1,4-Diazadiene Imido Complexes of Group V and VI Elements and Their Application in Chemical Vapour Deposition of TaN Films

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Erstgutachter: Herr Prof. Dr. J. Sundermeyer
Zweitgutachter: Herr Prof. Dr. M. Bröring

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Science does not believe in marvels,
but always looks forward to marvellous coincidences

Wilhelm Schwebel

To my parents
Prologue

This dissertation is written in a manuscript style; each chapter can be read independently, yet they all interact. Each chapter contains a separate summary, introduction, results and discussion part, conclusion, experimental section and literature references. It should be noted that the repetition of certain facts and the citation of literature from chapter to chapter is useful under these circumstances and cannot be avoided in order to retain the independence and clarity of each chapter.

In the „General Introduction“ an overview of complexes with early transition metals supported by 1,4–diazadiene ligands is given, whereas more details about specific topics are discussed in the introduction of the relevant chapter.

Finally, an overall summary, which combines the separate chapters and their results in common context, is provided.
Parts of this dissertation have been published

Publications


Alexei Merkoulov, Klaus Harms, and Jörg Sundermeyer, “Synthesis and Structural Characterisation of 1,4-Diazadiene Imido Tungsten Complexes”, Z. Anorg. Allg. Chem., accepted, in press

Patents


Presentations

“1,4-Diazadiene Imido Complexes – A Fruitful Liaison of $\pi$-Acidic and $\pi$-Basic Ligands”, 8th Seminar of PhD Students on Organometallic Chemistry, 2003, Hruba Scala, Czech Republic

“1,4-Diazadien-Imido-Komplexe der Metalle der Gruppe 5 und 6”, Anorganisches Kolloquium des FB Chemie, 2004, Philipps Universität Marburg
# Abbreviations

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<tr>
<td>acac</td>
<td>Acetylacetonate</td>
</tr>
<tr>
<td>all</td>
<td>Allyl, C\textsubscript{3}H\textsubscript{5}</td>
</tr>
<tr>
<td>Ar</td>
<td>Aromatic substituent</td>
</tr>
<tr>
<td>Ar\textsubscript{F}</td>
<td>2,3,4,5,6-Pentafluorophenyl</td>
</tr>
<tr>
<td>B</td>
<td>Base</td>
</tr>
<tr>
<td>Bz</td>
<td>Benzyl</td>
</tr>
<tr>
<td>Cp</td>
<td>Cyclopentadienyl</td>
</tr>
<tr>
<td>Cy</td>
<td>Cyclohexyl</td>
</tr>
<tr>
<td>R,R’–DAD</td>
<td>Substituted 1,4-diazadiene (R at nitrogen and R’ at carbon atoms)</td>
</tr>
<tr>
<td>DAD, dad</td>
<td>1,4-Diazadiene, if not specified 1,4-di-\textit{tert}-butyl-1,4-diaza-1,3-diene</td>
</tr>
<tr>
<td>Dip</td>
<td>2,6-Di-\textit{iso}-propylphenyl</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-Dimethoxyethane</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>DNMR</td>
<td>Dynamic NMR</td>
</tr>
<tr>
<td>EI</td>
<td>Electron Ionisation</td>
</tr>
<tr>
<td>Ind</td>
<td>Indenyl</td>
</tr>
<tr>
<td>\textit{iPr}</td>
<td>\textit{iso}-Propyl</td>
</tr>
<tr>
<td>L</td>
<td>Any ligand</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>Mes</td>
<td>Mesityl (2,4,6-trimethylphenyl)</td>
</tr>
<tr>
<td>MMA</td>
<td>Methyl methacrylate</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectroscopy</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>Py</td>
<td>Pyridine</td>
</tr>
<tr>
<td>\textit{tBu}</td>
<td>\textit{tert}-Butyl</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofurane</td>
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# Numbers

Compounds are labelled with full-size, bold numbers, e.g. \textbf{3}.

Numbers in square brackets indicate a reference (e.g. example [4] or elevated example\textsuperscript{[8]}).
Acknowledgments

First of all, I would like to thank my Ph.D. supervisor, Prof. Dr. Jörg Sundermeyer, for the interesting research topics and his readiness for fruitful advice and discussions throughout this work.

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Finally, I would like to thank Ekaterina Gauchenova for her endless patience and invaluable support.
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Zusammenfassung

Die vorliegende Arbeit beschreibt neue Perspektiven in der metallorganischen Chemie von 1,4-Diaza-1,3-dien- (R,R′–DAD) Liganden. Aus dem breiten Spektrum der bekannten R,R′–DAD Derivate wurde das 1,4-Di-tert-butyl-1,4-diazabuta-1,3-dien (tBu,H–DAD oder einfach DAD) ausgewählt. Diese Verbindung weist mehrere Vorteile auf, insbesondere eine leichte Synthese auch im großen Maßstab und einen hohen Dampfdruck, der für die Entwicklung flüchtiger metallhaltiger Komplexe notwendig ist. Der DAD Ligand ist redox-aktiv und kann in seiner zweifach reduzierten En-diamid Form DAD$^{2-}$ für das Design kovalenter Metallkomplexe verwendet werden.

Die gelungene Kombination von DAD und π-basischen Imido-Liganden hat eine neue Klasse flüchtiger DAD$^{2-}$ Komplexe von Niob und Tantal eröffnet, die in Gasphasenabscheidungsprozessen (CVD) für die Abscheidung von nitridischen Schichten der Idealzusammensetzung M$_{1.0}$N$_{1.0}$ – Diffusionsbarrierematerialien in der Mikroelektronik – getestet wurden (Kapitel VIII).
Verschiedene synthetische Methoden zur Darstellung der Schlüsselverbindungen 
\[(DAD)M(N^tBu)(\mu-Cl)]_2\) (A) und \[(DAD)M(N^tBu)(NH^tBu)]\) (B) mit M = Nb und Ta wurden 
erarbeitet und die Reaktionsbedingungen für \(MCl_5\) als Ausgangsstoff optimiert (Schema 1).

\[\text{Kapitel V}\]

\[\text{Kapitel VII}\]

\[\text{Kapitel IX}\]

\[\text{Kapitel I}\]

\[\text{Schema 1. Synthese der Schlüsselverbindungen } [(DAD)M(N^tBu)(\mu-Cl)]_2\) (A) und \[(DAD)M(N^tBu)(NH^tBu)]\) (B) mit M = Nb und Ta.\]

Die Reaktivität der dinuklearen Komplexe A und mononuklearen Pyridin-Addukte
\([(DAD)M(N^tBu)(Cl)(py)]\) mit M = Nb und Ta wurde in Bezug auf nucleophile Substitution, Reduktion und Metathese mit Aminen untersucht (Schema 2, Kapitel V und VI).
Zusammenfassung

Die synthetisierten Amido-Imido-Komplexe \([(\text{DAD})M(\text{N}^\text{T}Bu)(\text{NH}^\text{T}Bu)] \) (B) mit \(M = \text{Nb und Ta}\) zeigen hohe Reaktivität in metathetischen Reaktionen mit Aminen, organischen Säuren und Lithiumalkylen (Kapitel VII, Schema 3).
Die Amido-Gruppe in [(DAD)M(N^tBu)(NH^tBu)] (B) mit M = Nb und Ta reagiert hochselektiv unter Entwicklung von ^tBuNH_2 mit organischen Molekülen, die acidere Protonen besitzen, wie ^tBuOH und acacH. Analog Reaktionen mit primären Aminen führen zu verschiedenen Produkten abhängig von dem Amin-Substituenten. Durch Reaktion mit sterisch anspruchsvollem DipNH_2 wurden neue mononukleare Komplexe [(DAD)M(NDip)(NHDip)] erhalten, während im Fall von aciderem C_6F_5NH_2 nur die dinuklearen Verbindungen [(DAD)_2M_2(NC_6F_5)_3] und [(DAD)_2Nb(N^tBu)(NC_6F_5)_2] isoliert wurden. Durch Umsetzung von [(DAD)Ta(N^tBu)(NH^tBu)] mit Me_2NNH_2 gelingt erstmals die Darstellung eines Tantal-Hydrazido^2- Komplexes [(DAD)_2Ta(N^tBu)_2(NNMe_2)]. Das Amido-Wasserstoffatom in B kann durch Lithium in einer metathetischen Reaktion mit Lithiumalkylen substituiert werden. Die erhaltenen dinuclearen Lithium-tantalate bzw. -niobate [(DAD)M(N^tBu)_2Li]_2 zeigen Lewis
Zusammenfassung

Acidität gegenüber DAD und bilden mononucleare Komplexe des Typs \([(\text{DAD})\text{M}(\text{N}^\text{tBu})_2\text{Li(dad)}].\)

Die vollständige Reihe der Übergangsmetallkomplexe der Gruppe VI vom Typ \([(\text{DAD})\text{M}(\text{NR})_2]\) mit \(\text{M} = \text{Cr, Mo, W}\); \(\text{R} = \text{tBu und Mes}\) wurde hergestellt (Kapitel IV). Die Synthese von Molybdän- und Wolfram-Komplexen gelingt durch die Reaktion von \([\text{M}(\text{NR})_2\text{Cl}_2\text{L}_2]\), mit \(\text{L} = \text{DME und Pyridin, mit DAD in Anwesenheit von Magnesium. Unter gleichen Bedingungen liefert [Cr(NtBu)\text{Cl}_2] einen dinuclearen }d^1-d^1\text{ Komplex [Cr}_2(\text{N}^\text{tBu})_2(\mu-N^\text{tBu})_2(\mu-\text{DAD})] (C), der den ungewöhnlichen Koordinationsmodus eines verbrückenden DAD\(^2^−\text{Liganden aufweist. Die gewünschte Verbindung [(DAD)Cr(N}^\text{tBu})_2]\) wurde nach der Reaktion von \([\text{Cr(NtBu)\text{Cl}_2]}\) mit \(\text{Li}_2\text{DAD}\) isoliert.

Die Monoimido-DAD\(^2^−\text{-Komplexe von Wolfram [(DAD)W(NR)\text{Cl}_2], mit }\text{R} = \text{Ph und Cy, wurden durch die Reaktion zwischen [W(NR)\text{Cl}_4(L)] und }\text{Li}_2\text{DAD in guten Ausbeuten erhalten (Kapitel II). Der DAD\(^2^−\text{-Ligand scheint ein besserer Donor im Vergleich zu dem ortho-Phenylenediamid-Liganden [o-(Me}_3\text{SiN})_2\text{C}_6\text{H}_4]^{2^−}\text{ zu sein und reduziert deswegen die Lewis Acidität des Metallzentrums.}}\n
Der gemischte dinucleare Imido-Oxo-Komplex \([(\text{DAD})\text{Mo(N}^\text{tBu})(\mu-O)]_2\) wurde durch Umsetzung von \([\text{Mo(N}^\text{tBu})(\text{O})\text{Cl}_2(\text{dme})]\) mit \(\text{Li}_2\text{DAD}\) synthetisiert (Kapitel III).

Zusammenfassung

Die tetraedrischen Komplexe mit X ≠ NR’ und die tetragonal-pyramidalen Komplexe, in denen eine Dissoziation des X oder X’ Liganden nicht möglich ist, weisen keine Temperaturabhängigkeit der NMR-Spektren auf. Dies spricht entweder für eine schnelle supine–prone Umlagerung, die auf der NMR-Zeitskala nicht erfasst werden kann, oder für das Vorliegen nur eines Isomers, supine oder prone, in Lösung.

Das dynamische Verhalten, das für die Komplexe des Typs [(DAD)M(NtBu)(X)(py)] und [(DAD)M(NtBu)(µ-Cl)]2 (A) mit M = Nb und Ta, X = Cl und Bz beobachtet wurde, beruht auf einem intramolekularen Dissoziations/Assoziations-Mechanismus. Die thermodynamischen Parameter der Dissoziationsbarriere wurden anhand von NMR-Messdaten berechnet (Kapitel V).

Für die tetraedrischen Komplexe des Typs [(DAD)M(NR)2], M = Cr, Mo, W; R = tBu, Mes, sowie für die isoelektronische Einheit [(DAD)M(NtBu)2], M = Nb und Ta, in den Komplexen [(DAD)M(NtBu)2Li]2 und [(DAD)M(NtBu)2Li(dad)] wurde die Ringinversion in der Lösung beobachtet.

Über NMR-spektroskopischen Methoden wurde eine Aktivierungsentropie ΔS* nah Null für die Ringinversion in allen Komplexen gefunden. Die Aktivierungsenthalpie ΔH* hat den
Zusammenfassung

bedeutendsten Beitrag in der Aktivierungsenergie $\Delta G^\neq$ und deutet auf die Bildung eines flachen Übergangszustandes hin. Dieser Übergangszustand scheint im Fall des Chrom-Komplexes [(DAD)Cr(N\text{t}Bu)$_2$] im Vergleich zu Molybdän- und Wolframkomplexen besser stabilisiert zu sein, was sich in den enormen Differenzen von mehr als 50 $kJ\ mol^{-1}$ in $\Delta H^\neq$ und mehr als 200 K in den Koaleszenztemperaturen ausdrückt.

In einer Kooperation mit der Arbeitsgruppe um PD Dr. W. Stolz (WZMW, Philipps-Universität Marburg) wurden keramische Schichten mit ca. 50 Atomprozent Tantal mittels CVD aus den Komplexen [(DAD)Ta(N\text{t}Bu)(NH\text{t}Bu)], [(DAD)Ta(N\text{t}Bu)(\eta^3-BH$_4$)] und [(DAD)Ta(N\text{t}Bu)(\eta^3-C$_3$H$_5$)] erhalten (Kapitel VIII). Eine optimale Zersetzungstemperatur von ca. 400°C und Schichtenwachstumsraten von ca. 0.6 $nm/min$ entsprechen idealen Zielvorgaben an CVD-Precursoren. Die durchschnittliche Oxidationsstufe des Tantalts ist wesentlich kleiner als V – eine notwendige Voraussetzung für die Leitfähigkeit.

![Abgeschiedene Schichten und Si-Wafer](image)

**Fig. 1.** Bestimmung von Schichtdickewachstumsrate mittels Rasterelektronenmikroskop (REM) für [(DAD)Ta(N\text{t}Bu)(NH\text{t}Bu)] bei 400°C.

Die abgeschiedenen Schichten enthalten EDX-Untersuchungen zufolge Sauerstoff, der wahrscheinlich durch Reaktion der ungesättigten Valenzen der Oberfläche mit Luftsaerstoff eingebaut wird. Außerdem, wurde der Einbau von Kohlenstoff in die Schichten mittels EDX-Analyse festgestellt. Diese Tendenz gilt allgemein für die getesteten Imido/Amido-Tantal-Verbindungen, die N–C Bindungen enthalten. In dieser Hinsicht besitzen die DAD$^{2-}$-Komplexe keine Vorteile gegenüber die kommerziell verfügbaren CVD-Precursoren. Jedoch hat der Komplex [(DAD)Ta(N\text{t}Bu)(NH\text{t}Bu)] einige Vorteile im Vergleich zu handelsüblichen Tantal-Quellen, vor allem durch den günstigen Syntheseweg und die ausgezeichnete thermische Stabilität bis zum erwünschten Zersetzungspunkt.
General Introduction

Complexes on the basis of the 1,4-diaza-1,3-diene (R,R′-DAD) ligand backbone have been the focus of attention for many years. Due to several possible coordination modes and their red-ox activity, R,R′-DAD ligands can stabilize metals in a wide range of formal oxidation states.[1] While neutral R,R′-DAD is a strong π–acceptor stabilizing low-valent metal centres, the 2-electron reduced R,R′-DAD$^{2-}$ ligand, which is best described as an ene-diamido functionality, can be envisaged as a strong π–donor stabilizing high-valent metal centres.

The diversity of substituents at nitrogen and carbon atoms offers a perfect handle for the fine-tuning of electronic and steric ligand features in catalytic applications. For example, complexes of the late transition metals (in particular nickel and palladium) and DAD ligands with bulky electron-withdrawing aryl substituents at nitrogen are used extensively in olefin oligomerisation and polymerisation.[2]

In the last decade many publications were devoted to the chemistry of the reduced 1,4-diaza-1,3-diene (R,R′–DAD$^{2-}$) ligand with transition metals of groups IV[3, 4] and V.[5, 6] Some of them were supported by computational results[7] and experimental thermodynamic data of inversion observed in solution for the folded R,R′–DAD$^{2-}$ moiety.[8] However there is much less known about complexes of group VI elements with a reduced R,R′–DAD$^{2-}$ backbone.[9] Scheme 1 summarises characterised complexes of group V and VI elements with reduced R,R′–DAD$^{2-}$ ligands.
Scheme 1. Complexes with reduced R,R’–DADâ€”ligands of group V and VI elements.
Metal nitrides of the formula $M_{1.0}N_{1.0}$, where $M$ is a group IV or V element, possess a wide range of useful properties. Their hardness and good electrical conductivity allow using them as barrier materials in microelectronics. The barrier between copper and silicon layers prevent the copper atoms from diffusion into silicon dioxide layer or silicon wafers at high fabrication temperatures. Formation of copper silicides or copper-doped silicon at the copper–silicon interface can be efficiently inhibited by a nanometer scale layer of TaN as electroceramic material.\textsuperscript{10}

According to the most recent investigations\textsuperscript{1} thin TaN films are claimed to be the best up to date barrier material between copper and silicon substrate. They are better than TiN films, which exhibit columnar structure and create fast diffusion paths for copper atoms.\textsuperscript{11} The disordered grain boundary structure of TaN films makes diffusion of copper atoms ineffective.\textsuperscript{1}

The Chemical Vapour Deposition (CVD) might be the most preferable film-forming process and can realistically deliver the conformal coverage that is needed. In contrast to the Physical Vapour Deposition (PVD), in which highly reactive atoms or small molecules immediately adhere to growing film surfaces, molecules are able to absorb/desorb on the film surface in CVD.\textsuperscript{1} As a result, shape factor features are poorly realised by PVD techniques, especially on the sides and corners. Tested nitrogen containing metalorganic compounds (["Ta(NEt$_2$)$_5"], [Ta(N$^t$Bu)(NEt$_2$)$_3$] and dimer [Ta(N$^t$Bu)(NH$^t$Bu)Cl$_2$(NH$_2$Bu)$_2$]) produce either $TaN_5$ (isolator) or carbon rich films with large resistivity.\textsuperscript{1, 12} That is why the development of new precursors for CVD of TaN is a challenge and topic in applied coordination chemistry.

The chemistry of early transition metals has become a great breakthrough in the last decade owing to the usage of $\pi$–donor imido ligands, which were proved to be isolobal to the cyclopentadienyl ring.\textsuperscript{13} A fruitful liaison of the $\pi$–acidic R,Rˈ–DAD ligand and $\pi$–basic imido
ligand uncovers a new class of R,R′–DAD$_2$– imido complexes. The aim of this work was the
synthesis and characterisation of a new class of compounds with group V (niobium and
tantalum) and group VI (chromium, molybdenum and tungsten) elements with a combination of
π–basic imido groups (RN$_2^-$) and π–acidic $^1$Bu,H–DAD (or simply DAD) ligand.

References


Chapter I

Preparation of New Dimethoxymethane (DME) and Neutral 1,4-Diazadiene (DAD) Imido Complexes of Niobium and Tantalum

Introduction

The chemistry of niobium and tantalum has experienced a strong development in the last decades stimulated by the use of \( \pi \)-donor imido ligands, which were proved to be isolobal to the cyclopenadienyl ring [1]. The preparation of mono-imido starting materials was widely investigated and showed that metal pentachlorides have a strong tendency to form metalate complexes poorly soluble in organic solvents [2]. There are three possibilities to obtain soluble imido-complexes: usage of silated amines [3a], ZnCl\(_2\) as Lewis acid [2b] and Py as the donating ligand [3b]. While the pyridine ligand is suitable for further transformations, the last method is the simplest and the cheapest one. The reaction between MCl\(_5\) and excess primary amines leads to dimeric amido-imido compounds \([\text{M(NR)(NHR)(NH}_2\text{R)Cl}_2\text{]}_2\) [2a, 4] with one known exception, \( \text{R} = \text{iPr} \), whose dimeric structure is proposed to be in equilibrium with a monomeric one [4b, 5]. Such dimers react with Py to yield monomeric imido amido complexes that was recently shown in our workgroup [6].
The main concept of this work was the synthesis and characterisation of a new class of niobium and tantalum compounds displaying a combination of \( \pi \)-basic imido groups (RN\(^2\)) and \( \pi \)-acidic 1,4-diaza-1,3-diene (R,R’–DAD) ligands. There are four methods described in the literature for the preparation of complexes with early transition metals and R,R’–DAD\(^2\) dianion: reaction of metal halogenides with dilithium salts of R,R’–DAD \([7a]\), \textit{in situ} reduction of a metal centre in the presence of R,R’–DAD \([7b]\), oxidative addition of R,R’–DAD to a reduced metal centre \([7c]\) and double insertion of isocyanides into metal carbon bond followed by \textit{intra} molecular coupling \([7d]\).

The R,R’–DAD ligands are not only \( \pi \)-acids but they can build complexes with metals as anion radicals R,R’–DAD\(^–\) or ene-diamide R,R’–DAD\(^2\) dianions \([7, 8]\). Finally they may serve as chelate 4e\(^–\) \( \sigma \)-donors. The frontier orbitals of 1,4-diaza-1,3-butadiene are presented in Fig. 1 compared to those of 1,3-butadiene \([9]\). Such complexes with neutral R,R’–DAD ligands could be useful starting materials for the preparation of R,R’–DAD\(^2\) complexes. For example, dichloride complexes containing neutral R,R’–DAD ligand ought to be reduced with appropriate reducing agents in order to produce the corresponding R,R’–DAD\(^2\) complex.

![Front orbitals of 1,4-diaza-1,3-butadiene and 1,3-butadiene](image)

**Fig. 1.** The front orbitals of 1,4-diaza-1,3-butadiene and 1,3-butadiene \([9]\).
There are some crystallographically characterised examples for this ‘neutral R,R’–DAD’ coordination mode with the group IV and VI $d^0$ metal centres [10] (see Fig. 2).

![Complexes early transition metals with neutral R,R’–DAD ligands [10].](image)

Surprisingly, we did not find such examples of $d^0$ niobium or tantalum complexes. Thus we decided to synthesise and characterise a few imido complexes of niobium and tantalum with neutral DAD (1,4-di-tert-butyl-1,4-diazabuta-1,3-diene) ligand in order to get some examples for spectroscopic and structural comparison between complexes with reduced DAD$^{2-}$ and neutral DAD moiety. These DAD adducts also allow the approval of an alternative synthetic approach to DAD$^{2-}$ complexes by subsequent reduction.

**Results and discussion**

**Preparative studies**

Although the abbreviation ‘DAD’ is commonly used for the whole class of compounds only the 1,4-di-tert-butyl ($R = 'Bu, R' = H$) derivative was applied in this work. For this reason the DAD abbreviation, if not specified, is used for 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene. This derivative has some advantages, namely, it is very simple to synthesise even in large scale and it possesses a high vapour pressure and therefore can be easily sublimed or even distilled. It is
anticipated that complexes based on this particular H,tBu–DAD (or simply DAD) ligand should possess the high volatility, which is important for the CVD technique.

The reaction between MCl$_5$ (M = Nb, Ta) and neutral DAD ligand could lead to a mixture of compounds because the metal centres in the educts are too electrophilic and DAD ligand is able to create different bonding modes [8]. For example, reaction of NbCl$_5$ with [Li(thf)$_2$]$_2$DAD leads to the formation of four different products depending on the reactants’ proportion [10]. That is one complication along with the poor solubility of MCl$_5$. Consequently, the formation of imido moiety is preferable in the first step of the synthetic work.

The simplest way to obtain imido complexes with neutral DAD is to substitute DME with the more basic DAD ligand. The following six DME complexes were obtained by adhering to the known method [2b] and the not-previously described 1-3 were characterized by means of $^1$H-, $^{13}$C-NMR, mass and IR spectroscopy.

Four of them were transformed into DAD complexes 4-7 by adding one equivalent of DAD to a CH$_2$Cl$_2$ solution of the corresponding DME compound. The reaction provides a very good yield as well as pure substances. All obtained complexes 4-7 are air-sensitive solids with good solubility in polar solvents such as CHCl$_3$, CH$_2$Cl$_2$ or THF. This reaction is based on the different affinity of DAD and DME to Lewis acids. The question arises, if neutral DAD is a
sufficiently strong ligand to substitute chlorine anion in monoimido salts type \([\text{BH}^+]\_2\text{[M(NR)Cl]}_5\) and to produce the desirable neutral monoimido complexes with neutral DAD ligand.

This reaction was investigated with alkyl (\(^t\)Bu) and aryl (Dip) amines using Py and amine as a base. According to the results obtained from NMR monitoring in CDCl\(_3\) the target DAD complexes are in equilibrium with salts. Furthermore the equilibrium lies on the side of the metalate complexes and addition of ZnCl\(_2\) as a Lewis acid has no effect on this ratio. But the formation of the DAD adducts in equilibrium can be used in large scale reactions for preparation of DAD\(^{2–}\) complexes [(DAD)M(\(^t\)Bu)(\(\mu\)-Cl)]\(_2\) [11].

**Spectroscopic studies**

The \(^1\)H-NMR spectra for all DAD complexes 4-7 exhibit two doublets in the aromatic region approx. 8.3 ppm for methine CH-protons and two singlets in the aliphatic region approx. 1.5 ppm for \(^t\)Bu-groups, which should be assigned to protons of the DAD ligand. The methine signals are not always well resolved as doublets because of a very small (about 1.2 Hz) coupling constant. The same situation was observed in the \(^{13}\)C-NMR spectra: 2 signals for the CH-group and two sets of signals for the chemically non-equivalent \(^t\)Bu groups. Thus, on the basis of NMR experiments the asymmetrical coordination of DAD ligand in complexes is supposed to be similar to the crystallographically characterised DME complexes [2b].

In all electron ionisation mass spectra a very intense signal was observed for a cation [M – DAD]\(^+\). This is in contrast to the results for DAD\(^{2–}\) complexes, where the fragmentation of the DAD\(^{2–}\) ligand – notably the abstraction of isobutylene – was found (see Chapter III – VII).

Because we have not found crystallographically characterised examples of d\(^0\) niobium and tantalum complexes with neutral R,R\(^{−}\)–DAD ligands a crystal structure analysis of 5 was conducted.
X-ray studies

A crystal of 5 suitable for X-ray analysis was grown from concentrated CH$_2$Cl$_2$ solution by cooling to −30°C. The crystals contain one solvate molecule of CH$_2$Cl$_2$ per complex unit, which gets lost by drying in vacuum. The molecular structure is shown in Fig. 3; selected bond distances and angles are presented in Table 1.

![Molecular structure of 5•CH$_2$Cl$_2$.](image)

**Fig. 3.** The molecular structure of 5•CH$_2$Cl$_2$. The hydrogen atoms and solvate molecule of CH$_2$Cl$_2$ are omitted for clarity.

The coordination sphere of niobium is a slightly distorted octahedral. The imido group occupies the axial position and reveals the typical structural parameters for its 6e$^−$ bonding mode, namely, a short metal-nitrogen distance Nb(1)–N(1) of 1.7720(16) Å and an almost linear angle C(11)–N(1)–Nb(1) of 171.90(13)$°$ [1].

One nitrogen atom of DAD occupies the second axial position *trans* to the imido ligand with a long Nb–N distance of 2.460(2) Å. The other one lies in the equatorial plane with three chlorine atoms exhibiting a short Nb–N distance of 2.301(2) Å in accordance with the stronger thermodynamic *trans*-effect of NR$_2^−$ compared to Cl$^−$. The central atom Nb(1) and the four atoms of the DAD ligand N(2), C(1), C(2) and N(3) form flat metallocycle (σ$_{\text{plane}}$ = 0.004 Å; σ$_{\text{plane}}$ = $\sqrt{\frac{\sum_{i=1}^{n} d_i^2}{n-3}}$, where $n$ is the number of atoms and $d_i$ is the perpendicular distance to the calculated least-square plane; for example, this parameter for aromatic ring C$_6$H$_2$Cl$_3$ is 0.016 Å) [12].
The metal nitrogen distances are 2.301(2) and 2.460(2) Å and should be referred to 2e\(^-\) bond situation that makes DAD ligand 4e\(^-\) \(\sigma\)-donor coordinated to the d\(^0\) metal centre. As a result there are no large changes in the bond distances between free DAD ligand [13] and its complex 5 (see Table 2).

### Table 2. Comparison of the selected bond distances (Å) in reference compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nb – N</th>
<th>N – C</th>
<th>C – C</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Bu-DAD</td>
<td>—</td>
<td>1.264 – 1.267</td>
<td>1.468 (2)</td>
</tr>
<tr>
<td>5•CH(_2)Cl(_2)</td>
<td>2.46 – 2.30</td>
<td>1.27 – 1.28</td>
<td>1.471(3)</td>
</tr>
</tbody>
</table>

### Conclusion

Imido complexes of the type \([\text{MCl}_3(\text{NR})(\text{dad})]\) (M = Nb, Ta) with neutral DAD ligand can be easily prepared from DME adducts by ligand exchange. The DAD ligand was not found to be strong enough to cleave completely metalate complexes with the common formula \([\text{BH}^+\]_2[\text{M(NR)}\text{Cl}_3]\). Thus an order of ligand strength to the M(NR)Cl\(_3\)-moiety can be postulated: Py \(\gg\) Cl\(^-\) \(\approx\) DAD. The asymmetrical 4e\(^-\) donor-acceptor coordination mode of the DAD ligand in \([\text{M(NR)}\text{Cl}_3(\text{dad})]\) \(4–7\) proposed from the NMR spectra was proved by X-ray analysis.

### Experimental Part

**General:** All reactions and manipulations were carried out under argon using standard Schlenk tube technique or in a conventional nitrogen-filled glove box. Solvents were refluxed in
the presence of an appropriate drying agent and distilled: C₆D₆ and hexane (Na/K alloy), DME (Na/benzophenone), toluene (Na), and CH₂Cl₂ and CDCl₃ (CaH₂). Literature methods were employed for the synthesis of [Nb(NDip)Cl₃(dme)], [Ta(NDip)Cl₃(dme)], [Ta(N’Bu)Cl₃(dme)] [2b] and 1,4-ditert-butyl-1,4-diazabuta-1,3-diene (DAD) [14]. Melting points were measured with Büchi MP B-540 (uncorrected). C, H and N analyses were carried out with a Heraeus CHN-Rapid analyser. Mass spectra were taken on Varian MAT CH-7a (EI, 70 eV) and Finnigan TSQ 700 (ESI). ¹H- and ¹³C{¹H}-NMR spectra were recorded with Bruker ARX200, AMX300 and DRX500 spectrometers; chemical shifts are given in ppm referred to the ¹H (δ 7.15) and ¹³C (δ 128.0) residual signals of C₆D₆ and the ¹H (δ 7.24) and ¹³C (δ 77.0) residual signals of CDCl₃. Infrared spectra were recorded with Bruker IFS 88 FT; samples as Nujol mulls between KBr plates.

**Preparation of [M(NR)Cl₃(dme)] 1–3.** These compounds were synthesised with good yields (70–100 %) following to the procedure described for [Ta(NPh)Cl₃(dme)] [2b] using the corresponding substituted derivative 2,4,6-trichlorineaniline (H₂N-2,4,6-C₆H₂Cl₃) or 2,3,4,5,6-pentaflouroaniline (H₂NC₆F₅) instead of aniline. Typically 2 g of MCl₅ were suspended in 30 mL CH₂Cl₂. To this 2 mL of DME and 2 eq. of ZnCl₂ were added. The mixture was cooled down to 0°C and a solution of 1 eq. of ArNH₂ and 2 eq. of Py in 10 mL CH₂Cl₂ was added. This dissolved the precipitate and formed coloured solution (orange or yellow). The reaction mixture was stirred for 12h at room temperature. A precipitate formed was filtered off and washed with 15 mL of CH₂Cl₂. The solvent was removed in vacuum and a product extracted with 100 mL of toluene. Removing the solvent, washing with 20 mL of Et₂O and drying in vacuum produced pure product.

**[Nb(N-2,4,6-C₆H₂Cl₃)Cl₃(dme)] 1.** Light orange solid. Yield: 70%. Anal. Calcd. for C₁₀H₁₂NCl₆O₂Nb (M = 483.84 g mol⁻¹): C 24.82, H 2.50, N 2.89. Found: C 24.70, H 2.46, N 3.05. MS-ESI (CH₃CN): 481 (M⁺, 20%), 270(100%). ¹H-NMR (CDCl₃, 300 MHz, 300 K): not observed (m-C₆H₂Cl₃), 4.20 – 4.10 (m, 4H, CH₂-dme), 4.04 and 4.01 (s, 3H, CH₃-dme). ¹³C{¹H}-NMR (CDCl₃, 75 MHz, 300 K): 134.6 (o-C₆H₂Cl₃), 131.5 (p-C₆H₂Cl₃), 127.8 (m-C₆H₂Cl₃), 75.6 and 71.0 (CH₂), 69.7 and 63.1 (Me). IR (KBr, cm⁻¹): 1603(w), 1559(w), 1532(w), 1457(s), 1425(w), 1329(w), 1281(w), 1262(w), 1242(w), 1188(w), 1142(w), 1074(m), 1024(s), 990(w), 984(w), 856(s), 822(s), 802(w), 735(w), 719(m), 671(w), 613(w), 573(w), 446(w), 424(w). M.p. 175.3°C.

**[Nb(NC₆F₅)Cl₃(dme)] 2.** Orange solid. Yield: 85%. Anal. Calcd for C₁₀H₁₀Cl₃NF₃O₂Nb (M = 470.45 g mol⁻¹): C 25.53, H 2.14, N 2.98. Found: C 24.85, H 2.25, N 2.95. MS-EI: 381 (M⁺ – dme, 100%). ¹H-NMR (CD₃D₆, 300 MHz, 300 K): 3.43 and 3.27 (s, 3H,
CH₂-dme), 2.98 – 2.87 (m, 2H, CH₂-dme). ¹³C{¹H}-NMR (C₆D₆, 75 MHz, 300 K): 74.7 and 70.6 (CH₃-dme), 68.3 and 62.8 (CH₂-dme). ¹⁹F-NMR (C₆D₆, 188 MHz, 300 K): -147.9 (pseudo-d, 2F, o-C₆F₅), -158.5 (pseudo-t, 1F, p-C₆F₅), -164.1 (pseudo-t, 2F, m-C₆F₅). IR (KBr, cm⁻¹): 1643(w), 1607(w), 1510(s), 1462(m), 1360(w), 1345(m), 1279(w), 1236(s), 1190(w), 1171(w), 1074(w), 1061(s), 1026(s), 1009(w), 993(s), 930(w), 860(s), 820(m), 801(w), 650(w), 571(w), 419(w). M.p. 180.2°C.

[Ta(NC₆F₅)Cl₃(dme)] 3. Yellow solid. Yield: 99%. Anal. Calcd for C₁₀H₁₀Cl₃NF₅O₂Ta (M = 558.50 g mol⁻¹): C 21.51, H 1.80, N 2.51. Found: C 21.55, H 2.12, N 3.04. MS-EI: 466 (M⁺ – dme, 86%), 183 (100%). ¹H-NMR (CDCl₃, 500 MHz, 300 K): 4.29 – 4.27 and 4.20 – 4.18 (m, 2H, CH₂-dme), 4.21 and 4.08 (s, 3H, CH₃-dme). ¹³C{¹H}-NMR (CDCl₃, 125 MHz, 300 K): 76.2 and 71.5 (CH₃-dme), 70.7 and 63.9 (CH₂-dme). ¹⁹F-NMR (CDCl₃, 376 MHz, 300 K): -149.2 (pseudo-d, 2F, o-C₆F₅), -160.5 (pseudo-t, 1F, p-C₆F₅), -164.1 (pseudo-t, 2F, m-C₆F₅). IR (KBr, cm⁻¹): 3214(w), 3158(w), 3129(w), 3104(w), 3069(w), 1634(w), 1603(w), 1514(s), 1501(w), 1462(m), 1362(w), 1346(m), 1279(w), 1242(s), 1188(w), 1071(w), 1061(s), 1022(s), 1005(w), 990(s), 858(s), 818(w), 799(w), 748(w), 723(w), 698(w), 677(w), 640(w), 571(w), 469(w), 436(w), 426(w), 403(w). M.p. 152.9°C.

Preparation of [M(NR)Cl₃(dad)] 4–7. Typically about 500 mg of a starting material [M(NR)Cl₃(dme)] was dissolved in approx. 30 mL of CH₂Cl₂. One equivalent of DAD was added to this solution at room temperature. After 8h the solvent was removed in vacuum and the product washed with 10 mL hexane. All products can be recrystallised at room temperature from CH₂Cl₂ by layering it with hexane. Yields of analytically pure substances after recrystallisation are 52–88%.

[Nb(NDip)Cl₃(dad)] 4. Purple crystals. Yield: 52%. Anal. Calcd for C₂₂H₃₇Cl₃N₃Nb (M = 542.83 g mol⁻¹): C 48.68, H 6.87, N 7.74. Found: C 47.82, H 7.40, N 7.69. MS-EI: 373 (M⁺ – dad, 22%), 358 (M⁺ – dad – Me, 48%), 322 (M⁺ – dad – Me – Cl, 22%), 57 (100%). ¹H-NMR (CDCl₃, 300 MHz, 300 K): 8.23 and 8.19 (d, 1H, ¹J₃-H-H = 1.2 Hz, CH₃-dad), 7.12 – 6.99 (m, 3H, Ar-NDip), 4.66 (sept, 2H, ³J₃-H-H = 6.7 Hz, CH₃-NDip), 1.70 and 1.49 (s, 9H, ¹Bu-dad), 1.31 and 1.24 (d, 12H, ³J₃-H-H = 6.7 Hz, CH₃-NDip). ¹³C{¹H}-NMR (CDCl₃, 75 MHz, 300 K): 156.5 and 153.5 (CH-dad), 151.0 (o-NDip), not observed (ipsos-NDip), 127.6 (p-NDip), 122.7 (m-NDip), 67.0 and 66.2 (CMe₃-dad), 29.3 and 28.7 (CMe₃-dad), 27.9 (CH-NDip), 26.5 and 21.9 (CH₃-NDip). IR (KBr, cm⁻¹): 3054(w), 1599(w), 1427(w), 1398(w), 1391(w), 1383(w), 1368(w), 1362(w), 1346(w), 1333(w), 1279(m), 1258(w), 1236(w), 1204(w), 1192(m), 1148(w), 1115(w), 1103(w), 1080(w), 1059(w), 1047(w), 1036(w), 984(w), 974(m), 939(w), 932(w), 893(m),
870(m), 804(m), 762(s), 723(w), 635(w), 617(w), 567(w), 554(w), 536(w), 523(w), 507(m),
461(w), 449(w). M.p. 193°C(dec).

[Nb(N-\textsubscript{2,4,6-C}_6\textsubscript{6}H\textsubscript{2}Cl\textsubscript{3})Cl\textsubscript{3}(dad)] 5. Beige solid. Yield: 64%. Anal. Calcd. for C\textsubscript{16}H\textsubscript{22}N\textsubscript{3}Cl\textsubscript{6}Nb (M = 562.00 g mol\textsuperscript{-1}): C 34.20, H 3.95, N 7.48. Found: C 34.11, H 4.13, N 7.47. MS-EI: 393 (M\textsuperscript{+} – dad, 11%), 57 (100%). \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 300 MHz, 300 K): 8.22 (s, 2H, CH-dad), 7.29 (s, 2H, NC\textsubscript{6}H\textsubscript{2}Cl\textsubscript{3}), 1.71 and 1.49 (s, 9H, t\textsubscript{Bu}-dad).

13\textsuperscript{C}{\textsuperscript{1}H}-NMR (CDCl\textsubscript{3}, 75 MHz, 300 K): 156.7 and 154.0 (C\textsubscript{H}-dad), 137.6 (o-C\textsubscript{6}H\textsubscript{2}Cl\textsubscript{3}), 131.7 (p-C\textsubscript{6}H\textsubscript{2}Cl\textsubscript{3}), 128.1 (m-C\textsubscript{6}H\textsubscript{2}Cl\textsubscript{3}), 66.7 and 66.6 (CMe\textsubscript{3}-dad), 29.4 and 28.7 (CMe\textsubscript{3}-dad). IR (KBr, cm\textsuperscript{-1}): 3092(w), 3057(w), 1749(w), 1591(w), 1557(m), 1532(w), 1522(w), 1456(s), 1425(w), 1398(m), 1391(w), 1368(w), 1348(w), 1319(m), 1262(w), 1236(w), 1206(w), 1190(m), 1146(m), 1092(w), 1074(w), 1038(w), 1015(w), 980(m), 972(s), 926(w), 893(m), 872(s), 822(s), 810(w), 758(w), 727(m), 635(w), 613(m), 581(w), 509(w). M.p. 239°C(dec).

[Ta(N\textsubscript{t}Bu)Cl\textsubscript{3}(dad)] 6. Beige solid. Yield: 60%. Anal. Calcd for C\textsubscript{14}H\textsubscript{29}Cl\textsubscript{3}N\textsubscript{3}Ta (M = 526.71 g mol\textsuperscript{-1}): C 31.93, H 5.55, N 7.98. Found: C 31.97, H 5.45, N 7.78. MS-EI: 512 (M\textsuperscript{+} – Me, 3%), 342 (M\textsuperscript{+} – dad – Me, 19%), 57 (100%). \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 200 MHz, 300 K): 8.33 and 8.23 (d, 1H, 3\textsubscript{J}H-H = 1.1 Hz, C\textsubscript{H}-dad), 1.65, 1.64 and 1.43 (s, 9H, N\textsubscript{t}Bu and \textsubscript{t}Bu-dad).

13\textsuperscript{C}{\textsuperscript{1}H}-NMR (CDCl\textsubscript{3}, 75 MHz, 300 K): 157.5 and 154.3 (C\textsubscript{H}-dad), 66.9 and 66.6 (CMe\textsubscript{3}-dad), 31.5, 29.7 and 28.5 (CMe\textsubscript{3}-dad and NCMe\textsubscript{3}). IR (KBr, cm\textsuperscript{-1}): 1601(w), 1400(w), 1391(w), 1368(w), 1358(w), 1271(s), 1240(w), 1217(w), 1190(w), 1180(w), 1080(w), 1038(w), 974(m), 930(w), 897(w), 870(m), 806(w), 760(m), 721(w), 669(w), 617(w), 602(w), 550(w), 534(w), 509(w). M.p. 239°C(dec).

[Ta(NDip)Cl\textsubscript{3}(dad)] 7. Purple crystals. Yield: 88%. Anal. Calcd for C\textsubscript{22}H\textsubscript{37}Cl\textsubscript{3}N\textsubscript{3}Ta (M = 630.87 g mol\textsuperscript{-1}): C 41.89, H 5.91, N 6.66. Found: C 38.52, H 5.66, N 6.30. MS-EI: 461 (M\textsuperscript{+} – dad, 10%), 524 (M\textsuperscript{+} – dad – Me, 35%), 162 (100%). \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 500 MHz, 300 K): 8.41 and 8.33 (s, 1H, CH-dad), 7.17 (d, 2H, 3\textsubscript{J}H-H = 7.8 Hz, m-DipN), 6.83 (t, 1H, 3\textsubscript{J}H-H = 7.8 Hz, p-DipN), 4.54 (sept, 2H, 3\textsubscript{J}H-H = 6.7 Hz, CH-DipN) 1.72 and 1.51 (s, 9H, \textsubscript{t}Bu-dad), 1.28 and 1.22 (d, 12H, 3\textsubscript{J}H-H = 6.7 Hz, CH\textsubscript{2}-DipN). IR (KBr, cm\textsuperscript{-1}): 3051(w), 1607(w), 1598(w), 1399(w), 1344(m), 1298(w), 1259(w), 1236(w), 1191(w), 1150(w), 1104(w), 1080(w), 1046(w), 991(w), 973(m), 934(w), 894(w), 868(m), 842(w), 804(w), 762(m), 723(w), 697(w). M.p. 209°C(dec).
References


[11] see Chapter V


Chapter II

Synthesis and Structural Characterisation of 1,4-Diazadiene Imido Tungsten Complexes

Abstract

The reaction of \([\text{W}(\text{NR})\text{Cl}_4(\text{L})]\) (R = Ph, Cy; L = thf) and \(\text{Li}_2\text{DAD}\) (DAD = 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene) leads to the formation of \([(\text{DAD})\text{W}(\text{NR})\text{Cl}_2]\), R = Ph (1), R = Cy (2). Both compounds are examples of a growing class of complexes displaying an uncommon combination of two highly charged sterically demanding 6-electron donor ligands, \(\text{NR}^2\) and \(\text{DAD}^{2–}\), at one coordination site. Surprisingly both complexes show weak Lewis acidity and don’t react with \(\sigma\)-donors such as \(\text{PMe}_3\) and \(\text{THF}\). The crystal structure determination of 1 reveals a mononuclear structure with folded \(\text{DAD}^{2–}\) moiety. In accordance with spectroscopic data and the \(\text{W–N, C–N and C–C bond lengths of the DAD ligand, the obtained compounds should be described as W(VI) imido ene-diamido species.}

Introduction

Stable alkylidene complexes of group VI metals in high oxidation states are useful catalysts in olefin metathesis reaction and its applications ROMP and ADMET [1, 2]. The most convenient synthetic approach to such complexes is dialkylation of halogen derivatives followed by \(\alpha–\text{H–elimination of RH}\) [2]. Boncella and co-workers have investigated a class of imido compounds supported by the bidentate dianion of \(\text{N,N’-bissilylated o-phenylene diamine}\) [3]. We continue our previous investigations [4] on complexes based on the sixth group metals and a very promising combination of \(\pi\)-donor imido and redox active \(\pi\)-acceptor 1,4-diaza-1,3-diene ligands \(\text{R,R’–DAD}\). Here we report the synthesis and complete spectroscopic and structural characterisation of two chloro functionalised tungsten(VI) complexes \([(\text{DAD})\text{W}(\text{RN})\text{Cl}_2]\) with \(\text{R} = \text{Ph}\) and \(\text{Cy}\), DAD = 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene (R = \(\text{tBu}\), R’ = H), which may act
as key compounds for further modifications and especially for the preparation of tetra coordinated alkylidene complexes.

**Results and discussion**

R,R’–DAD is a redox active ligand with low-lying $\pi^*$–orbitals [5]. Reduction with elemental lithium leads to the known ene-diamide Li$_2$DAD [6]. The target complexes 1 and 2 were synthesised from monoimido compounds [W(NPh)Cl$_4$(thf)] [7a] or [W(NCy)Cl$_4$]$_2$ [7b] and Li$_2$DAD in THF at –80°C. Extraction with toluene followed by crystallisation leads to yellow-brown solids with moderate solubility in toluene and good solubility in polar solvents, such as CH$_2$Cl$_2$, CHCl$_3$ or THF.

![Chemical Reaction](attachment:image.png)

The $^1$H- and $^{13}$C-NMR spectra of the diamagnetic compounds 1 and 2 reveal sharp singlets for chemically equivalent tert-butyl groups. No dynamic behaviour for the DAD ligand was observed in the temperature range of 180–400 K. This is in contrast to [(DAD)(C$_5$R$_5$)TiX] complexes [8] where inversion of the pyramidal configuration at both DAD nitrogen atoms was observed in the low temperature limiting NMR spectra. It is interesting to compare $\delta_C$ and $\delta_H$ of the \{CH–CH\} bridge of the DAD ligand of [(DAD)W(NR)Cl$_2$] 1 and 2 and the literature known Lewis base adduct [W(NtBu)$_2$Cl$_2$(dad)] [9] (Table 1). The shift of signals to higher fields in 1 and 2 in comparison with the adduct [W(NtBu)$_2$Cl$_2$(dad)] is a first indication that DAD is bonded in its reduced ene-diamido (DAD$^{2–}$) form. This tendency was observed for other known R,H–DAD$^{2–}$ complexes of d-electron poor transition metals [6, 8,10].

**Table 1.** $^1$H and $^{13}$C chemical shifts for 1, 2 and reference [W(NtBu)$_2$Cl$_2$(dad)] [9].

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### Table II

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\delta_H$</th>
<th>$\delta_C$</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>C$_6$D$_6$</td>
<td>6.41</td>
<td>–</td>
</tr>
<tr>
<td>1</td>
<td>CDCl$_3$</td>
<td>7.05</td>
<td>110.5</td>
</tr>
<tr>
<td>2</td>
<td>C$_6$D$_6$</td>
<td>6.58</td>
<td>111.6</td>
</tr>
<tr>
<td>[W(N^tBu)$_2$Cl$_2$(dad)]</td>
<td>CD$_2$Cl$_2$</td>
<td>8.13</td>
<td>153.2</td>
</tr>
</tbody>
</table>

In the EI mass-spectra, peaks referring to molecular ions of 1 and 2 were observed. No molecular ions for free DAD in its oxidized neutral form typically found for DAD Lewis base adducts were observed. In both cases, molecular fragments [M – Me$_2$C=CH$_2$]$^+$ and [M – 2 Me$_2$C=CH$_2$]$^+$ appear without any traces of [DAD]$^+$ or [M – DAD]$^+$. According to the fragmentation pattern, the DAD ligand is strongly bonded to the metal centre. This again may be taken as an indication for an interaction of a formally W(VI) metal atom with DAD in its fully reduced form DAD$_2^-$ (form A and not B).

![Diagram](image1)

For the phenyl derivative 1 a single crystal suitable for an X-ray structure analysis was grown. The molecular structure is shown in Figure 1, selected bond distances and angles in Table 2. The coordination sphere of tungsten is a square pyramid with a basal plane defined by two chlorine and nitrogen atoms of the DAD moiety. In accordance with the common definition [6c, 8, 10] for folded R,R’–DAD$_2^-$ ligands in cyclopentadienyl complexes, we observe the supine conformation as the most stable ground state conformer of 1 of two possible conformers.
Although the molecule has no crystallographically imposed symmetry plane, the data show very similar parameters for bond distances and angles within the chelate DAD$^{2-}$ ligand. For example $W(1)$–$N(1)$ 1.958(2) Å and $W(1)$–$N(2)$ 1.964(2) Å are in the deviation range of 3σ and can be considered equal. This explains the existence of only one signal in $^1$H- and $^{13}$C-NMR for tert-butyl groups as well as for protons of the {CH–CH} bridge of DAD$^{2-}$. These DAD $W$–$N$ bond lengths of $1$ are considerably shorter than those found in the Lewis adduct $[W(N^tBu)_2Cl_2(dad)]$, where DAD acts as a neutral 4e$^-$ donor. Table 3 displays, that the shortening of $W$–$N$ bonds is accompanied by a lengthening of both $C$–$N$ bonds and a shortening of the $C$–$C$ bond, when the DAD is bonded in its reduced ene-diamido form [3c, 6, 8–11]. In contrast to the Lewis adduct $[W(N^tBu)_2Cl_2(dad)]$ the metal centre in $1$ and $[^6Bu,Me$–DAD$]W(NPh)(NSiMe_3)C_6H_4$ [3c] does not lie in the plane defined by $C_2N_2$ moiety of DAD ligands forming folded conformation. The folding is not accompanied by a high degree of

![Figure 1. Molecular structure of 1 (ORTEP).](image-url)
pyramidalisation at the N atoms as the sum of angles at nitrogen atoms of 1 are very close to 360° (Table 3).

**Table 3.** Comparison of bond lengths (Å) and angles (°) within the DAD moiety.

<table>
<thead>
<tr>
<th>Complex</th>
<th>W–N</th>
<th>N–C</th>
<th>Σ°N</th>
<th>W–E(C₂N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.958(2)</td>
<td>1.367(3)</td>
<td>359.2(5)</td>
<td>1.1033(1)</td>
</tr>
<tr>
<td></td>
<td>1.964(2)</td>
<td>1.368(3)</td>
<td>359.2(5)</td>
<td>1.1033(1)</td>
</tr>
<tr>
<td>[([t-Bu,Me–DAD)W(NPh)(NSiMe₃)₂C₆H₄] [3c]</td>
<td>1.957(3)</td>
<td>1.393 (5)</td>
<td>359.6(7)</td>
<td>1.285(2)</td>
</tr>
<tr>
<td></td>
<td>2.025(3)</td>
<td>1.385 (5)</td>
<td>356.3(7)</td>
<td>1.285(2)</td>
</tr>
<tr>
<td>W(N'Bu)₂Cl₂(dad)] [9]</td>
<td>2.507(7)</td>
<td>1.24(1)</td>
<td>360.0</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>2.533(7)</td>
<td>1.27(1)</td>
<td>360.0</td>
<td>0.038</td>
</tr>
<tr>
<td>[DAD] [11]</td>
<td></td>
<td>1.264(2)</td>
<td>1.468(2)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.267(2)</td>
<td>1.470(2)</td>
<td>–</td>
</tr>
</tbody>
</table>

Preliminary studies on the reactivity show, that 1 and 2 don’t form stable adducts with σ–donor ligands such as THF or PMe₃. This is in contrast to o-phenylene diamido complex [W(NPh)Cl₂(NSiMe₃)₂C₆H₄] [3a, b] described by Boncella. Luck of Lewis acidity can be explained by the –M effect of the benzene ring, which is absent in our case. Furthermore it is well known, that the Me₃Si group possesses weak π–acceptor properties, while Me₃C is a +I substituent, making the nitrogen atoms better σ, π–donors.

**Conclusions**

We present new tungsten(VI) key complexes with two W–Cl functions for further transformations, that are supported by two strong, sterically demanding and redox active σ, π–donor ligands with flexible electron count: the imido ligand may act as a 4-6 electron donor, the ene-diamido ligand as a 6-8 electron donor. With respect to known o-phenylene diamido compounds, the newly synthesized complexes are more electron rich and less Lewis acidic. The DAD²⁻ ligand turned out to be stereorigid and strongly bonded, a precondition for further use of this synthon in catalysis.
Experimental Part

General: All reactions and manipulations were carried out under argon using standard Schlenk tube techniques. Solvents were refluxed in the presence of an appropriate drying agent and distilled: C₆D₆ and hexane (Na/K alloy), THF (Na/benzophenone) and toluene (Na), CH₂Cl₂ and CDCl₃ (CaH₂). Literature methods were employed for the synthesis of starting materials [W(NR)Cl₄(L)] (R = Ph, Cy) [7], 1,4-di-tert-butyl-1,4-diaza-but-a-1,3-diene (DAD) [12] and Li₂DAD [6c]. Melting points were measured with a Büchi MP B-540 (uncorrected). C, H and N analyses were carried out with a Heraeus CHN-Rapid analyser. Mass spectra were taken on Varian MAT CH-7a (EI, 70 eV). ¹H- and ¹³C{¹H}-NMR spectra were recorded with Bruker AMX300 and DRX500; chemical shifts were referenced to the residual signals of C₆D₆: ¹H (δ 7.15) and ¹³C (δ 128.0); CDCl₃: ¹H (δ 7.24) and ¹³C (δ 77.0). Infrared spectra were recorded with Bruker IFS 88 FT; samples as Nujol mulls between KBr plates.

Preparation of [W(NPh)(DAD)Cl₂] 1. A solution of Li₂DAD (1.86 g, 10.2 mmol) in 50 mL THF was added dropwise to a solution of [W(NPh)Cl₄(thf)] (5.00 g, 10.2 mmol) in 100 mL THF at –80°C, changing the colour of the reaction mixture from green to dark brown. After warming to RT the solution was stirred for 8 h. The evaporation of the solvent produced brown oil, which was extracted with two portions of 250 mL toluene. The analytical pure compound was obtained after recrystallisation from CH₂Cl₂/hexan. Yield 2.97 g (57%). M.p. 243°C (dec.).

Anal. Calcd. for C₁₆H₂₅N₃Cl₂W (M = 514.15 g·mol⁻¹): C 37.38, H 4.90, N 8.17. Found: C 37.15, H 4.87, N 8.24. MS–EI: 515 (M⁺, 26%), 459 (M⁺ – Me₂C=CH₂, 16%), 403 (M⁺ – 2 Me₂C=CH₂, 67%), 57 (100%). ¹H-NMR (C₆D₆, 200 MHz, 300 K): 7.20 (d, 3J_H–H= 7.9 Hz, 2H, o-Ph), 6.93 (pseudo-t, 3J_H–H= 7.7 Hz, 2H, m-Ph), 6.69 (t, 3J_H–H= 7.5 Hz, 1H, o-Ph), 6.41 (s, 2H, CH-DAD), 1.31 (s, 18H, tBu-DAD). ¹H-NMR (CDCl₃, 300 MHz, 300 K): 7.38 (pseudo-t, 3J_H–H= 7.8 Hz, 2H, m-Ph), 7.23 (d, 3J_H–H= 7.8 Hz, 2H, o-Ph), 7.14 (t, 3J_H–H= 7.5 Hz, 1H, o-Ph), 7.05 (s, 2H, CH-DAD), 1.51 (s, 18H, tBu-DAD). ¹³C{¹H}-NMR (CDCl₃, 75 MHz, 300 K): 128.4, 127.8 and 126.2 (Ph), 110.5 (CH-DAD), 62.7 (C(CH₃)₃-DAD), 30.1 (C(CH₃)₃-DAD). IR (KBr, cm⁻¹): 3057(w), 3032(w), 1585(m), 1402(w), 1394(w), 1367(s), 1259(m), 1224(w), 1205(s), 1116(w), 1091(w, b), 1066(m), 1040(w), 1030(w), 1020(w), 995(w), 956(w), 918(w), 908(w), 864(w), 833(m), 798(m), 791(w), 760(s), 717(w), 688(m), 619(w), 586(w), 553(w), 534(w), 523(w), 509(w). Tm.p. 243°C (dec).

X-ray diffraction experiment. A crystal suitable for X-ray was grown by cooling CH₂Cl₂/tolune (1:1) solution to –30°C. Crystal data: Molecular formula C₁₆H₂₅Cl₂N₃W, formular weight 514.14 g·mol⁻¹, a = 10.5842(11), b = 15.9211(11), c = 11.9470(11) Å, β =
103.474(8)°, \( V = 1957.8(3) \text{ Å}^3 \), \( Z = 4 \), \( D_{\text{calc}} = 1.744 \text{ g cm}^{-3} \), monoclinic, space group \( P2_1/n \).

**Data collection:** Stoe IPDS2, Mo-K\( \alpha \) radiation (\( \lambda = 0.71073 \text{ Å} \)), graphite monochromatic, 190(2) K, crystal size 0.27x0.16x0.11 mm\(^3\), \( \omega \)-scan, 2.17 ≤ 2\( \Theta \) ≤ 25, -12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -12 ≤ l ≤ 14, 15737 reflections measured, 3433 independent (\( R_{\text{int}} = 0.035 \)), \( \mu(\text{MoK\( \alpha \)}) = 6.173 \text{ mm}^{-1} \), numerical absorption correction.

**Structural Analysis and Refinement:** The structure was solved by direct methods (SHELXS-97), refinement was done by full matrix least squares on \( F^2 \) (SHELXL-97 [13]); all non-hydrogen atoms were refined with anisotropic temperature factors; H(1) and H(2) were located and refined isotropically, the other hydrogen atoms using a riding model and isotropic temperature factors of \( U(H) = 1.2U_{\text{eq}}(C) \) for CH and \( 1.5U_{\text{eq}}(C) \) for CH\(_3\), 214 refined parameters, final \( R1 = 0.016 \) for 3035 reflections with \( I > 2\sigma(I) \), \( wR2 = 0.0372 \) for all data, largest difference peak and hole 0.688/-0.690 e \text{ Å}^{-3} near the W atom.

**CCDC 264372 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.**

**Preparation of [W(NCy)(DAD)Cl\(_2\)]** 2. This compound was synthesised with 70% yield using the same procedure as for 1 from [W(NCy)Cl\(_4\)]\(_2\) M.p. 204.8°C. Anal. Calcd. for C\(_{16}\)H\(_{31}\)N\(_3\)Cl\(_2\)W (M = 520.20 g·mol\(^{-1}\)): C 36.94, H 6.01, N 8.08. Found: C 37.67, H 6.25, N 8.08.

**References**


[4] A. Merkoulov, K. Harms and J. Sundermeyer, in press; Alexei Merkoulov, Jörg Sundermeyer, 8th Seminar of PhD Students on Organometallic Chemistry, 2003, Hruba Scala, Czech Republic; see also Chapter IV and V.


Chapter III

Synthesis and Investigations on the Crystal Structure of a Dinuclear Diazadiene Molybdenum Oxo-Imido with an Unique $N_3Mo(\mu-O)_2MoN_3$ Core

Summary

Ligand metathesis of a diimido and dioxo precursor complexes $[\text{Mo}(X)_2\text{Cl}_2(\text{dme})]$ ($X = \text{O}, \text{N}^\text{tBu}$) leads to the mixed oxo-imido derivative $[\text{Mo}(\text{N}^\text{tBu})(\text{O})\text{Cl}_2(\text{dme})]$ (1). By treatment with $\text{Li}_2\text{DAD}$ (DAD = 1,4-di-tert-butyl-1,4-diaza-1,3-diene), 1 is converted into the diazadiene complex $[(\text{DAD})\text{Mo}(\text{N}^\text{tBu})(\text{O})]_2$ (2). The crystal structure determination on a non merohedrel twin of 2 revealed a dinuclear molecular structure with close to symmetrical bridging oxygen atoms. The smaller oxo ligand tends to be a better bridging functionality than the imido oxygen: The unprecedented $N_3Mo(\mu-O)_2MoN_3$ configuration is favored with respect to a $\text{ON}_2Mo(\mu-N)_2MoN_2\text{O}$ core. Compared to other known molybdenum DAD complexes, 2 reveals some degree of pyramidalization at the N atoms of the DAD ligand. In accord with the Mo–N, N–C and C–C bond distances, complex 2 is best described as an ene-diamido complex of formally six valent molybdenum.

Introduction

Complexes on the basis of the 1,4-diaza-1,3-diene (R,R’–DAD) ligand backbone have been the focus of attention for many years. Due to several possible coordination modes and their redox activity, R,R’–DAD ligands can stabilize metals in a wide range of formal oxidation states.\textsuperscript{[1]} While R,R’–DAD is a strong $\pi$–acceptor stabilizing low-valent metal centers, the 2-electron reduced R,R’–DAD$^2$– ligand, best described as ene-diamido functionality, can be envisaged as a strong $\pi$–donor stabilizing high-valent metal centres. The diversity of substitutes
at nitrogen and carbon atoms offers a perfect handle for the fine-tuning of electronic and steric ligand features in catalytic applications. For example, complexes of the late transition metals and DAD ligands with bulky electron-withdrawing aryl substituents at nitrogen are used extensively in olefin oligomerisation and polymerization.\[2\]

Following our previous investigations\[3\] of high valent N-organo imido complexes of group VI metals having other strong $\pi$–donor ligands such as cyclopentadienyl, oxo, alkylidene or metalated phosphorus ylide ligands, we set out to follow up the chemistry of ene-diamido ligands with imido and oxo complexes of molybdenum. Here we wish to report the synthesis of an oxo-imido key complex $[\text{Mo}(\text{N}_t\text{Bu})(\text{O})\text{Cl}_2(\text{dme})] \ (1)$ and its conversion into DAD derivative $[(\text{DAD})\text{Mo}(\text{N}_t\text{Bu})(\text{O})]_2 \ (2)$ (DAD = 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene).

### Results and discussion

The oxo-imido complex $1$ is formed in good yield by ligand metathesis between the known dioxo and diimido complexes $[\text{Mo}(\text{O})_2\text{Cl}_2(\text{dme})]^{[4]}$ and $[\text{Mo}(\text{N}_t\text{Bu})_2\text{Cl}_2(\text{dme})]^{[5a]}$ in DME (Scheme 1). In accordance with the spectroscopic data and with related structurally characterized $d^0$ oxo-imido complexes$^{[5b]}$, $1$ probably has an octahedral structure with trans chloro ligands and the strongest $\pi$–donor ligands $\text{O}^2–$ and $\text{NR}^2–$ in cis configuration. Reduction of DAD by lithium in THF affords the ene-diamide $\text{Li}_2\text{DAD}$.[$^6]$ The latter reacts with $1$ to form the ene-diamido title complex $2$ in fair yield of 59 percent. $2$ is a hexane soluble, dark purple diamagnetic compound. $^1\text{H}$- and $^{13}\text{C}$-NMR data reveal equivalent tert-butyl groups at the DAD and imido N atoms as well as equivalent methine protons at the C$_2$ bridge of DAD.

An alternative synthetic approach to DAD$^{2–}$ complex $2$ failed. Complex $[\text{Mo}(\text{N}_t\text{Bu})(\text{O})\text{Cl}_2(\text{dme})] \ (1)$ reacts with one equivalent of DAD to yield $[\text{Mo}(\text{N}_t\text{Bu})(\text{O})\text{Cl}_2(\text{dad})] \ (3)$ but the following reduction with $\text{C}_8\text{K}$ surprisingly produces only small amounts of the desirable product $2$. The formation of complex $3$ was confirmed with reaction in NMR tube and characterised by $^1\text{H}$- and $^{13}\text{C}$-NMR spectroscopy.

Indeed, the NMR data for $2$ are consistent with either a mononuclear tetrahedral structure or a binuclear species with either a mirror plane or a center of inversion. The EI mass spectra show mononuclear molecular ions $[(\text{DAD})\text{Mo}(\text{N}_t\text{Bu})(\text{O})]$ as the highest peaks. In order to gain further insight into the nature of the title complex, single crystals for an X-ray crystal structure determination were grown from a hexane solution.
Scheme 1. Preparation of oxo-imido complex 2.

Data collection and structure refinement

A crystal with the dimensions 0.35 x 0.15 x 0.15 mm was mounted on a glass fibre using the "oil drop method". Data was collected at T = 193 K with a STOE IPDS area detector system using graphite monochromated Mo-Kα radiation. The crystal was orthorhombic with a = 19.913(2), b = 18.437(2), c = 9.547(2) Å and happened to be a non-merohedrel twin with only minor overlapping of the reflections. Only one orientation matrix was used during the integration of the intensities. Overlapping reflections were ignored. This procedure led to 13576 integrated intensities; 2877 were independent (R\text{int} = 12.26%); the completeness was 90% for Θ\text{max} = 25°. No absorption correction was applied (C\text{28H58M}o\text{2N}6O\text{2}: M = 702.68, μ = 7.46 cm\text{−1} for Z = 4). Structure solution (direct methods) and refinement in the space group Pnma was performed using the SHELX-97 programs, all non hydrogen atoms anisotropic, hydrogens with fixed isotropic temperature factors using a riding model. In the final stage of the refinement two residual peaks in the difference Fourier map (distance 3.09 Å) were interpreted as disorder positions of atoms Mo(1) and Mo(2) (non crystallographic transformation nearly to "x, y, .5-z"). The ratio of the occupancies (all atoms of the main part versus atoms Mo(3) and Mo(4)) refined to 0.907 : 0.093, no disordered positions of the light atoms could be located; final residuals: wR2 = 11.28 % (for all unique reflections), conventional R1 = 4.86 % (for 1346 reflections with I > 2σ(I)), 205 refined parameters.
Fig. 1. Molecular structure of the 2.

Fig. 2. Coordination polyhedra and disorder in the crystal structure of 2. Open bonds: minor part of disorder, positions of light atoms calculated.

**Molecular structure of 2**

The molecular structure of 2 in the crystal is shown in Fig. 1, selected bond distances and angles in Table 1. Fig. 2 displays the disorder and inner coordination spheres. The title complex 2 is binuclear in the solid state. Both molybdenum atoms are tetragonal pyramidal coordinated by five atoms, an axial imido nitrogen atom, two basal nitrogen atoms of the DAD ligand, and two oxygen atoms of the central planar Mo$_2$(µ-O)$_2$ core. All six basal atoms N$_2$O$_2$N$_2$ lie in the same plane. Both imido ligands adopt an anti collinear orientation. There is a crystallographic mirror plane defined by the two metal centres and the two Mo–N(imido) vectors. Although there is no inversion symmetry unit, the Mo$_2$(µ-O)$_2$ core can be considered as symmetrical by means of bond lengths’ standard deviation; Mo–O bond distances are 1.958(5)
and 1.951(5) Å. These bond distances correlate with the value for Mo–O single bonds, e.g. in A\[^{8a}\] approx. 1.95 Å (Scheme 2).

### Table 1. Selected distances (Å) and angles (°) in 2.

<table>
<thead>
<tr>
<th>Bond/Crystallographic Position</th>
<th>Distance/ Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-N(1)</td>
<td>1.333(11)</td>
</tr>
<tr>
<td>C(1)-C(1_8)</td>
<td>1.42(2)</td>
</tr>
<tr>
<td>C(2)-N(1)</td>
<td>1.493(13)</td>
</tr>
<tr>
<td>C(6)-N(2)</td>
<td>1.464(13)</td>
</tr>
<tr>
<td>C(9)-N(3)</td>
<td>1.345(11)</td>
</tr>
<tr>
<td>C(9)-C(9_8)</td>
<td>1.389(17)</td>
</tr>
<tr>
<td>C(10)-N(3)</td>
<td>1.501(13)</td>
</tr>
<tr>
<td>C14-N(4)</td>
<td>1.471(14)</td>
</tr>
<tr>
<td>Mo(1)-N(2)</td>
<td>1.716(8)</td>
</tr>
<tr>
<td>Mo(1)-O(1_8)</td>
<td>1.959(5)</td>
</tr>
<tr>
<td>Mo(1)-O(1)</td>
<td>1.959(5)</td>
</tr>
<tr>
<td>Mo(1)-N(1)</td>
<td>2.036(8)</td>
</tr>
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<td>2.036(8)</td>
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<td>Mo(2)-N(3)</td>
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<td>Mo(2)-N(3_8)</td>
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<td>Mo(3)-Mo(4)</td>
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<td>N(2)-Mo(1)</td>
<td>106.2(3)</td>
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<tr>
<td>N(2)-Mo(1)-O(1)</td>
<td>106.2(3)</td>
</tr>
<tr>
<td>O(1_8)-Mo(1)-</td>
<td>76.8(3)</td>
</tr>
<tr>
<td>N(2)-Mo(1)-N(1)</td>
<td>111.4(3)</td>
</tr>
<tr>
<td>O(1_8)-Mo(1)-</td>
<td>142.2(3)</td>
</tr>
<tr>
<td>O(1)-Mo(1)-N(1)</td>
<td>89.4(3)</td>
</tr>
<tr>
<td>N(2)-Mo(1)</td>
<td>111.4(3)</td>
</tr>
<tr>
<td>O(1_8)-Mo(1)-</td>
<td>89.4(3)</td>
</tr>
<tr>
<td>O(1)-Mo(1)</td>
<td>142.2(3)</td>
</tr>
</tbody>
</table>

To date, no other structurally characterized example of an \( \text{N}_3\text{Mo}(\mu-O)\text{MoN}_3 \) coordination polyhedron is known for direct comparison (CCSD search 3’2004). However, a similar framework has been found in a dinuclear thiolato(oxo) complex of the type \( \text{S}_2(\text{O})\text{Mo}(\mu-O)\text{Mo(S}_2\text{O}) \) \( A \). In contrast to 2, the two square pyramids with their apical Mo–O vectors in \( A \) are in a syn configuration to each other.
Several molybdenum R,R’–DAD complexes have been described in literature, examples are given in B–E.\textsuperscript{[8, 9]} Type B\textsuperscript{[8b]} represents a 4-electron Lewis base adduct of the diazadiene ligand to a formally six-valent molybdenum centre, characterized by long Mo–N distances of \( \sim 2.40 \, \text{Å} \), short N–C distances of \( \sim 1.27 \, \text{Å} \) and long C–C distances of \( \sim 1.48 \, \text{Å} \) and perfectly planar N atoms. It is anticipated for a metal of d\textsuperscript{0} electron configuration, that there is no M→L backbonding in B. This is demonstrated by negligible differences between the discussed bond lengths in free DAD\textsuperscript{[10]} and B (Table 2). However, due to its low-lying \( \pi^* \)–orbitals, neutral R,R’–DAD can easily be reduced by more electron rich metal centers to form the coordinated radical anion [R,R’–DAD]\textsuperscript{−\textsuperscript{[1, 11]}} and ene-diamido [R,R’–DAD]\textsuperscript{2−} ligands.\textsuperscript{[1, 6, 8c, 8d, 12, 13]} Examples for molybdenum complexes with fully reduced R,R’–DAD moiety are C\textsuperscript{[8c]} and D.\textsuperscript{[8d]}

The structural parameters of their MN\textsubscript{2}C\textsubscript{2} units are similar to phenylene-1,2-diamido systems E\textsuperscript{[9]} (Table 2). Typically, flat\textsuperscript{[12]} and folded\textsuperscript{[13]} ene-diamido units MN\textsubscript{2}C\textsubscript{2} are known. In folded conformations, the metal is located out of the N\textsubscript{2}C\textsubscript{2} plane (E\textsuperscript{NCCN}) as indicated by the distance \( d(M-E_{NCCN}) \) which is listed in Table 2. In close to flat conformations as found in C and D, the Mo atom is only \( \sim 0.3 \, \text{Å} \) out of plane. Perfectly flat conformations are found in R,R’–DAD adducts such as B. Similar to B the nitrogen atoms of C and D are close to planar (sum of angles

\[ \text{Scheme 2. Related DAD complexes and reference compounds.} \]
at N atoms $\Sigma^\circ N \sim 360^\circ$). By comparing the M–N, N–C, and C–C bond distances, our title complex 2 is best described as an ene-diamide of d$^5$-Mo(VI) and not as neutral diazadiene adduct at d$^2$-Mo(IV). In contrast to C and D, the Mo atom of 2 is located 0.951(1) Å out of the N$_2$C$_2$ plane and the sum of angles at the nitrogen atoms, $\Sigma^\circ N$ 355(2) and 357(2), indicates a trend for pyramidalization, similar to that found for phenylene-diamido complexes of type E. Table 2 reveals the trend, that the shortening of the Mo–N and C–C bonds is accompanied by a lengthening of N–C bonds and a higher degree of pyramidalization at the N atoms. Currently we are investigating the scope of this statement by exploring other diazadiene imido complexes of the early transition metals.

Table 2. Comparison of the selected bond distances (Å) and angles (°) in reference compounds.

<table>
<thead>
<tr>
<th></th>
<th>Mo – N</th>
<th>N – C</th>
<th>C – C</th>
<th>d(M–E$^{NCCN}$)</th>
<th>$\Sigma^\circ N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBu-DAD</td>
<td>—</td>
<td>1.264 – 1.267</td>
<td>1.468 (2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>2.388 – 2.399</td>
<td>1.267 – 1.271</td>
<td>1.476 (3)</td>
<td>0</td>
<td>360.0 (5)</td>
</tr>
<tr>
<td>C</td>
<td>2.081 – 2.092</td>
<td>1.353 (4)</td>
<td>1.363 (2)</td>
<td>0.3295(1)</td>
<td>360.0 (3)</td>
</tr>
<tr>
<td>D</td>
<td>1.957 – 2.075</td>
<td>1.354 – 1.392</td>
<td>1.344 (8)</td>
<td>0.3047(5)</td>
<td>359 (1)</td>
</tr>
<tr>
<td>E</td>
<td>1.996 – 2.078</td>
<td>1.373 – 1.407</td>
<td>1.409 – 1.452</td>
<td>0.085 – 1.148</td>
<td>356.3 – 360.0</td>
</tr>
<tr>
<td>2</td>
<td>2.017 – 2.036</td>
<td>1.333 – 1.345</td>
<td>1.389 – 1.420</td>
<td>0.951 (1)</td>
<td>355.5 – 357.2</td>
</tr>
</tbody>
</table>

Experimental Part

**General:** All reactions and manipulations were carried out under argon using standard Schlenk tube techniques. Solvents were refluxed in the presence of an appropriate drying agent and distilled: C$_6$D$_6$ and hexane (Na/K alloy), THF and DME (Na/benzophenone) and toluene (Na). Literature methods were employed for the synthesis of starting materials [Mo(O)$_2$Cl$_2$(dme)]$_4$,[4] [Mo(N$^\circ$Bu)$_2$Cl$_2$(dme)]$_5$,[5] and 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene (DAD),[14] and Li$_2$DAD.[6] Melting points were measured with a Büchi MP B-540 (uncorrected). C, H and N analyses were carried out with a Heraeus CHN-Rapid analyser. Mass spectra were taken on Varian MAT CH-7a (EI, 70 eV). $^1$H- and $^{13}$C($^1$H)-NMR spectra were recorded with Bruker AMX300 and DRX500; chemical shifts were referenced to the $^1$H (δ 7.15) and $^{13}$C (δ 128.0) residual signals of the C$_6$D$_6$. Infrared spectra were recorded with Bruker IFS 88 FT; samples as Nujol mulls between KBr plates.
Preparation of [Mo(N\text{t}Bu)(O)Cl\text{2}(dme)] 1. Under argon [Mo(N\text{t}Bu)\text{2}Cl\text{2}(dme)] (400 mg, 1.00 mmol) and [Mo(O)\text{2}Cl\text{2}(dme)] (290 mg, 1.00 mmol) were dissolved in DME (10 mL) and refluxed for 3 days. Volatiles were removed in vacuum and the yellow-green product was extracted into 30 mL toluene. Yield 500 mg (73%). M.p. 71°C. Anal. Calcd. for C\textsubscript{8}H\textsubscript{19}NCl\textsubscript{2}O\textsubscript{3}Mo (M = 344.09 g·mol\textsuperscript{-1}): C 27.93, H 5.57, N 4.07. Found: C 25.39, H 5.55, N 4.01.

\textsuperscript{1}H-NMR (C\textsubscript{6}D\textsubscript{6}, 300 MHz, 300 K): 3.41 (s, 6H, Me), 3.02 (s, 4H, CH\textsubscript{2}), 1.41 (s, 9H, N\text{t}Bu).

\textsuperscript{13}C {\textsuperscript{1}H}-NMR (C\textsubscript{6}D\textsubscript{6}, 75 MHz, 300 K): 70.6 (s, CH\textsubscript{2}), 63.2 (bs, Me), 27.8 (s, N\text{t}Bu). IR (KBr, cm\textsuperscript{-1}): 3160 (m, vb), 1587 (m), 1405 (w), 1362 (s), 1276 (w), 1259 (w), 1228 (s, b), 1188 (w), 1162 (w), 1137 (w), 1108 (w), 1086 (s), 1044 (s, b), 1005 (vw), 961 (m), 910 (s), 861 (s), 826 (m), 799 (m), 725 (w), 627 (w), 592 (w), 572 (m), 515 (w).

Preparation of [(DAD)Mo(N\text{t}Bu)(\mu-O)]\textsubscript{2} 2. To a solution of 1 (500 mg, 1.45 mmol) in THF (20 mL) at –80°C was added dropwise a solution of Li\textsubscript{2}DAD (265 mg, 1.45 mmol) in THF (20 mL). Within 30 min the reaction mixture reached room temperature. After 8h at room temperature, THF was removed at reduced pressure and the product was extracted with two portions of hexane (30 mL). The analytical pure dark-violet compound was obtained by crystallisation from hexane at –80°C. Yield: 300 mg (59%). M.p. 190°C (dec.). Anal. Calcd. for C\textsubscript{28}H\textsubscript{58}N\textsubscript{6}O\textsubscript{2}Mo\textsubscript{2} (M = 702.69 g·mol\textsuperscript{-1}): C 47.86, H 8.32, N 11.96. Found: C 47.44, H 8.02, N 11.55. MS-EI: 353 (M/2\textsuperscript{+}, 1%), 338 (M/2\textsuperscript{+} – Me, 2%), 57 (100%).

\textsuperscript{1}H-NMR (C\textsubscript{6}D\textsubscript{6}, 500 MHz, 300 K): 6.75 (s, 2H, CH-DAD), 1.51 (s, 18H, \text{t}Bu-DAD), 1.38 (s, 9H, N\text{t}Bu).

\textsuperscript{13}C {\textsuperscript{1}H}-NMR (C\textsubscript{6}D\textsubscript{6}, 125 MHz, 300 K): 119.9 (CH-DAD), 74.6 (N\text{C}(CH\textsubscript{3})\textsubscript{3}), 72.2 (CH\textsubscript{2}-DME), 64.4 and 63.7 (C(CH\textsubscript{3})\textsubscript{3}-dad), 58.7 (CH\textsubscript{3}-DME), 29.2 and 28.5 (C(CH\textsubscript{3})\textsubscript{3}-dad) 27.9 (NC(CH\textsubscript{3})\textsubscript{3}).

Reaction of [Mo(N\text{t}Bu)(O)Cl\text{2}(dme)] 1 with DAD. 50 mg of [Mo(N\text{t}Bu)(O)Cl\text{2}(dme)] (145 \textmu mol) were dissolved in approx. 0.8 mL dry C\textsubscript{6}D\textsubscript{6} and 1.2 equivalent of DAD (29 mg, 172 \textmu mol) was added. The formation of the product [Mo(N\text{t}Bu)(O)Cl\text{2}(dad)] 3 was found to be quantitative according to amount of evolved DME and supported by the \textsuperscript{1}H-\textsuperscript{13}C-NMR spectra. \textsuperscript{1}H-NMR (C\textsubscript{6}D\textsubscript{6}, 500 MHz, 300 K): 7.00 and 6.91 (s, 1H, CH-dad), 3.32 (s, 4H, free CH\textsubscript{2}-DME), 3.11 (s, 6H, free CH\textsubscript{3}-DME), 1.60 (s, 9H, \text{t}Bu-dad), 1.57 (s, 9H, N\text{t}Bu) 1.43 (s, 9H, \text{t}Bu-dad).

\textsuperscript{13}C {\textsuperscript{1}H}-NMR (C\textsubscript{6}D\textsubscript{6}, 125 MHz, 300 K): 152.8 and 152.1 (C\textsubscript{H}-dad), 74.6 (NC(CH\textsubscript{3})\textsubscript{3}), 72.2 (CH\textsubscript{2}-DME), 64.4 and 63.7 (C(CH\textsubscript{3})\textsubscript{3}-dad), 58.7 (CH\textsubscript{3}-DME), 29.2 and 28.5 (C(CH\textsubscript{3})\textsubscript{3}-dad) 27.9 (NC(CH\textsubscript{3})\textsubscript{3}).
Chapter III

References


Chapter III


Chapter IV

Dynamic Effects in 1,4-Diaza-1,3-diene Complexes
[M(NR)₂(DAD)] of Chromium Triad Metals

Abstract

The complete set of group VI complexes with the common formula [(DAD)M(NR)₂] (DAD = 1,4-diaza-1,4-di-tert-butyl-buta-1,3-diene; M = Cr, Mo, W; R = 'Bu, Mes) was synthesised. The ¹H-NMR spectra show temperature dependence for all compounds. The X-ray structure of [(DAD)Cr(N'tBu)₂] and [(DAD)Mo(N'tBu)₂] were solved in order to gain insight into the nature of the dynamic behaviour in solution. From the NMR experiments thermodynamic parameters of the energetic barriers have been calculated. A side product in the synthesis of [(DAD)Cr(N'tBu)₂], a dinuclear d¹–d¹ complex [Cr₂(N'tBu)₂(µ-N'tBu)₂(µ-DAD)] with rather unusual bridging ene-diamido, ligand was isolated and characterised under slightly different reaction conditions.

Introduction

In the last decade a number of publications were devoted to the chemistry of the reduced 1,4-diaza-1,3-diene (R,R'-DAD) ligand with transition metals of groups IV[¹,²] and V[³,⁴]. Some of them were supported by computational results[⁵] and experimental thermodynamic data for the energy of inversion of the folded R,R'-DAD²– moiety.[⁶] Much less is known about complexes of group VI elements with reduced R,R'-DAD²– backbone.[⁷] Our recent investigations of monoimido complexes of molybdenum [(DAD)Mo(N'tBu)(µ-O)]₂[⁸a] and tungsten [(DAD)W(N'tBu)Cl₂]⁸b carrying the reduced DAD²– ligand at a d⁰ metal centre of coordination number five reveal folded MN₂C₂ rings, but do not show temperature dependent NMR spectra that may indicate dynamic processes.
All known structurally characterised $R,R’$–DAD$_2^-$ complexes of group VI elements reveal coordination numbers five and six. We were interested in investigating the influence of the coordination number on the dynamic behaviour in solution and set out to synthesise tetrahedrally coordinated complexes supported by two strong $\pi$-donor imido ligands, in particular, diimido DAD$^-$ compounds of Cr, Mo and W (DAD = 1,4-diaza-1,4-di-tert-butylbuta-1,3-diene).

**Results and discussion**

**Preparative studies**

The standard method for the preparation of $R,R’$–DAD$_2^-$ complexes with earlier transition metals is the reaction of dilithium salts [Li$_2$(R,R’–DAD)], which usually contain four solvent molecules of THF or Et$_2$O, with metal halides. The known salts [Li$_2$DAD(THF)$_4$]$^{[21]}$ and
[Li₂DAD(Et₂O)₄]^{3c} can be easily obtained as crystalline materials by reaction of DAD with lithium in the corresponding solvent.

According to the $^1$H- and $^{13}$C-NMR spectra the amount of solvent molecules depends on the time of drying in vacuum. Furthermore, the orange crystals change their colour and slowly turn yellow with time when kept in a Glove Box. After drying at 25°C/10⁻⁴ mbar for 48 hours the spectra do not show any signals of solvate molecules. The obtained substance seems to have the constitution Li₂DAD and is insoluble in hexane, poorly soluble in toluene and much better in Et₂O or THF forming in the solution the solvates described above. Unfortunately we were not able to grow crystals for an X-ray structure analysis of the obtained Li₂DAD compound. In comparison with its solvate forms the Li₂DAD has some advantages. First of all, it does not change its composition with time and consequently is better for precise weighing. As an alternative method a standard solution of Li₂DAD in THF or Et₂O can be prepared and used in further reactions.\[4d]\ In this work the abbreviation Li₂DAD is used for the solvate-free form, which may be stored in a Glove Box.

Surprisingly, no diamagnetic compound was observed after the addition of Li₂DAD solution to a solution of [Cr(NᵗBu)₂Cl₂]^{9} in THF or Et₂O at −78°C. However, when the same reagents are mixed at room temperature and THF or toluene as solvent is rapidly added, the target complex [(DAD)Cr(NᵗBu)₂] (1) can be isolated by fractional sublimation with poor yield (approx. 20%). Complex 1 is extremely soluble in hexane and aromatic solvents. It has limited solubility in DMSO and slowly decomposes in this solvent at room temperature.
A single crystal of 1 suitable for X-ray analysis was obtained from the gas phase by warming a closed, evacuated Schlenk tube with 50 mg of 1 to 30°C. The molecular structure of 1 is presented in Fig. 2 and selected bond lengths and angles are listed in Table 1. This is the first example of the structurally characterised chromium complex with R,R’–DAD₂⁻ ligand.[10]

![Molecular structure of (DAD)Cr(N₆Bu)₂](image)

**Fig. 2.** The molecular structure of [(DAD)Cr(N₆Bu)₂] 1 with thermal ellipsoids at 50% probability. Space group P 2₁/c, Z = 4.

**Table 1.** Selected bond lengths (Å) and angles (°) for 1.

<table>
<thead>
<tr>
<th>Bond Lengths &amp; Angles</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(1)–N(13)</td>
<td>1.630(2)</td>
</tr>
<tr>
<td>Cr(1)–N(18)</td>
<td>1.650(2)</td>
</tr>
<tr>
<td>Cr(1)–N(4)</td>
<td>1.942(2)</td>
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<td>Cr(1)–C(2)</td>
<td>2.534(3)</td>
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<td>Cr(1)–C(3)</td>
<td>2.540(3)</td>
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<tr>
<td>N(4)–C(3)</td>
<td>1.342(4)</td>
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<td>N(1)–C(2)</td>
<td>1.334(4)</td>
</tr>
<tr>
<td>C(2)–C(3)</td>
<td>1.386(4)</td>
</tr>
<tr>
<td>N(1)–Cr(1)–N(4)</td>
<td>86.16(9)</td>
</tr>
<tr>
<td>N(13)–Cr(1)–N(18)</td>
<td>114.8(1)</td>
</tr>
<tr>
<td>N(13)–Cr(1)–C(14)</td>
<td>178.4(2)</td>
</tr>
<tr>
<td>Cr(1)–N(13)–C(14)</td>
<td>151.6(2)</td>
</tr>
</tbody>
</table>

The coordination polyhedron of the chromium atom in 1 is a distorted tetrahedron formed by four nitrogen atoms. The imido moieties exhibit short chromium–nitrogen bond lengths Cr(1)–N(13) 1.630(2) Å and Cr(1)–N(18) 1.650(2) Å. These distances are in good agreement with the range of 1.60–1.64 Å found in the structurally characterised d⁰ diimido complex of chromium [Cr(N₆Bu)₂Cl₂].[11] The imido metal–nitrogen–carbon angles in 1 differ from each other. One imido group Cr(1)–N(13)–C(14) shows an almost perfect linear
conformation of 178.4(2)°, while the second one exhibits some deviation from the ideal \(sp\)-hybridisation of the nitrogen atom, 151.6(2)° for \(\text{Cr}(1)–\text{N}(18)–\text{C}(19)\). In spite of such differences in the angle values they still correlate to the range of 159–173° found in the crystal structure of [\(\text{Cr}(\text{N}^3\text{Bu})_2\text{Cl}_2\)].

The DAD\(^2\^-\text{Cr}\) metallacycle exhibits a folded conformation in solid state. The metal centre is not located in the plane defined by \(\text{N}_2\text{C}_2\) atoms of the DAD\(^2\^-\) moiety with a metal–to–plane distance of 0.9070(4) Å. With respect to the definition of *prone* and *supine* conformers [4d, 6, 12] for the folded \(\text{R},\text{R}’–\text{DAD}^2\^-\) ligand in cyclopentadienyl complexes we suggest using it also in the presence of the isolobal \(\text{RN}^2\^-\) ligand.

Unfortunately, in folded tetrahedral DAD\(^2\^-\) complexes with two equal substituents the *supine-prone* nomenclature is not applicable. For further discussion a new definition is suggested for this case. For example, with respect to the group \(\text{X}_1\) the complex \([\text{DAD}\text{M}(\text{X}_1)(\text{X}_2)]\), \(\text{X}_1 = \text{X}_2\), exhibits *supine* conformation and with respect to the \(\text{X}_2\) a *prone* one. Thus, group \(\text{X}_1\) can be considered to be pro-*supine* and \(\text{X}_2\) pro-*prone*.

Applying this terminology to the molecular structure of 1 the imido group \(\text{N}(18)–\text{C}(19)\) has a pro-*supine* position and \(\text{N}(13)–\text{C}(14)\) has a pro-*prone* one.

Two nitrogen–chromium distances \(\text{Cr}(1)–\text{N}(1)\) 1.930(2) Å and \(\text{Cr}(1)–\text{N}(4)\) 1.942(2) Å indicate strong \(\pi\)-interaction between chromium and nitrogen atoms. Furthermore, in comparison with the free DAD ligand\(^{[13]}\) and its donor–acceptor complex with \(d^0\) Lewis acids [\(\text{Mo(O)}_2\text{Cl}_2(\text{dad})\)]\(^{[14]}\) and tungsten [\(\text{W}(\text{N}^3\text{Bu})_2\text{Cl}_2(\text{dad})\)]\(^{[15]}\) the decrease of C–C bond distance and
the increase of C–N bond distances is observed in 1 (Table 2). The same tendency was found in other structurally characterised R,R’–DAD\(^{2–}\) \(d^0\) complexes with elements of group IV\(^[[1, 2]\), V\(^[[3, 4]\) and VI\(^[[7, 8]\) in which the \(C_2N_2\) backbone exhibits very similar structural parameters in the reduced state. Selected parameters for the DAD\(^{2–}\) ligand in reference complexes [(DAD)Mo(N\(^t\)Bu)(\(\mu\)-O\)]\(^2[8a]\) and [(DAD)W(N\(^t\)Bu)Cl\(_2\)]\(^[8b]\) are presented in Table 2.

### Table 2. Selected structural parameters (distances in Å) of the DAD\(^{2–}\) ligand in 1 and reference complexes [Mo(O)\(_2\)Cl\(_2\)(dad)], [W(N\(^t\)Bu)\(_2\)Cl\(_2\)(dad)], [(DAD)Mo(N\(^t\)Bu)(\(\mu\)-O)]\(_2\) and [(DAD)W(N\(^t\)Bu)Cl\(_2\)]. In the formulas “DAD” represents the dianionic form DAD\(^{2–}\) and “dad” represents the donor–acceptor bonded ligand.

<table>
<thead>
<tr>
<th>Complex</th>
<th>DAD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C – C</td>
</tr>
<tr>
<td>1</td>
<td>1.386(4)</td>
</tr>
<tr>
<td>DAD(^{[13]})</td>
<td>1.468(2)</td>
</tr>
<tr>
<td></td>
<td>1.470(2)</td>
</tr>
<tr>
<td>Mo(O)(_2)Cl(_2)(dad)(^{[14]})</td>
<td>1.476(3)</td>
</tr>
<tr>
<td></td>
<td>1.271(3)</td>
</tr>
<tr>
<td>[(DAD)Mo(N(^t)Bu)((\mu)-O)](^2[8a])</td>
<td>1.39(1)</td>
</tr>
<tr>
<td></td>
<td>1.42(1)</td>
</tr>
<tr>
<td>[W(N(^t)Bu)(_2)Cl(_2)(dad)](^{[15]})</td>
<td>1.45(1)</td>
</tr>
<tr>
<td></td>
<td>1.27(1)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>[(DAD)W(N(^t)Bu)Cl(_2)](^{[8b]})</td>
<td>1.375(4)</td>
</tr>
<tr>
<td></td>
<td>1.368(3)</td>
</tr>
</tbody>
</table>

* no data for standard deviation was obtained from *.cif file
** Mo and \(C_2N_2\) moiety define a crystallographic mirror plane

In spite of the short distances of approx. 2.5 Å between the metal centre and carbon atoms of the double bond in 2, the latest computations\(^{[5a, b, d]}\) suggest that there is no considerable chemical interaction. In contrast, the short M–N bond distances below 2 Å indicate a strong metal–nitrogen interaction with DAD\(^{2–}\) moiety. Therefore the reduced DAD\(^{2–}\) moiety has to be considered as an ene-diamido ligand in 1.

As already mentioned, the DAD\(^{2–}\) ligand in 1 exhibits the folded conformation producing geometrical non-equivalence of the two imido groups. Thus three signals with relative
intensities 9:9:18 are expected for $^1$Bu groups in the $^1$H-NMR spectra and three sets of signals in $^{13}$C-NMR. Surprisingly, the room temperature $^1$H-NMR spectrum of 1 consists of two sharp singlets of equal intensities in the aliphatic region and two sets of $^1$Bu signals were observed in the $^{13}$C-NMR spectra. In order to throw light on this phenomenon we have measured the temperature-dependent spectra of 1.

![Fig. 3. The $^1$H-DNMR spectra for [(DAD)Cr(N$^1$Bu)$_2$] (1), d$_8$-toluene (500 MHz).](image)

The dynamic picture obtained for 1 is presented in Fig. 3. One of the two signals is split into two singlets with equal intensities, while the second one does not exhibit any line broadening. The coalescence temperature is ~190 K. Additionally, the CH protons of the DAD$^{2-}$ ligand are sharp singlets within the range of temperatures. This renders the DAD$^{2-}$ ligand to be in symmetrical surrounding, because an AA’ spin system must be observed in the asymmetrical case.$^{[16]}$ Thus the split signals have to be referred to as two non-equivalent imido groups, which are also expected from X-ray studies.
The magnetic equivalence of the two imido groups is caused by an *inversion* of the \( \text{DAD}^{2-} \) moiety, similar to that found in the isolobal complexes \([\text{Cp}_2(R,R'-\text{DAD})M]\), \((M = \text{Ti, Zr, Hf})\).\(^{[6b]}\) The complex with planar \( \text{DAD}^{2-} \) ligand seems to be the transition state of the *inversion* in both cases.

The ‘flipping’ of the \( \text{DAD}^{2-} \) double bond is an alternative term for this phenomenon. In terms of ‘pro-supine’–‘pro-prone’ nomenclature one imido group changes its mode from ‘pro-supine’ to ‘pro-prone’, while the second one is automatically forced to change from ‘pro-prone’ to ‘pro-supine’.

In order to increase the yield of \([\text{DAD}]\text{Cr(NTBu)}_2\) (1) an alternative method, based on *in situ* reduction of \([\text{Cr(NTBu)}_2\text{Cl}_2]\) with magnesium in the presence of the DAD ligand, was applied. Surprisingly, in an EI mass spectrum of the product an intensive peak referred to as a dinuclear molecular ion was observed. This synthetic method yielded a new dimeric \(d^{10}-d^{10}\) product 2 instead of mononuclear complex 1. In this case, the first reaction step is probably the reduction of the starting monomeric complex into the bridged dimeric species \([\text{Cr(NTBu)}(\mu-N^t\text{Bu})\text{Cl}]_2\).\(^{[9]}\) Further reduction in presence of DAD leads to the formation of 2.
A single crystal of 2 suitable for X-ray analysis was obtained by cooling a concentrated hexane solution to –30°C. The molecular structure of 2 is presented in Fig. 4; selected bond lengths and angles are listed in Table 3.

**Fig. 4.** The molecular structure of 5•C₆H₁₄ with thermal ellipsoids at 50% probability. Space group P nma, Z = 4. The disordered methyl groups at C(12) and solvent hexane molecule are not shown for clarity.

**Table 3.** Selected bond lengths (Å) and angles (°) for 2.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(1)–N(1)</td>
<td>1.653(2)</td>
</tr>
<tr>
<td>Cr(1)–N(2)</td>
<td>1.854(2)</td>
</tr>
<tr>
<td>Cr(1)–N(3)</td>
<td>1.821(2)</td>
</tr>
<tr>
<td>Cr(1)–N(4)</td>
<td>1.824(2)</td>
</tr>
<tr>
<td>Cr(1_7)–N(1_7)</td>
<td>1.653(2)</td>
</tr>
<tr>
<td>Cr(1_7)–N(2_7)</td>
<td>1.854(2)</td>
</tr>
<tr>
<td>Cr(1_7)–N(3)</td>
<td>1.821(2)</td>
</tr>
<tr>
<td>Cr(1_7)–N(4)</td>
<td>1.824(2)</td>
</tr>
<tr>
<td>N(2_7)–C(100_7)</td>
<td>1.402(3)</td>
</tr>
<tr>
<td>N(2)–C(100)</td>
<td>1.402(3)</td>
</tr>
</tbody>
</table>
2 is a dimer with two bridging imido and one bridging DAD ligands. Each Cr atom has a distorted tetrahedral coordination sphere formed by two bridging and one terminal imido nitrogen atoms and one nitrogen atom from the DAD ligand.

A crystallographic mirror plane in the molecule is defined by atoms N(3), N(4), C(1) and C(12). As a consequence the bridging imido moieties are symmetrical within each bridge. Furthermore, the Cr$_2$N$_2$ unit can be considered as full symmetrical one within range of 3$\sigma$, the Cr(1)–N(3) distance being 1.821(2) Å and the Cr(1)–N(4) distance 1.824(2) Å. These values are very close to those found in the dinuclear chromium(V) compound [Cr(NDip)(µ-N$^t$Bu)Cl]$_2$.$^{[11]}$ The Cr–N distances lie in both cases between 1.79–1.84 Å and the Cr–Cr distance of 2.4411(4) Å is slightly shorter in 2 than in [Cr(NDip)(µ-N$^t$Bu)Cl]$_2$, where d(Cr–Cr) is approx. 2.49 Å. The two terminal imido ligands have very short Cr–N bond lengths of 1.653(2) Å and close to linear Cr–N–C angles of 158.0(2)$^\circ$. The latter is in good agreement with these parameters in 1 and [Cr(N$^t$Bu)$_2$Cl]$_2$.$^{[11]}

![Fig. 5. Different bridging coordination modes for R,R’–DAD ligands in dinuclear complexes with M–M bonding and their designation.$^{[10,17]}$](image)

Several coordination modes are found for bridging R,R’–DAD ligand in dinuclear complexes with M–M bonding.$^{[10]}$ Structurally characterised complexes containing modes A and B have been known for a long time,$^{[17]}$ while coordination mode C is relative new and only one example, namely [Mn$_2${µ–(η$^1$,η$^2$–Ph$_2$–DAD)}$_2$(THF)$_2$]$^{[18]}$, of such coordination type has been described to date. In the coordination modes A and B one or two carbon atoms take part in the bonding to one of two metal centres. In contrast to this, in the case C the DAD ligand is bonded only through nitrogen atoms to metals.
Chapter IV

The bonding mode in 2 differs from all types A–C. It is similar to C, because no carbon–metal interaction is possible, but each nitrogen atom is bonded only to one chromium atom. This defines the difficulty by ascribing a definite bonding situation between M–M moiety and the DAD ligand in 2. An additional complexity consists in there being several ligand oxidation states: neutral R,R′–DAD, anion–radical R,R′–DAD− and dianion R,R′–DAD2−.[1-7, 17, 19] Furthermore, the DAD ligand in 2 is bonded to two metal centres, which makes the comparison with monomeric species not completely adequate.

Nevertheless, the comparison with Cr(VI) mononuclear complexes [Cr(N′Bu)2Cl2][11] and [Cr(N)(N′Pr2)3][20a], Cr(V) dinuclear complexes [Cr(NDip)(μ-N′Bu)Cl]2[11] and [Cr(μ-N)(N′Pr2)2]2[20b] reveals, that the bonding situation between chromium and nitrogen of the DAD ligand should be considered as an example of a 4e− amido one (Table 4). The Cr(1)–N(2) and Cr(1,7)–N(2,7) distances of 1.854(2) Å in 2 are even shorter than the same M–N bond length in the mononuclear chromium DAD2− complex 1 (1.930(2) and 1.942(2) Å). Furthermore, there is a crystallographically characterised example [Cr(CO)4(Cy,R′–DAD)] of the formal Cr(0) with the neutral Cy,R′–DAD ligand (Fig. 6).[21] In this case the ligand is coordinated to the metal by two donor–acceptor 2e− bonds with M–N bond lengths of 2.176(3) and 2.1863(3) Å. As a consequence the C2N2 moiety exhibits bond parameters similar to the free DAD[13] ligand: C–C bond length is 1.438(5) Å and C–N bond lengths are 1.278(5) and 1.266(5) Å.

Fig. 6. Reference chromium complexes [Cr(N′Bu)2Cl2][11] [Cr(N)(N′Pr2)3][20a] [Cr(NDip)(μ-N′Bu)Cl]2[11] [Cr(μ-N)(N′Pr2)2]2[20b] and [Cr(CO)4(Cy,R′–DAD)].[21]
Table 4. Typical M–N distances in the imido and amido bonding situation.

<table>
<thead>
<tr>
<th>Complex</th>
<th>M–N type</th>
<th>d(M–N), Å</th>
</tr>
</thead>
</table>
| [Cr(NBu₂)₂Cl₂]¹¹ | imido | 1.60(1)  
|          |         | 1.62(1)  
|          |         | 1.63(1)  
|          |         | 1.64(1)  |
| [Cr(N)NiPr₂₃]²⁰a | amido | 1.840(3)  
|          |         | 1.842(3)  
|          |         | 1.844(2)  |
| [Cr(μ-N)NiPr₂₂]²⁰b | amido | 1.839(3)  
|          |         | 1.842(3)  
|          |         | 1.845(3)  
|          |         | 1.845(3)  |
| [Cr(NC₆H₃iPr₂-2,6)(μ-NBu)Cl₂]¹¹ | bridging imido | 1.79(2)  
|          |         | 1.80(2)  
|          |         | 1.83(2)  
|          |         | 1.84(2)  |
| [Cr(CO)₄(Cy,R′–dad)]²¹ | amino | 2.176(3)  
|          |         | 2.186(3)  |
| 1        | imido   | 1.630(2)  
|          |         | 1.650(2)  |
|          | DAD²⁻   | 1.930(2)  
|          |         | 1.942(2)  |
| 2        | imido   | 1.653(2)  |
|          | bridging imido | 1.821(2)  
|          |         | 1.824(2)  |
|          | DAD²⁻   | 1.854(2)  |

The dimetallacycle Cr(1)–Cr(1₇)–N(2₇)–C(100₇)–C(100)–N(2) in 2 is not absolutely flat but exhibits a very large extent of planarity, with σ_{plane} = 0.065 Å (σ_{plane} = \sqrt{\sum_{i=1}^{n} d_i^2 / n - 3}, where n is the number of atoms and d_i is the perpendicular distance to the calculated least-square plane).²²²² The largest deviation from the plane is 0.064(2) Å.

The deviation from planarity can be also discussed using the plane defined by the N₂C₂ atoms of the DAD ligand. This moiety is absolutely planar because of the crystallographic mirror plane. Two chromium atoms are located slightly out of the N₂C₂ plane with a metal–to–plane distance of 0.2847(3) Å.

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Short C(100)–C(100_7), 1.357(5) Å, and long C(100)–N(2) and C(100_7)–N(2_7), 1.402(3) Å, distances compared to the free DAD ligand[13] and complex [Cr(CO)_4(Cy,R’–dad)][21] give additional assurance that complex 2 is the unique example of a bridging mode for the flat DAD^2– ligand coordinated to the M–M (d^1–d^1) backbone.

Complex 2 exhibits temperature-independent ^1H- and ^13C-NMR spectra in the range of 180–320 K. The ^13C-NMR spectra for 2 show 7 signals as expected, which can be divided into three groups. In the aromatic area one signal for the CH group with δ = 117.5 ppm is assigned to the DAD^2– ligand. Three signals in the region of 55–70 ppm for tertiary carbon atoms as well as three peaks in the aliphatic region of 30–35 ppm correspond to the three different tBu-groups: imido, bridging imido and DAD^2–. In the ^1H-NMR spectra 4 signals with relative intensities 2:18:18:18 are observed. In the aliphatic region between 1 and 2 ppm three singlets belong to tBu-groups. The last signal with the smallest intensities is assigned to the CH group of the DAD^2– ligand. Surprisingly this signal is extremely shifted to high field with a chemical shift of approximately 3.5 ppm.

Indeed, studies on the reaction of [Cr(N^tBu)_2Cl_2] with Li_2DAD in toluene at room temperature confirm formation of three diamagnetic products: mononuclear complex 1 (approx. 30%), dinuclear complex 2 (approx. 15%) and free DAD ligand (approx. 55%). This again underlies the tendency of chromium to take part in redox reactions and to form dinuclear d^1–d^1 species as by-products.

In contrast to chromium the last two members of the triad, molybdenum and tungsten, are more difficult to reduce in their highest oxidation state. They form stable adducts with neutral Lewis bases, such as DME or pyridine to complete their coordination sphere. In this situation the in situ reduction can be a good method to obtain diimido DAD^2– complexes starting from diimido dichloride educts.

The target DAD^2– complexes 3-6 were obtained by reaction of known compounds [Mo(N^tBu)_2Cl_2(dme)],[23a], [Mo(NMes)_2Cl_2(dme)],[23b] [W(N^tBu)_2Cl_2py_2],[23c] and [W(NMes)_2Cl_2(dme)][23d] with Mg in the presence of DAD using THF as solvent. The products were isolated in yield 28%–60%. Other reducing agents, such as C_8K or Li, either produced lower yields or the desired product wasn’t obtained.
The \(^{1}\text{Bu}\) imido derivatives 3 and 5 are well soluble in hexane. They exhibit high volatility and can be sublimed at 100°C/10\(^{-2}\) mbar. In contrast, the complexes with aromatic mesityl imido ligand 4 and 6 show poor solubility in hexane, but dissolve in toluene or benzene. They cannot be purified by sublimation, but can be crystallised from aromatic solvents. Compounds 3-6 are partially soluble in DMSO but decompose slowly in this solvent at room temperature.

The EI mass spectra of 3-6 contain peaks, which correlate to molecular ions. The abstraction of methyl radical and isobutylene was found to be the specific pathway of fragmentation for these complexes.

A single crystal of 3 suitable for X-ray analysis was obtained by cooling a concentrated hexane solution to –80°C. Selected bond lengths and angles for 3 are listed in Table 5 and the molecular structure is shown in Fig. 7.

The coordination geometry at the Mo atom in 3 is a slightly distorted tetrahedron, formed by four nitrogen atoms. For comparison of structural features the previously reported tetrahedral complex \([\text{Mo}(\text{NDip})_2(\text{NHDip})_2]\)\(^{24}\) and structurally characterised molybdenum complexes with reduced R,H–DAD ligands (Fig. 8) can be used.
Fig. 7. The ORTEP representation of 3 with thermal ellipsoids at 40% probability. Space group P 2\textsubscript{1}/c, Z = 4. The disordered methyl groups at C(11) and C(15) are not shown.

Table 5. Selected bond lengths (Å) and angles (°) for 3.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(1)–N(1)</td>
<td>2.012(2)</td>
<td>C(1)–C(2)</td>
<td>1.394(4)</td>
</tr>
<tr>
<td>Mo(1)–N(2)</td>
<td>2.011(2)</td>
<td>N(2)–C(2)</td>
<td>1.362(4)</td>
</tr>
<tr>
<td>Mo(1)–N(3)</td>
<td>1.755(2)</td>
<td>Mo(1)–N(3)–C(11)</td>
<td>164.2(2)</td>
</tr>
<tr>
<td>Mo(1)–N(4)</td>
<td>1.745(2)</td>
<td>Mo(1)–N(4)–C(15)</td>
<td>164.7(2)</td>
</tr>
<tr>
<td>Mo(1)–C(1)</td>
<td>2.493(3)</td>
<td>Mo(1)–N(4)–C(15)</td>
<td>164.7(2)</td>
</tr>
<tr>
<td>Mo(1)–C(2)</td>
<td>2.493(3)</td>
<td>N(1)–Mo(1)–N(2)</td>
<td>85.82(9)</td>
</tr>
<tr>
<td>N(1)–C(1)</td>
<td>1.358(4)</td>
<td>N(3)–Mo(1)–N(4)</td>
<td>113.8(1)</td>
</tr>
</tbody>
</table>

Both imido fragments in 3 possess almost linear Mo–N–C angles, 164.1(2)° and 164.7(2)° respectively, and short Mo–N distances, 1.756(2) and 1.745(2) Å. In [Mo(NDip)\textsubscript{2}(NHDip)\textsubscript{2}] the imido Mo–N bond lengths are 1.764(2) and 1.753(2) Å, and the imido Mo–N–C angles are 155.7(3) and 172.3(3)°, which correspond to M≡N triple bonds.
**Chapter IV**

![Structural diagrams](image)

**Fig. 8.** Structurally characterised DAD\(^2^-\) complexes of molybdenum.\(^{[7b-e, 8a]}\)

**Table 6.** Selected structural parameters (distances in Å) of the DAD\(^2^-\) ligand in 3 and reference complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>C – C</th>
<th>N – C</th>
<th>M – N</th>
<th>M – C</th>
<th>M – (DAD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.394(4)</td>
<td>1.358(4)</td>
<td>2.011(2)</td>
<td>2.493(3)</td>
<td>1.1507(2)</td>
</tr>
<tr>
<td>DAD(^{[13]})</td>
<td>1.468(2)</td>
<td>1.264(2)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mo(O(_2)Cl(_2))(dad)(^{[14]})</td>
<td>1.476(3)</td>
<td>1.267(4)</td>
<td>2.388(2)</td>
<td>3.138(3)</td>
<td>0.00*</td>
</tr>
<tr>
<td>[Cp(Dip,H–DAD)MoCl(_3)](^{[7c]})</td>
<td>1.363(2)</td>
<td>1.351(2)</td>
<td>2.092(1)</td>
<td>2.960(2)</td>
<td>0.3295(1)</td>
</tr>
<tr>
<td>[Cp(iPr,H–DAD)MoI(_2)](^{[7d]})</td>
<td>1.372(4)</td>
<td>1.335(3)</td>
<td>2.067(2)</td>
<td>2.924(2)</td>
<td>0.1276(4)</td>
</tr>
<tr>
<td>[(iPr,H–DAD)Mo(_2)(OiPr)(_4)(µ-OiPr)(_2)](^{[7b]})</td>
<td>1.344(8)</td>
<td>1.354(7)</td>
<td>1.957(5)</td>
<td>2.840(6)</td>
<td>0.3047(5)</td>
</tr>
<tr>
<td>[(iPr,H–DAD)(_2)MoCl(_2)](^{[7e]})</td>
<td>1.369(4)</td>
<td>1.332(3)</td>
<td>2.038(2)</td>
<td>2.901(3)</td>
<td>0.1222(2)</td>
</tr>
<tr>
<td>[(DAD)Mo(N(^t)Bu)(µ-O)](_2)](^{[8a]})</td>
<td>1.39(1)</td>
<td>1.33(1)</td>
<td>2.018(8)</td>
<td>2.676(9)</td>
<td>0.958(1)</td>
</tr>
</tbody>
</table>

*Mo and C\(_2\)N\(_2\) moiety form crystallographic mirror plane*
The comparison of the structural features of \( R,H\)-DAD\(^{2-} \) ligands in known molybdenum complexes is presented in Table 6. The above-mentioned tendency of the decrease of C–C bond distance and increase of C–N bond distances in \( R,R'\)-DAD\(^{2-} \) moiety compared to the non-reduced ligand and its donor–acceptor complexes is also observed for 3. The structural parameter in \( R,R'\)-DAD\(^{2-} \)M metallacycle are in good agreement with those found in other molybdenum complexes (Table 6). The short M–N and C–C bonds point out that the DAD ligand in 3 should be considered an as an ene-diamido type.

It is interesting that the Mo atom of 3 is located 1.1507(2) Å out of the \( N_2C_2 \) plane, while the larger part of the reference complexes exhibits close to planar metallacycles with metal–to–ligand plane distance in the range of 0.1–0.3 Å. A large deviation from planarity has been previously observed only in the dinuclear complex \([(DAD)Mo(N^tBu)(\mu-O)]_2^{[8a]} \), where this distance is approx. 1 Å. Thus the DAD\(^{2-} \)M moiety in 3 exhibits a folded conformation, which results in non-equivalence of the imido ligands, and the similar dynamic behaviour observed for \([(DAD)Cr(N^tBu)_2] \) (1) is also expected for \([(DAD)Mo(N^tBu)_2] \) (3).

Surprisingly, in the room temperature \(^1\)H- and \(^13\)C-NMR spectra of 3-6 two sets of sharp signals for non-equivalent imido ligands are observed. In order to throw light on this phenomenon the \(^1\)H-NMR spectra were recorded at different temperatures. These DNMR spectra for 3, 4 and 6 are presented in Fig. 9, Fig. 10 and Fig. 11, respectively.

![Fig. 9. The \(^1\)H-DNMR spectra for \([(DAD)Mo(N^tBu)_2] \) (3) in d\(^6\)-DMSO (500 MHz).](image)
Fig. 10. The $^1$H-DNMR spectra for [(DAD)W(N$^t$Bu)$_2$] (4) in d$_6$DMSO (500 MHz).

Fig. 11. The $^1$H-DNMR spectra for [(DAD)W(NMes)$_2$] (6) in d$_6$DMSO (500 MHz). The relative intensities are not maintained.
For all complexes 3-6 the signals of imido groups coalesce or begin to coalesce with increasing temperature. This temperature dependence was also observed for 1, but the most amazing difference between chromium complex 1 and molybdenum/tungsten complexes 3-6 lies in the observed temperature ranges. Indeed, two equivalent imido groups were found in the NMR spectra of 1 at room temperature, while in the spectra of 3-6 the imido groups are non-equivalent at this temperature. Thus, a NMR sample of 1 has to be cooled down in order to reach the coalescence point, a corresponding sample of 3-6 has to be warmed up.

In spite of the difference in coalescence temperatures for 1 and 3-6 of about 200 K, this dynamic behaviour seems to have the same origin. It has been suggested to assign this behaviour to the inversion of the DAD$^{2–}$ moiety as discussed for 1. The complex with planar DAD$^{2–}$ ligand is considered to be the transition state of such inversion.

**Activation parameters of the DAD$^{2–}$ inversion**

In order to estimate the thermodynamic parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) of the inversion barrier in 1 the standard Band-Shape Analysis$^{[25]}$ and the Win-Dyna 32 program$^{[26]}$ were applied. A problem arises with the method for such measurements in the case of compounds 3-6. Because the coalescence point is not reached or not sufficiently exceeded, estimated values of the rate constants applying Band-Shape Analysis cannot be perfectly reliable. The Selective Inversion-Recovery experiments$^{[27]}$ were not successful due to lack of difference in the chemical shifts of peaks, which have to be measured. So the most precise but time-consuming 2D-EXSY method for this range of the rate constants was applied.$^{[28]}$

$^d$-$\text{t}$-Toluene was used for complexes 1, 3-4 and $^d$-$\text{C}_6\text{D}_5\text{Br}$ for 5-6, because the rate constant values are considerably smaller for the latter compounds and so higher temperatures had to be applied. These solvents are aromatic and the solvent effect on the calculated thermodynamic parameters should be negligible. For computations $^t$Bu signals of the imido groups for complexes 1, 3 and 5 and all mesityl signals for complexes 4 and 6 were taken. The values of the rate constants were calculated at different temperatures and this dependence was used in the standard Eyring equation$^{[25]}$ to determine the thermodynamic parameters for the inversion of the DAD$^{2–}$ ligand in complexes 1 and 3-6:

$$k = \frac{\sigma k_B T}{h} \cdot e^{-\frac{\Delta H^\ddagger - T\Delta S^\ddagger}{RT}}$$


where \( k_B \) is Boltzmann’s constant, \( T \) is absolute temperature, \( h \) is Planck’s constant and \( R \) is the universal gas constant. The transmission constant \( \sigma \) was taken equal to one for this type of barrier. The logarithmic variant allows calculating \( \Delta H^e \) and \( \Delta S^e \) values from experimental data of the rate constants \( k \) depending on the temperature \( T \). By plotting the experimental data in a half-logarithmic way \( \Delta H^e \) and \( \Delta S^e \) values can be obtained from a linear fit.

\[
\lg \left( \frac{k}{T} \right) = 10.32 - \frac{\Delta H^e}{19.13} \left( \frac{1}{T} \right) + \frac{\Delta S^e}{19.13}
\]

The fitting program \( PFIT45W^{[29]} \) was applied to arrays of the experimental data (Fig. 12 and Fig. 13), in which a temperature uncertainty of 0.5 K and a relative uncertainty of 10% (for 2D-EXSY) and 20% (for 1D-Band-Shape) in rate constants were taken to estimate the error of the fitted parameters.

\[\text{Fig. 12. Eyring equation plot for complex 1.}\]
Fig. 13. Eyring equation plot for complexes 3-4 (d⁸-toluene) and 5-6 (d⁵-C₆D₅Br). For reason of accuracy three different mixing times (tₚ) at certain temperatures were applied.[²⁸]

The activation enthalpy ΔH° and entropy ΔS° values are presented in Table 7. The calculated values of the free Gibbs energies ΔG°₂₉₈ for complexes 1 and 3-6 (approx. 40–90 kJ·mol⁻¹) correlate with those (approx. 50–70 kJ·mol⁻¹) found in the isolobal biscyclopentadienyl (R,R’–DAD)₂⁻ complexes of group IV elements [Cp₂(R,R’–DAD)M], (M = Ti, Zr, Hf). This range of energies was also predicted for the ring inversion by DFT calculations.[⁵ᵃ] According to these calculations steric factors are supposed to be of little relevance for the bending of the DAD⁻ ring. The high energy of the unfavourable planar conformation has electronic nature.[⁵ᵃ] This means that a value near to zero is expected for the activation entropy ΔS° and a strong positive value for the activation enthalpy ΔH°.

Table 7. The activation enthalpy ΔH° and entropy ΔS° values for the ring inversion in the DAD⁻ complexes 1 and 3-6.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Tₑ, K</th>
<th>ΔG°₂₉₈, kJ·mol⁻¹</th>
<th>ΔH°, kJ·mol⁻¹</th>
<th>ΔS°, J·mol⁻¹·K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>197</td>
<td>36 ± 3</td>
<td>40 ± 1</td>
<td>12 ± 7</td>
</tr>
<tr>
<td>3</td>
<td>&gt; 400</td>
<td>81 ± 2</td>
<td>85 ± 1</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>4</td>
<td>~ 390</td>
<td>83 ± 2</td>
<td>83 ± 1</td>
<td>1 ± 3</td>
</tr>
<tr>
<td>5</td>
<td>&gt;&gt; 405</td>
<td>92 ± 3</td>
<td>91 ± 2</td>
<td>−2 ± 4</td>
</tr>
<tr>
<td>6</td>
<td>~ 390</td>
<td>98 ± 4</td>
<td>94 ± 2</td>
<td>−13 ± 6</td>
</tr>
</tbody>
</table>

* in d⁶-DMSO for 3-6 and in d⁸-toluene for 1
Indeed, these quantum mechanical predictions are in good agreement with experimental
data for complexes 1 and 3-6. The $\Delta S^\neq$ values are in the range of $-10 - +10 \, J\text{-mol}^{-1}\text{-K}^{-1}$ and estimated $\Delta H^\neq$ values are strong positive 40 – 90 $kJ\text{-mol}^{-1}$. The activation enthalpy decreases in complexes [(DAD)M(NR)$_2$] from tungsten to chromium and as a consequence the coalescence temperature lies below room temperature for the chromium complex 1, while for the molybdenum and tungsten complexes 3-6 coalescence can be reached only at high temperatures.

Although entropy does not play a big energetic role in the inversion it can be considered to depend on the metal nature and substituent in the imido ligand. The substitution of tBu groups with the more bulky mesityl group in the imido ligand decreases activation entropy $\Delta S^\neq$ (approx. 10 $J\text{-mol}^{-1}\text{-K}^{-1}$). A similar effect can be observed by metal substitution; for example, activation entropy values for tungsten complexes are about 10 $J\text{-mol}^{-1}\text{-K}^{-1}$ smaller than for the same complexes of molybdenum and chromium. Nevertheless the enthalpy part is the most important one and the change in activation entropies has almost no effect on the standard free Gibbs activation energies $\Delta G^\neq_{298}$ for the ring inversion.

**Conclusions**

The DAD$^{2-}$ complex [(DAD)Cr(N$^t$Bu)$_2$] (1) was obtained by the reaction of [Cr(N$^t$Bu)$_2$Cl$_2$] with Li$_2$DAD in THF or toluene at room temperature. The molecular structure of 1 reveals a folded conformation for the DAD$^{2-}$M metallacycle and exhibits the first example of a structurally characterised chromium complex with fully reduced R,R’–DAD$^{2-}$ ligand. In situ reduction of [Cr(N$^t$Bu)$_2$Cl$_2$] with Mg powder in the presence of DAD led to formation of the dinuclear $^{1-1}$ complex [Cr$_2$(N$^t$Bu)$_2$(μ–N$^t$Bu)$_2$(μ–DAD)] (2), which, according to its molecular structure, exhibits an unusual Cr–Cr bridging coordination of the DAD$^{2-}$ ligand.

The reaction of molybdenum and tungsten bisimido dichloride complexes of the type [M(NR)$_2$Cl$_2$L$_2$] with DAD in the presence of magnesium led to the formation of bisimido DAD$^{2-}$ complexes [(DAD)M(NR)$_2$], M = Mo, R = tBu (3), Mes (4); M = W, R = tBu (5), Mes (6). According to the molecular structure of 3 the DAD$^{2-}$ ligand has a folded conformation creating magnetic non-equivalence of the imido substituents.

The NMR spectra of 1 and 3-6 confirm the presence of two non-equivalent imido substituents: at 180 K for 1 and at room temperature for 3-6. These signals coalesce or begin to coalesce with increasing temperature. Based on the NMR experiments (1D Band Shape Analysis for 1 and 2D-EXSY for 3-6) calculations of the thermodynamic parameters ($\Delta H^\neq$ and $\Delta S^\neq$) for the
DAD$^{2-}$ ring inversion reveal activation entropy values $\Delta S^\neq$ close to zero for all complexes. The activation enthalpy has the most prominent contribution in the formation of the ‘flat’ transition state that correlates with quantum mechanical computations.$^{[5a]}$ This transition state seems to be significantly stabilised in the case of chromium compared to molybdenum and tungsten as indicated by a huge difference $> 50$ kJ mol$^{-1}$ in activation enthalpies and $> 200$ K in coalescence temperatures.

**Experimental Part**

**General:** All reactions and manipulations were carried out under argon using standard Schlenk tube techniques. Solvents were dried in the presence of an appropriate drying agent and distilled: C$_6$D$_6$, toluene and hexane (Na/K alloy); THF (Na/benzophenone); d$^6$-DMSO (molecular sieve 4Å); d$^5$-C$_6$D$_5$Br (CaH$_2$). Literature methods were employed for the synthesis of starting materials [Cr(N$_t$Bu)$_2$Cl$_2$]$^{[9]}$ [Mo(N$_t$Bu)$_2$Cl$_2$(dme)]$^{[23b]}$ [Mo(NMes)$_2$Cl$_2$(dme)]$^{[23c]}$ [W(N$_t$Bu)$_2$Cl$_2$py$_2$]$^{[23d]}$ [W(NMes)$_2$Cl$_2$(dme)]$^{[23d]}$ 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene (DAD)$^{[30]}$ and Li$_2$DAD.$^{[4d]}$ Melting points were measured with a Büchi MP B-540 (uncorrected). Elemental analyses (C, H, N) were carried out with a Heraeus CHN-Rapid analyser. Mass spectra were taken on Varian MAT CH-7a (EI, 70 eV). $^1$H- and $^{13}$C{$^1$H}-NMR spectra were recorded with Bruker AMX300 and DRX500 spectrometer; chemical shifts were referenced (in ppm) to the $^1$H ($\delta$ 7.15) and $^{13}$C ($\delta$ 128.0) residual signals of the C$_6$D$_6$, $^1$H ($\delta$ 2.03) and $^{13}$C ($\delta$ 20.3) residual signals of the methyl group of d$^8$-toluene, and $^1$H ($\delta$ 2.49) residual signals of the d$^6$-DMSO. Infrared spectra were recorded with Bruker IFS 88 FT as Nujol mulls between KBr plates.

**Preparation of [(DAD)Cr(N$_t$Bu)$_2$]** 1. [Cr(N$_t$Bu)$_2$Cl$_2$] (1.00 g, 3.8 mmol) and 690 mg of Li$_2$DAD (3.8 mmol) were mixed as solids in a Glove Box. To the mixture 50 mL of THF were rapidly added at room temperature. After an extreme exothermic reaction the solution was stirred for 8h at room temperature. Removing the solvent in vacuum followed by hexane extraction yielded a red-brown oily crude product. Further purification by sublimation at 50°C/10$^{-4}$ mbar onto a glass tube cooled with liquid nitrogen produced a mixture of the product and free DAD ligand. The sublimate was dried in vacuum (10$^{-1}$ mbar) at room temperature for 12h. This afforded 300 mg (22% yield) of pure product as a red solid. M.p. 70.5°C. Anal. Calcd. for C$_{18}$H$_{38}$N$_4$Cr (M = 362.53 g·mol$^{-1}$): C 59.64, H 10.57, N 15.45. Found: C 58.92, H 10.80, N
Chapter IV

13.33. MS-EI: 362 (M\(^+\), 2%), 347 (M\(^+\) – Me, 2%), 291 (M\(^+\) – Me – Me\(_2\)C=CH\(_2\), 1%), 57 (100%). \(^1\)H-NMR (C\(_6\)D\(_6\), 300 MHz, 300 K): 6.42 (s, 2H, CH-DAD), 1.43 (s, 18H, N\(^{t}\)Bu), 1.33 (s, 18H, \(^{t}\)Bu-DAD). \(^1\)H-NMR (d\(_8\)-toluene, 500 MHz, 300 K): 6.35 (s, 2H, CH-DAD), 1.35 (s, 18H, N\(^{t}\)Bu), 1.27 (s, 18H, \(^{t}\)Bu-DAD). \(^1\)H-NMR (d\(_8\)-toluene, 500 MHz, 180 K): 6.18 (s, 2H, CH-DAD), 1.68 (s, 9H, N\(^{t}\)Bu), 1.30 (s, 18H, \(^{t}\)Bu-DAD), 1.23 (s, 9H, N\(^{t}\)Bu).

\(^{13}\)C\({}^1\)H-NMR (C\(_6\)D\(_6\), 75 MHz, 300 K): 123.4 (C\(_H\)-DAD), 32.9 (NC(C(CH\(_3\)))\(_3\)), 32.5 (C(C(CH\(_3\)))\(_3\)-DAD). IR (KBr, cm\(^{-1}\)): 3025(w), 1360(m), 1284(w), 1256(w), 1242(m ), 1215(s), 1130(w), 1089(w), 1049(w), 1025(w), 805(m ), 771(w), 723(w), 669(w), 644(w), 603(w), 577(w), 521(w), 464(w).

Preparation of \([\text{Cr}_2(N^{t}\text{Bu})_2(\mu–N^{t}\text{Bu})_2(\mu–\text{DAD})]\) 2. 1.00 g of \([\text{Cr}(N^{t}\text{Bu})_2\text{Cl}_2]\) (3.77 mmol), 634 mg of DAD (3.77 mmol) and 92 mg (3.77 mmol) Mg powder [31] were mixed and 50 mL THF were added. The mixture was stirred for 48h and the solvent was removed in vacuum. The product was extracted with 3 portions of 30 mL hexane. The solvent was reduced to 10 mL and a first crop of 350 mg of pure product was obtained as black crystals by cooling at –30°C. The second crop of 375 mg was obtained from the filtrate by concentration and crystallisation at –30°C. Yield: 725 mg (69%). M.p. 315°C (dec). Anal. Calcd. for C\(_{26}\)H\(_{56}\)N\(_6\)Cr\(_2\) (M = 556.77 g·mol\(^{-1}\)): C 56.09, H 10.14, N 15.09. Found: C 52.48, H 9.63, N 14.05. MS-EI: 556 (M\(^+\), 27%), 541 (M\(^+\)– Me, 21%), 57 (100%). \(^1\)H-NMR (C\(_6\)D\(_6\), 300 MHz, 300 K): 3.58 (s, 2H, C\(_H\)-DAD), 1.87 (s, 18H, N\(^{t}\)Bu), 1.31 (s, 18H, \(^{t}\)Bu-DAD), 1.13 (s, 18H, \(^{t}\)Bu-DAD).

\(^{13}\)C\({}^1\)H-NMR (C\(_6\)D\(_6\), 75 MHz, 300 K): 117.5 (C\(_H\)-DAD), 69.5 and 66.9 (NC(C(CH\(_3\)))\(_3\)), 58.2 (C(C(CH\(_3\)))\(_3\)-DAD), 35.1 (NC(C(CH\(_3\)))\(_3\)), 32.5 (C(C(CH\(_3\)))\(_3\)-DAD). IR (KBr, cm\(^{-1}\)): 1465(s), 1351(s), 1204(s), 1182(s), 1108(m), 1089(w), 1049(w), 1025(w), 805(m), 771(w), 723(w), 669(w), 644(w), 603(w), 577(w), 521(w), 464(w).

Preparation of \([\text{DAD})\text{Mo}(N^{t}\text{Bu})_2]\) 3. 1.69 g of DAD (10.0 mmol) and 0.24 g of Mg powder (10.0 mmol) were added to a solution of \([\text{Mo}(N^{t}\text{Bu})_2\text{Cl}_2(\text{dme})]\) (4.00 g, 10.0 mmol) in 50 mL THF under ice cooling. The reaction mixture was stirred for 24h at room temperature. The solvent was removed in vacuum and the complex was extracted with 2 portions of 100 mL hexane. The solvent was removed in vacuum and the complex was extracted with 2 portions of 100 mL hexane. After removing of the solvent in vacuum, pure orange solid product was obtained by sublimation at 90°C/10\(^{-2}\) mbar. Yield 2.44 g (60%). M.p. 79°C. Anal. Calcd. for C\(_{18}\)H\(_{38}\)N\(_4\)Mo (M = 406.47 g·mol\(^{-1}\)): C 53.19, H 9.42, N 13.78. Found: C 52.62, H 9.35, N 13.65. MS-EI: 408 (M\(^+\), 41%), 393 (M\(^+\) – Me, 100%), 352 (M\(^+\) – Me\(_2\)C=CH\(_2\), 3%), 337 (M\(^+\) – Me – Me\(_2\)C=CH\(_2\), 23%), 296 (M\(^+\) – 2 Me\(_2\)C=CH\(_2\), 3%), 281 (M\(^+\) – Me – 2 Me\(_2\)C=CH\(_2\), 6%). \(^1\)H-NMR (C\(_6\)D\(_6\), 300 MHz, 300 K): 6.05 (s, 2H, CH-DAD), 1.56 (s, 9H, N\(^{t}\)Bu), 1.33 (s, 18H, \(^{t}\)Bu-DAD), 1.26 (s, 9H, N\(^{t}\)Bu).
$^{13}$C{\textsuperscript{1}H}-NMR (C\textsubscript{6}D\textsubscript{6}, 75 MHz, 300 K): 113.4 (CH-DAD), 66.7 and 65.9 (NC(CH\textsubscript{3})\textsubscript{3}), 55.9 (C(CH\textsubscript{3})\textsubscript{3}-DAD), 33.6 and 33.1 (NC(CH\textsubscript{3})\textsubscript{3}), 32.0 (C(CH\textsubscript{3})\textsubscript{3}-DAD). IR (KBr, cm\textsuperscript{-1}): 3182(w), 3010(w), 1414(w), 1361(s), 1262(w), 1246(m), 1217(s), 1120(w), 1055(w), 1021(w), 936(w), 875(w), 814(w), 773(w), 724(w), 673(w), 638(w), 605(w), 581(w), 551(w), 518(w), 470(w).

Preparation of [(DAD)Mo(NMes)]\textsubscript{4} 4. 322 mg of DAD (1.9 mmol) and 46 mg of Mg powder (1.9 mmol) were added to a solution of [Mo(NMes)\textsubscript{2}Cl\textsubscript{2}(dme)] (1.00 g, 1.9 mmol) in 50 mL THF under ice cooling. The reaction mixture was stirred for 24h at room temperature. The solvent was removed in vacuum and the complex was extracted by hot hexane until the extract was colourless. The concentration of the solution and crystallisation at –80°C produced 350 mg (35 % yield) of the orange compound. M.p. 179.8°C. Anal. Calcd. for C\textsubscript{28}H\textsubscript{42}N\textsubscript{4}Mo (M = 530.61 g·mol\textsuperscript{-1}): C 63.38, H 7.98, N 10.56. Found: C 61.02, H 7.83, N 9.82. MS-EI: 532 (M\textsuperscript{+}, 55%), 517 (M\textsuperscript{+} – Me, 3%), 57 (100%). \textsuperscript{1}H-NMR (C\textsubscript{6}D\textsubscript{6}, 300 MHz, 300 K): 6.81 and 6.78 (s, 2H, m-Mes), 6.14 (s, 2H, CH-DAD), 2.62 and 2.34 (s, 6H, o-Mes), 2.17 and 2.12 (s, 3H, p-Mes), 1.31 (s, 18H, tBu-DAD).

Preparation of [(DAD)W(N\textsuperscript{t}Bu)\textsubscript{2}] 5. 610 mg of DAD (3.6 mmol) and 90 mg of Mg powder (3.7 mmol) were added to a solution of [W(N\textsuperscript{t}Bu)\textsubscript{2}Cl\textsubscript{2}py\textsubscript{2}] (2.00 g, 3.6 mmol) in 50 mL THF under ice cooling. The reaction mixture was stirred for 24h at room temperature. The solvent was removed in vacuum and the complex was extracted with 2 portions of 100 mL hexane. After removing of the solvent in vacuum pure yellow-orange solid product was obtained by sublimation at 100°C/10\textsuperscript{-2} mbar. Yield 590 mg (28%). M.p. 73.5°C. Anal. Calcd. for C\textsubscript{18}H\textsubscript{38}N\textsubscript{4}W (M = 494.38 g·mol\textsuperscript{-1}): C 43.73, H 7.75, N 11.33. Found: C 43.19, H 7.72, N 11.27. MS-EI: 494 (M\textsuperscript{+}, 28%), 479 (M\textsuperscript{+} – Me, 100%), 438 (M\textsuperscript{+} – Me\textsubscript{2}C=CH\textsubscript{2}, 5%), 423 (M\textsuperscript{+} – Me – Me\textsubscript{2}C=CH\textsubscript{2}, 9%), 367 (M\textsuperscript{+} – Me – 2 Me\textsubscript{2}C=CH\textsubscript{2}, 3%), 311 (M\textsuperscript{+} – Me – 3 Me\textsubscript{2}C=CH\textsubscript{2}, 4%). \textsuperscript{1}H-NMR (C\textsubscript{6}D\textsubscript{6}, 300 MHz, 300 K): 6.27 (s, 2H, CH-DAD), 1.89 (s, 9H, N\textsuperscript{t}Bu), 1.64 (s, 18H, \textsuperscript{1}Bu-DAD), 1.62 (s, 9H, N\textsuperscript{t}Bu). \textsuperscript{13}C{\textsuperscript{1}H}-NMR (C\textsubscript{6}D\textsubscript{6}, 75 MHz, 300 K): 109.2 (CH-DAD), 65.4 and
65.3 (NC(CH₃)₃), 56.3 (C(CH₃)₃-DAD), 34.3 and 34.1 (NC(CH₃)₃), 32.0 (C(CH₃)₃-DAD). IR (KBr, cm⁻¹): 3026(w), 1489(w), 1402(w), 1364(m), 1354(w), 1294(m), 1248(s), 1219(s), 1163(w), 1144(w), 1113(w), 1067(w), 1026(w), 972(w), 872(m), 814(w), 808(w), 774(m), 721(w), 660(w), 598(w), 673(w), 544(w), 519(w), 476(w).

Preparation of [(DAD)W(NMes)₂] 6. DAD (550 mg, 3.3 mmol) and Mg powder (80 mg, 3.3 mmol) were added to a solution of [W(NMes)₂Cl₂(dme)] (2.00 g, 3.3 mmol) in 50 mL THF. The reaction mixture was stirred for 24h at room temperature. The solvent was removed in vacuum and the complex was extracted by hot hexane until the extract was colourless. The concentration of the solution and crystallisation at –80°C produced 710 mg (47 % yield) of the yellow solid. M.p. 205.3°C. Anal. Calcd. for C₂₈H₄₂N₄W (M = 618.52 g·mol⁻¹): C 54.37, H 6.84, N 9.06. Found: C 54.18, H 6.59, N 8.94. MS-EI: 618 (M⁺, 100%), 562 (M⁺ – Me₂C=CH₂, 8%), 547 (M⁺ – Me – Me₂C=CH₂, 5%), 506 (M⁺ – 2 Me₂C=CH₂, 15%). ¹H-NMR (C₆D₆, 300 MHz, 300 K): 6.89 and 6.85 (s, 2H, m-Mes), 5.99 (s, 2H, C–H-DAD), 2.64 and 2.36 (s, 6H, o-Mes), 2.21 and 2.18 (s, 3H, p-Mes), 1.28 (s, 18H, ’Bu-DAD). ¹H-NMR (CDCl₃, 300 MHz, 300 K): 6.84 and 6.74 (s, 2H, m-Mes), 6.30 (s, 2H, CH-DAD), 2.37 (s, 6H, o-Mes), 2.28 and 2.18 (s, 3H, p-Mes), 2.10 (s, 6H, o-Mes), 1.40 (s, 18H, ’Bu-DAD). ¹³C{¹H}-NMR (CDCl₃, 75 MHz, 300 K): 133.3, 132.5, 129.1, 129.0, 127.6 and 127.4 (Ar-Mes), 107.5 (CH-DAD), 58.1 (C(CH₃)₃-DAD), 31.6 (C(CH₃)₃-DAD), 20.8 and 20.7 (p-Mes), 19.7 and 19.0 (o-Mes). IR (KBr, cm⁻¹): 2723(w), 1422(w), 1366(w), 1352(m), 1327(s), 1289(m), 1248(w), 1213(s), 1167(w), 1111(w), 1063(w), 1028(w), 1015(w), 988(m), 941(w), 887(m), 853(m), 828(w), 781(w), 735(w), 723(w), 604(w).

References


[16] Chapter V.


[31] Magnesium powder was dried in vacuum ($10^{-2}$ mbar) at 200°C for 4h before use.
Chapter V

Dynamic Processes in the New DAD Niobium and Tantalum Complexes of the Types [(DAD)M(NR)(X)(L)] and [(DAD)M(NR)(µ-Cl)]2

Introduction

Complexes on the basis of the 1,4-diaza-1,3-diene (R,R’-DAD) ligand backbone have been the focus of attention for many years. Due to several possible coordination modes and their redox activity, R,R’-DAD ligands can stabilize metals in a wide range of formal oxidation states [1]. While neutral R,R’-DAD is a strong π-acceptor stabilizing low-valent metal centers, the 2-electron reduced R,R’-DAD\textsuperscript{2–} ligand, which is best described as an ene-diamido functionality, can be envisaged as a strong π-donor stabilizing high-valent metal centres.

\[ \text{R,R'} \text{—DAD} \]

\[ \text{DAD} \]

There are four methods described in the literature for the preparation of complexes of early transition metals with the R,R’-DAD\textsuperscript{2–} anion: reaction of metal halogenides with dilithium salts of R,R’-DAD (Li\textsubscript{2}R,R’-DAD) [2a], in \textit{situ} reduction of a metal centre in the presence of R,R’-DAD [2b], oxidative addition of R,R’-DAD to a reduced metal centre [2c] and double insertion of isocyanides into metal carbon bonds followed by \textit{intra} molecular coupling [2d].
In order to show that chloro complexes of early transition metals with neutral R,R’–DAD ligands can be reduced to R,R’–DAD\(^{2–}\) complexes, a set of niobium and tantalum imido compounds with neutral DAD ligand, DAD = 1,4-di-\textit{tert}-butyl-1,4-diaza-1,3-diene, was synthesised and characterised [3].

\[ \text{M(OAr)}_2\text{R}_2 \xrightarrow{\Delta} \text{CNR'} \]

\[ \text{M} = \text{Ti, Zr} \]
\[ \text{R} = \text{CH}_3, \text{CH}_2\text{Ph} \]
\[ \text{Ar} = \text{Dip, 2,6-\textit{Bu}_{2}\text{Ph}} \]
\[ \text{R'} = 2,6-\text{Me}_{2}\text{Ph} \]
The prominent application of niobium and tantalum imido complexes containing DAD$^2$-ligand was supposed to be the CVD (Chemical Vapour Deposition) of Mn films and especially of TaN. The metal nitrides of the formula $M_{1.0}N_{1.0}$, where M is a group IV or V element, possess a wide range of useful properties. For example, their hardness and good electrical conductivity allow to use them as barrier materials in microelectronics [4].

One of the possible precursors is $t$Bu imido $t$Bu amido complex of the type $[(DAD)M(NH)tBu(NtBu)]$ [5], $M = Nb$ and Ta. The latter complexes can be obtained on large scale, but there are only a few possibilities to modify them in order to obtain precursors with new chemical and physical properties such as volatility, reductive decomposition paths etc. Here the chloro and chloropyridine complexes $[(DAD)M(NtBu)(µ-Cl)]_2$ and $[(DAD)M(NtBu)(Cl)(py)]$ are reported, which provide the possibility for further transformation by nucleophilic substitution of the chloride ligand. An example of such substitution by a benzyl ligand is also presented. Additionally, complexes $[(DAD)M(NAr)(µ-Cl)]_2$, $M = Nb$ and Ta, were synthesised by reducing $[M(NAr)Cl_3(dad)]$, $M = Nb$ and Ta. The dynamic behaviour of these complexes in solution was investigated and the thermodynamic activation parameters for the observed phenomenon were estimated.

**Results and discussion**

**Synthetic studies**

The known salts $[Li_2DAD(THF)_4]$ [6a] and $[Li_2DAD(Et_2O)_4]$ [6b] can be easily obtained as crystalline materials by the reaction of DAD with lithium in the corresponding solvent.

According to the $^1$H- and $^{13}$C-NMR spectra the amount of solvent molecules depends on the time of drying in vacuum. Furthermore the orange crystals change their colour and slowly
turn yellow with time when kept in a Glove Box. After drying at 25°C/10^{-4} \text{ mbar for 48 hours the spectra do not show any signals of solvate molecules. The obtained substance seems to have Li}_2\text{DAD constitution and is insoluble in hexane, poorly soluble in toluene and much better in Et}_2\text{O or THF forming in the solution the solvates described above [6a, b]. Unfortunately, we were not able to grow crystals for an X-ray structure analysis of the obtained Li}_2\text{DAD compound. In comparison with its solvate forms the Li}_2\text{DAD has some advantages. First of all, it does not change its composition with time and consequently it is better for precise weighing. As an alternative method a standard solution of Li}_2\text{DAD in THF or Et}_2\text{O can be prepared and used in further reactions [6c]. In this work the abbreviation Li}_2\text{DAD is used for the solvate-free form, which may be kept in a Glove Box.}

Chloro pyridine complexes of niobium and tantalum [(DAD)M(N^tBu)(Cl)(py)], M = Nb (1) and Ta (2), can be obtained in good yield from the reaction of [M(N^tBu)Cl_3py_2] [7] and Li}_2\text{DAD in THF. 1 and 2 are very well soluble in THF, aromatic solvents, Et}_2\text{O and poorly soluble in hexane. Single crystals suitable for X-ray analysis were obtained by layering an Et}_2\text{O solution of 1 or 2 with hexane. The molecular structures of 1 and 2 are presented in Fig. 1 and Fig. 2.}

The coordination sphere of niobium and tantalum in 1 and 2 is tetragonal pyramidal with the base plane formed by atoms N(1), N(4), Cl(1) and N(13); the imido nitrogen N(19) occupies the apex. The angles N(19)–M(1)–X, where X is an atom forming the base plane and M is Nb (1) or Ta (2), are in the range of 102–111°. The metal–to–base plane distance are very similar in the both complexes, 0.6760(2) Å for 1 and 0.6750(1) Å for 2.

The imido moiety exhibits standard parameters [8] for its 6e⁻ mode in both complexes 1 and 2: short M–N bond distances (less than 1.8 Å) and almost linear M–N–C angles (larger than 170°).
Fig. 1. The molecular structure of [(DAD)Nb(N^tBu)(Cl)(py)] 1 with thermal ellipsoids at 40% probability. Positions C(2) and C(2a), as well as C(3) and C(3a), are disordered; the site occupation factors are 0.82:0.18. Space group P 2_1/c, Z = 4. Selected bond length [Å] and angles [°]: Nb(1)–N(1) 2.025(2), Nb(1)–N(4) 2.021(2), Nb(1)–N(13) 2.309(2), Nb(1)–N(19) 1.754(2), Nb(1)–Cl(1) 2.4977(9), N(1)–C(2) 1.402(4), N(1)–C(2a) 1.62(2), N(4)–C(3) 1.409(4), N(4)–C(3a) 1.59(2), C(3)–C(2) 1.369(5), C(2a)–C(3a) 1.39(2), N(1)–Nb(1)–N(4) 84.47(9), N(19)–Nb(1)–Cl(1) 106.42(8), N(19)–Nb(1)–N(1) 110.66(10), N(19)–Nb(1)–N(4) 111.76(10), N(19)–Nb(1)–N(13) 102.37(9), Nb(1)–N(19)–C(20) 172.7(2).

Fig. 2. ORTEP plot of [(DAD)Ta(N^tBu)(Cl)(py)] 2 with thermal ellipsoids at 30% probability (hydrogen atoms are omitted for clarity). Space group P 2_1/c, Z = 4. Selected bond length [Å] and angles [°]: Ta(1)–N(1) 2.009(2), Ta(1)–N(4) 2.009(2), Ta(1)–N(13) 2.290(2), Ta(1)–N(19) 1.769(2), Ta(1)–Cl(1) 2.4836(9), N(1)–C(2) 1.397(4), N(4)–C(3) 1.390(4), C(2)–C(3) 1.371(5), N(1)–Ta(1) 2.009(2), N(4)–N(19) 3.126(3), N(19)–Ta(1)–Cl(1) 107.22(8), N(19)–Ta(1)–N(1) 110.6(1), N(19)–Ta(1)–N(4) 111.5(1), N(19)–Ta(1)–N(13) 102.28(9), Nb(1)–N(19)–C(20) 173.2(2).
In its solid state the DAD$_2^–$ M metallocycle exhibits a folded conformation. The metal centre is not located in the plane formed by the N$_2$C$_2$ atoms of the DAD$_2^–$ moiety with metal–to–plane distances of more than 1 Å (Table 1). In comparison with the free DAD ligand [9] and its donor–acceptor complex with d$^0$ niobium [Nb(NC$_6$H$_2$Cl$_3$)Cl$_3$(dad)] [3] a decrease in C–C bond distance and an increase in C–N bond distances is observed (Table 1). The same tendencies were found in other structurally characterised R,R’–DAD$_2^–$ d$^0$ complexes with niobium and tantalum [2c, 6b, 6c, 10], in which MC$_2$N$_2$ backbone exhibits very close structural parameters. For illustration, the selected parameters for the DAD$_2^–$ ligand in reference complex [Cp(DAD)NbCl$_2$] [2c] are presented in Table 1.

### Table 1. Selected distances [Å] and angles [°] of DAD$_2^–$ and imido ligands in complexes 1, 2, 4, 6, 10 and reference complexes [Cp(DAD)NbCl$_2$] [2c] and [Nb(NC$_6$H$_2$Cl$_3$)Cl$_3$(dad)] [3].

<table>
<thead>
<tr>
<th>Complex</th>
<th>DAD$_2^–$</th>
<th>imido</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.369(5)</td>
<td>1.402(4)</td>
</tr>
<tr>
<td></td>
<td>1.39(2)$^*$</td>
<td>1.62(2)$^*$</td>
</tr>
<tr>
<td>2</td>
<td>1.371(5)</td>
<td>1.390(4)</td>
</tr>
<tr>
<td>4</td>
<td>1.367(8)</td>
<td>1.382(7)</td>
</tr>
<tr>
<td>6</td>
<td>1.364(8)</td>
<td>1.390(7)</td>
</tr>
<tr>
<td></td>
<td>1.367(8)</td>
<td>1.383(8)</td>
</tr>
<tr>
<td>10</td>
<td>1.359(6)</td>
<td>1.377(5)</td>
</tr>
<tr>
<td>ref. [2c]</td>
<td>1.402(6)</td>
<td>1.354(6)</td>
</tr>
<tr>
<td>DAD [9]</td>
<td>1.468(2)</td>
<td>1.267(2)</td>
</tr>
<tr>
<td>ref. [3]</td>
<td>1.471(3)</td>
<td>1.270(3)</td>
</tr>
</tbody>
</table>

*disorder with the site occupation factor of 0.18 (prone isomer)
With respect to the definition of *prone* and *supine* conformers [6c, 11, 12] for the folded R,R’–DAD₂⁻ ligand in cyclopentadienyl complexes we can suggest using it also in the presence of the isolobal RN₂⁻ ligand. In the molecular structure of niobium complex 1 both *supine* and *prone* isomers are present. The disorder of the carbon atoms at position C(2) and C(3) with the site occupation factor of 18% leads to *prone* conformation. It is interesting, that this effect was not observed for tantalum complex 2 and only one *supine* isomer is present.

In spite of the short distances of approx. 2.5 Å between the metal centre and the carbon atoms of the double bond in 1 and 2 the latest computations [10b, 13] suggest that there is no considerable chemical interaction. In contrast, the short M–N bond distances of around 2 Å indicate strong metal–nitrogen multiple bonds with the DAD₂⁻ moiety. For example, these M–N distances in [Nb(NC₆H₂Cl₃)Cl₃(dad)], where the DAD ligand is a neutral chelate σ–donor, are 2.301(2) and 2.460(2) Å [3]. Therefore, the reduced DAD₂⁻ moiety has to be considered as an ene-diamido ligand. It should be mentioned that the nitrogen atoms of the DAD₂⁻ ligand in 1 and 2 have different surroundings that should lead to magnetically non-equivalent 'Bu groups and methine protons.

In the room temperature ¹H-NMR spectra of 1 and 2 the DAD₂⁻ ligand exhibits broad peaks for methine protons at δH 6.2 ppm and 'Bu groups at δH 1.4 ppm, while pyridine and 'Bu imido signals are sharp in the ¹H- and ¹³C-NMR spectra within the temperature limit of 200–400 K (Fig. 3 – Fig. 6). In the ¹H-NMR spectra at 200 K the CH signals of the DAD₂⁻ ligand consist of two doublets. The signals of the methine carbon atoms cannot be localised in the ¹³C-NMR spectra at room temperature but appear as two singlets in the region of 100–110 ppm at 230 K. The 'Bu peaks are also broadened in the ¹³C-NMR spectra at room temperature splitting into two sets of signals at 230 K. These data are consistent with the asymmetrical surroundings of the DAD₂⁻ ligand at low temperatures, which is expected from X-ray studies of 1 and 2. When warming up a dynamic process seems to take place, which is discussed in detail below in DNMR studies.
Fig. 3. The $^1$H-DNMR spectra of 1 (400 MHz, d$_8$-toluene, aliphatic area).

Fig. 4. The $^1$H-DNMR spectra of 1 (400 MHz, d$_8$-toluene, aromatic area).
**Fig. 5.** The $^1$H-DNMR spectra of 2 (400 MHz, d$_8$-toluene, aliphatic area).

**Fig. 6.** The $^1$H-DNMR spectra of 2 (400 MHz, d$_8$-toluene, aromatic area).

In the EI mass spectra of 1 and 2 ions [(DAD)M(N'Bu)(Cl)]$^+$ without pyridine ligand were detected as the peaks of the highest m/z value. The abstraction of one and two isobutylene fragments was also observed in the spectra forcing at least one of them to arise from the $^1$Bu
group of the DAD\textsuperscript{2–} ligand. Sublimation of the complexes 1 and 2 leads to a loss of the pyridine ligand and the chloro complexes 3 and 4 are formed.

![Chemical structure](image)

Complexes 3 and 4 are volatile compounds, which are well soluble in THF, Et\textsubscript{2}O and toluene and sparingly soluble in hexane. The cooling of a concentrated toluene solution of 4 to –30°C afforded single crystals suitable for an X-ray diffraction analysis. The molecular structure of 4 is presented in Fig. 7.

![Molecular structure](image)

**Fig. 7.** The molecular structure of [(DAD)Ta(N\textsuperscript{t}Bu)(μ-Cl)]\textsubscript{2} 4 with thermal ellipsoids at 50% probability. Space group P b c a, Z = 8. Selected bond length [Å] and angles [°]: Ta(1)–N(1) 1.987(4), Ta(1)–N(4) 1.993(4), Ta(1)–N(13) 1.750(4), Ta(1)–Cl(1) 2.548(1), Ta(1)–Cl(1\textsubscript{5}) 2.560(1), N(1)–C(2) 1.390(7), N(4)–C(3) 1.382(7), C(3)–C(2) 1.367(8), Ta(1)–N(13)–C(14) 173.6(4), N(13)–Ta(1)–Cl(1\textsubscript{5}) 101.3(2), N(13)–Ta(1)–Cl(1) 100.7(2), N(13)–Ta(1)–N(4) 113.1(2), N(13)–Ta(1)–N(1) 112.8(2).
The molecular structure of \([(\text{DAD})\text{Ta}(\text{NtBu})(\mu-\text{Cl})]_2\) \(4\) consists of two \([(\text{DAD})\text{Ta}(\text{NtBu})\text{Cl}]\) units, which can be also found in the molecular structures of \(1\) and \(2\). The chloro ligand from the one unit, instead of pyridine ligand compared to \(1\) and \(2\), coordinates to the metal centre in the second unit to complete its tetragonal pyramidal coordination sphere. The molecule contains a crystallographic centre of inversion, which renders the ligands in both polyhedra to be crystallographically and magnetically equivalent. Chlorine atoms \(\text{Cl}(1)\) and \(\text{Cl}(1_5)\) and nitrogen atoms of the DAD\(^2\-) ligands form the base planes of the pyramids, while imido nitrogen atoms occupy the apexes. The metal–to–base plane distance of 0.6599(2) Å in \(4\) correlates with the value of 0.6750(1) Å in \(2\). Two tetragonal pyramids are connected at the shared edge of the base planes so that the imido ligands and double bonds of the DAD\(^2\-) moiety are in trans configuration. The bridging chloro core is slightly asymmetrical with bond distances \(\text{Ta}(1)–\text{Cl}(1)\) and \(\text{Ta}(1)–\text{Cl}(1_5)\) of 2.548(1) Å and 2.560(1) Å, respectively. As expected these are somewhat longer than in the monomeric complex \(2\) (2.4977(9) Å) because of their bridging character.

Each pyramidal core has folded supine conformation and underlines the tendency of the DAD\(^2\-) ligand to have a shorter C–C bond length and a longer C–N bond length compared to the free ligand’s parameters discussed above for \(1\) and \(2\) (Table 1).

In contrast to \(1\) and \(2\) not only DAD\(^2\-) but also imido signals are broadened in the room temperature NMR spectra of \(3\) and \(4\). These signals are temperature dependent and this behaviour is presented in Fig. 8 – Fig. 11.

![Fig. 8. The \(^1\)H-DNMR spectra of \(3\) (500 MHz, d\(^8\)-toluene, aliphatic range).](image-url)
Fig. 9. The $^1$H-DNMR spectra of 3 (500 MHz, $d^8$-toluene, aromatic range).

Fig. 10. The $^1$H-DNMR spectra of 4 (500 MHz, $d^8$-toluene, aliphatic range).
At low temperatures the $CH$ signals of the DAD$^{2-}$ ligand split into two singlets with intensities 2:3 in the NMR spectra of 3 and 4. This is in contrast to the spectra of 1 and 2, for which two doublets with equal intensities were observed. The signal of the imido $t$Bu group also splits into two singlets at low temperatures, while only one singlet was observed in the spectra of 1 and 2 at different temperatures. Although at first sight this phenomenon differs from that observed for chloro pyridine complexes [(DAD)M(N$t$Bu)(Cl)(py)], $M = Nb$ (1) and Ta (2), these dynamic processes are assumed to have a similar origin, which is discussed below in the DNMR part.

Actually the sublimation of 1 and 2 is not preferable for large scale preparation of 3 and 4 but shows possible formation of the monomeric species [(DAD)M(N$t$Bu)(Cl)] in solution. On the other hand the chloro-pyridine complexes 1 and 2 were quantitatively obtained from 3 and 4 by adding pyridine.

Alternatively complex 4 can be obtained in good yield by reducing [Ta(N$t$Bu)Cl$_3$(dad)] [3] containing neutral DAD ligand with CsK in THF.

Fig. 11. The $^1$H-DNMR spectra of 4 (500 MHz, d$_8$-toluene, aromatic range).
Indeed, the best preparation method of [(DAD)M(N\text{tBu})(\mu-\text{Cl})]_2, M = \text{Nb (3)} and \text{Ta (4)}, is the large scale in situ synthesis directly from MCl_5. In this synthesis the equilibrium between [M(N'\text{Bu})Cl_3(dad)] and metatate complex [tBuNH_3]^[+][M(N'\text{Bu})Cl]^{2-} in the presence of DAD is used [3]. The tBuNH_3Cl formed can be filtered off after adding the same volume of hexane as CH_2Cl_2 taken for reaction. The reduction of the filtrate residue with C_8K or Li in THF yields the desired product [(DAD)M(N'\text{Bu})(\mu-\text{Cl})]_2 in good over-all yield, while applying Mg as the reducing agent does not lead to the formation of the desired product. Possibly, in the case of Mg the product formed is rapidly reduced to d^1 species. This is in good accord with reductive studies on 3 and 4 [14], in which the reduction in THF was found to be unselective. Evidently Li as a reducing agent is advantageous for large-scale syntheses, whereas for small amounts (approx. 1g scale) C_8K was found to give somewhat better yields.

\[
\begin{align*}
\text{MCl}_5 & \xrightarrow{3 \text{ tBuNH}_2} \text{CH}_2\text{Cl}_2 \quad \left[ \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array} \right]_2 \quad 2\text{ tBuNH}_3 \\
\text{M} = \text{Nb (3) (47\%)} \quad \text{Ta (4) (50 - 60\%)} \\
\end{align*}
\]

Similar to the monomeric chloro pyridine complexes [(DAD)M(N'\text{Bu})(\text{Cl})(\text{py})], M = \text{Nb (1) Ta (2)}, the EI mass spectra of 3 and 4 show mononuclear molecular ions [(DAD)M(N'\text{Bu})(\text{Cl})]^+ as the peaks of the highest m/z value. It can be explained by the easy dissociation of the dimeric species in the gas phase. Actually the EI mass spectra of the pyridine containing complexes 1 and 2 and their dimeric analogues without pyridine 3 and 4 are very similar exhibiting almost the same fragmentation pathways and intensities of the observed peaks. In both cases the volatile particle is the fragment [(DAD)M(N'\text{Bu})(\text{Cl})]^+. 87
Reaction of 1 and 2 with BzMgCl yields benzyl complexes 5 and 6 containing pyridine ligand. The yields in this reaction are not very good because of the extremely high solubility of the products, which cannot be completely recovered from solution by crystallisation.

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{M} & \quad \text{Cl} \\
\text{N} & \quad \text{M} \\
\text{N} & \quad \text{M} \\
\text{Cl} & \quad \text{BzMgCl, THF} \\
& \quad - \text{MgCl}_2
\end{align*}
\]

\[
\begin{align*}
\text{M} & \quad \text{Nb} \ (5) \ (39\%) \\
& \quad \text{Ta} \ (6) \ (38\%)
\end{align*}
\]

A crystal suitable for X-ray analysis was obtained by cooling a concentrated hexane solution of 6 to –80°C. In the crystal structure of 6 (Fig. 12) two independent molecules are present but their structural parameters are very similar and can be considered to be equal within the limits of 3σ (σ – standard deviation).

The coordination sphere of tantalum in 6 is similar to that found in complexes 1, 2 and 4: tetragonal pyramidal, where imido ligand occupies the apex. Two DAD\textsuperscript{2–} nitrogen atoms, one chlorine atom and one benzylic carbon atom form the base plane, the metal–to–plane distance being 0.6702(2) Å. The molecule exhibits supine conformation and parameters typical for the DAD\textsuperscript{2–} ligand, which are summarised in Table 1.

The metal–carbon bond length Ta(1)–C(1) of 2.309(6) Å correlates within ranges of 2.137-2.334 Å found in other tantalum benzyl complexes [15]. The corresponding metal–carbon–carbon angle Ta(1)–C(1)–C(2) of 120.6(3)° indicate that there is no interaction between the benzylic aromatic ring and tantalum. Indeed, the Ta(1)–C(2) bond length of 3.315(5) Å is considerably longer than the Ta(1)–C(1) bond length, while these distances should be comparable in the case of η\textsuperscript{2}– [16] or η\textsuperscript{3}–benzyllic [17] coordination. For example, in dibenzyl complex [{(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}SiMe\textsubscript{3})Nb(η\textsuperscript{2}–Bz)(η\textsuperscript{1}–Bz)}\textsubscript{2}(µ–1,4-NC\textsubscript{6}H\textsubscript{4}N)] the Nb–C bond lengths to benzylic carbon atoms are 2.22(2), 2.25(2) and 2.29(2) Å, while the distances to ipso carbon atoms are significantly different in η\textsuperscript{1} and η\textsuperscript{2} modes: 3.15(2) and 3.21(2) Å for η\textsuperscript{1}, 2.52(2) and 2.57(2) Å for η\textsuperscript{2} coordination. Furthermore, the C–C bonds in the aromatic ring of 6 are in the range of 1.38–1.40 Å demonstrating that almost no distortion in the aromatic system occurs, which should be observed in the case of η\textsuperscript{2} and η\textsuperscript{3} bonded benzyl complexes [16, 17].

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Fig. 12. The molecular structure of [(DAD)Ta(N^tBu)(Bz)(py)] 6 with thermal ellipsoids at 50% probability (one of two independent molecules is shown). Space group P 1̅, Z = 4. Selected bond length [Å] and angles [°]: Ta(1)–N(1) 2.016(5), Ta(1)–N(2) 2.014(4), Ta(1)–N(3) 2.311(4), Ta(1)–N(4) 1.772(4), Ta(1)–C(1) 2.309(6), Ta(1)–C(2) 3.315(5), N(2)–C(9) 1.383(8), N(1)–C(8) 1.404(7), C(8)–C(9) 1.364(8), Ta(1)–N(4)–C(23) 173.9(4), Ta(1)–C(1)–C(2) 120.6(3), N(1)–Ta(1)–N(2) 84.9(2), N(4)–Ta(1)–C(1) 106.2(2), N(4)–Ta(1)–N(3) 97.9(2), N(4)–Ta(1)–N(1) 115.4(2), N(4)–Ta(1)–N(2) 112.3(2).

The tendency of Lewis acidity to weaken when substituting the chloro ligand with benzyl one is represented as bond elongation between the tantalum and nitrogen atom of the pyridine ligand in 6 (2.309(4) and 2.311(4) Å) compared to 2 (2.290(2) Å).

As well as in the case of chloro complexes 1 and 2 according to the EI mass spectroscopic studies the pyridine ligand does not seem to be strongly bonded with the metal centre, the ions [(DAD)M(N^tBu)(Bz)]^+ being detected as the peaks of the highest m/z value.

The $^1$H-DNMR spectra of 5 and 6 show coalescence not only for DAD$_2^-$ signals, but also for the benzyl group and the pyridine ligand. These spectra for 5 are presented in Fig. 13 – Fig. 16.
Fig. 13. $^1$H-DNMR spectra of 5 (aliphatic range), the second signal of benzyl CH$_2$-group is shown in Fig. 14 (500 MHz, d$^8$-toluene).
Fig. 14. Splitting of the benzyl CH$_2$ signal in the $^1$H-DNMR spectra for 5. The second split doublet lies in aliphatic range Fig. 13 (500 MHz, d$_8$-toluene).

Fig. 15. The $^1$H-DNMR spectra of 5 (500 MHz, d$_8$-toluene, aromatic range).
Fig. 16. Splitting of the o-pyridine signal in 5, the second split signal overlaps with residual protons of d₈-toluene and is not shown (500 MHz, d₈-toluene).

Despite this complicated image, the dynamic processes can be divided into four independent parts. The first process is similar to that found for chloro pyridine complexes 1 and 2, which leads to coalescence of the DAD²⁻ signals (1 and 2); the second one is the limitation of rotation around the metal–carbon bond of the benzyl ligand leading to the appearance of two doublets for stereotopic protons of the CH₂ group (7); the third one is the further ‘freezing’ of motion in benzyl ligand, which limits rotation around the H₂C–Cᵢₚs bond and is responsible for the broadening of o- and m- signals (8, 9) in phenyl ring and shows no effect on the p-proton (10); the last one is limited rotation of the pyridine ligand around the metal–nitrogen bond, which seems to be responsible for the splitting of o- and m-pyridine signals (3 and 4), while the p-proton (5) does not show any changes except normal small deviations in chemical shift with temperature.

Complexes without pyridine ligand [(DAD)M(N'Bu)(Bz)], M = Nb (7) and Ta (8), were synthesised by reaction of 3 and 4 with BzMgCl in THF. Benzyl derivatives 7 and 8 are viscous liquids at room temperature and can be distilled in high vacuum.
The $^1$H-NMR spectra of 7 and 8 consist of a singlet at approx. 6.0 ppm for methine protons and a singlet at 1.3 ppm for $^1$Bu groups of the DAD$^{2-}$ ligand, indicating symmetrical surrounding of the DAD$^{2-}$ moiety. The benzyl group exhibits a sharp singlet at approx. 2.3 ppm for $CH_2$ protons and the expected aromatic signals for a symmetrical monosubstituted phenyl ring.

It is interesting that in contrast to the NMR spectra of 5 and 6 those for 7 and 8 are temperature independent in the region of 180–400 K. These data are consistent either with a $\eta^1$–bonded benzyl ligand with a rapid rotation around the M–C bond or with the symmetrical $\eta^2$ coordination [16]. Actually, there is no $^1$H- and $^{13}$C-NMR evidence for a $\eta^2$ or $\eta^3$ coordination mode.

The EI mass spectra of the complexes without pyridine ligand 7 and 8 are very similar to the spectra of their analogues with pyridine 5 and 6. This correlates with observations, which were made for the pairs of chloro complexes with and without pyridine 1, 2 versus 3, 4.

Other substituted imido chloro complexes of niobium and tantalum carrying the DAD$^{2-}$ ligand can be obtained from imido trichloride complexes with neutral DAD ligand. Reduction of $[M(NDip)Cl_3(dad)]$, $M = Nb$ and $Ta$ [3], with $C_8K$ in THF leads to formation of the DAD$^{2-}$ complexes 9 and 10 with aryl imido moiety.
Surprisingly, yields in this reaction for the aromatic Dip substituent are pretty small compared to the 'Bu derivative (71% see above). 9 and 10 are yellow solids, which are poorly soluble in hexane and toluene. The molecular ions [(DAD)M(NDip)(Cl)]\(^+\) were found to be the peaks of the highest m/z value in the EI mass spectra of 9 and 10. A crystal of 10 suitable for X-ray analysis was obtained by cooling a toluene solution saturated at 100°C to room temperature. The molecular structure of 10 is presented in Fig. 17.

**Fig. 17.** The molecular structure of 10•C\(_5\)H\(_5\)CH\(_3\) with thermal ellipsoids at 40% probability (a solvate molecule of toluene is omitted for clarity). Space group P 2\(_1\)/n, Z = 2. Selected bond length [Å] and angles [°]: Ta(1)–N(1) 1.997(2), Ta(1)–N(4) 1.983(3), Ta(1)–N(13) 1.774(3), Ta(1)–Cl(1) 2.593(1), Ta(1)–Cl(1\_3) 2.555(1), N(1)–C(2) 1.377(5), N(4)–C(3) 1.385(5), C(2)–C(3) 1.359(6), N(13)–Ta(1)–Cl(1\_3) 105.80(9), N(13)–Ta(1)–Cl(1) 105.0(1), Ta(1)–N(13)–C(14) 176.3(3), N(13)–Ta(1)–N(1) 110.9(1), N(13)–Ta(1)–N(4) 109.6(1).
The molecular structure of [(DAD)Ta(NDip)(µ-Cl)]$_2$ 10 is similar to that found for 1Bu analogue 4. It consists of two tetragonal pyramids connected at the shared edge of the base planes. A crystallographic centre of inversion renders the two pyramidal units to be crystallographically and magnetically equivalent. Bridging chlorine atoms Cl(1) and Cl(1_5) and nitrogen atoms of the DAD$^{2-}$ ligands form the base planes, while imido nitrogen atoms occupy apexes in anti configuration to each other. The metal–to–base plane distance is 0.6864(1) Å. The Ta$_2$(µ-Cl)$_2$ core is slightly asymmetrical with bond distances Ta(1)–Cl(1) and Ta(1)–Cl(1_5) of 2.593(1) Å and 2.555(1) Å, respectively. Each pyramidal core has supine conformation, which was also observed in complex [(DAD)Ta(N$^t$Bu)(µ-Cl)]$_2$ 4. The folded C$_2$N$_2$M metallocycle exhibits short M–N bond lengths of 1.997(2) and 1.983(3) Å, the short C–C bond length of 1.359(6) Å and long C–N bond lengths of 1.377(5) and 1.385(5) Å, which are in good agreement with those in 1, 2, 4, 6 and reference complex [Cp(DAD)NbCl$_2$] (Table 1).

It is interesting to note that 2,6-di-isopropylphenylimido complexes 9 and 10 do not show dynamic behaviour in solution similar to 3 and 4. Their $^1$H- and $^{13}$C-NMR spectra consist of signals for the DAD$^{2-}$ ligand in the symmetrical surrounding in the range of 180–400 K. Below 200 K the spectra of 10 display similar features to those for mononuclear complex [(DAD)Ta(NDip)(NHDip)] [5]: the one set of CH and CH$_3$ isopropyl signals split in the $^1$H-NMR spectra into two sets of signals with 1:1 intensities.

For both complexes roughly estimated barriers [18] at the coalescence temperatures ($\Delta G_{190}^{190} = 37 \pm 2$ kJ/mol for 10 and $\Delta G_{188}^{188} = 36 \pm 2$ kJ/mol for [(DAD)Ta(NDip)(NHDip)] [5]) of approx. 40 kJ·mol$^{-1}$ can be referred to the freezing of rotation around the carbon nitrogen bond of the bulky Dip group (the absolute statistical error of 2 K for the temperature and relative error of 100% for the rate constant were taken to calculate accuracy).
MS Studies

For the dimeric compounds 3, 4, 9 and 10 only peaks referred to the monomeric form were detected as the signals of the highest m/z value in the electron impact ionisation mass spectra. This indicates a low dissociation barrier in these complexes and is in good agreement with their volatility.

In contrast to the spectra of the d^0 complexes with neutral DAD ligand of the type [M(NR)Cl_3(dad)] [3], where ions without an intact DAD moiety were observed, the abstraction of isobutylene from the DAD^2− unit was found to be the specific pattern for the complexes 1-10. First of all, it means that DAD^2− ligand is strongly bonded to the metal and the desired reductive abstraction of neutral DAD accompanied by formation of reduced M(III) species does not take place. Actually, if this decomposition pathway is the most prominent one in CVD experiments, then the presence of carbon in the TaN films can arise from the rest of the DAD^2− ligand.
IR Studies

There are several important conclusions, which can be made from the comparison of the IR spectra of DAD$^{2-}$ complexes and neutral DAD ligand. First of all, the very intensive absorption at 1631 cm$^{-1}$, which refers to the absorption of C=N double bond of the free ligand, disappears in the spectra of 1-10. Two other strong absorptions at around 1361 cm$^{-1}$ and around 1211 cm$^{-1}$ can be found in all complexes somewhat shifted to shorter wavelengths compared to the DAD ligand. Other two medium absorptions in the spectra of 1-10 at approx. 870 cm$^{-1}$ and 760 cm$^{-1}$ seem to originate from the DAD ligand, but here assignment is more complicated because other organic groups are present in the molecules. The wave numbers for methine C–H stretching mode in the DAD$^{2-}$ complexes are found in the range of 3050-3010 cm$^{-1}$ demonstrating the considerable weakening of the C–H bond in comparison with the free ligand (3266 cm$^{-1}$) caused by large changes in electron density distribution in the reduced moiety.

NMR studies

All complexes 1-10 are diamagnetic substances. The non-reduced DAD ligand and its complexes with d$^0$ metal centres exhibit signals for $CH$ groups in the $^1$H-NMR spectra at low field ($\delta_H$ approx. 8.0 ppm) and in the $^{13}$C-NMR spectra in the region around 150 ppm [3]. In contrast, in the reduced DAD$^{2-}$ moiety all signals are shifted to high field: $\delta_{(CH)}$ of about 5-7 ppm in $^1$H-NMR and 90-100 ppm in $^{13}$C-NMR. The influence on the signals of $^1$Bu-groups is considerably smaller: signals are shifted to low field in comparison with signals of the free DAD, approx. 0.2 ppm in $^1$H-NMR and approx. 2 ppm in $^{13}$C-NMR. The symmetrical chelate nature of the folded DAD$^{2-}$ ligand allows the observation of some dynamic processes in solution. That will be discussed in the following paragraph.

DNMR studies

Dynamic effects in solution can be observed on signals of the DAD$^{2-}$ ligand if it has asymmetrical surroundings in a complex. In the imido DAD$^{2-}$ complexes of type A (Fig. 18) with different substituents X and Y the DAD$^{2-}$ signals should consist of two doublets (AA’ system) for methine protons and two singlets for $^1$Bu groups in the $^1$H-NMR spectra. In the $^{13}$C-
NMR spectra two signals for the methine carbon atoms and two sets of signals for $^1$Bu groups are expected. If the rapid exchange between the substituents X and Y takes place either intermolecularly via dissociation/association or intramolecularly via pseudo-rotation [19], then the molecule gets a new symmetry plane. This forces the DAD$^{2-}$ signals to be magnetically equivalent on the NMR time scale and two singlets in $^1$H-NMR and three signals in $^{13}$C-NMR spectra should be detected.

Fig. 18. Geometry and dynamics of the DAD$^{2-}$ ligand in imido complexes of niobium and tantalum.
There are two other possible mechanisms of ligand rearrangement, which should be considered for the DAD$^{2-}$ ligand. The mechanism of rotation around the metal–to–diene centroid axis was postulated for some complexes with $\eta^4$–butadiene$^{2-}$ ligands, which are at first sight similar to the DAD$^{2-}$ one [20]. Alternatively a ‘flipping’ mechanism with ring inversion, in which planar $\eta^2$–bonded metallocycle is the transition state can be considered. This mechanism is more consistent with experimental data for complexes of early transition metals with substituted $\eta^4$–butadiene$^{2-}$ ligands [11a].

The ‘flipping’ of the double bond (inversion of the R,R’–DAD$^{2-}$M ring) was proposed as a mechanism of molecular rearrangement in pseudo tetrahedral complexes of the elements group IV with different substituted R,R’–DAD$^{2-}$ ligands [Cp$_2$(R,R’–DAD)M] (M = Ti, Zr, Hf) [12]. In this case the dynamic behaviour was observed on the signals of cyclopentadienyl rings and not R,R’–DAD$^{2-}$ ligands. The molecule with planar metallocycle seems to be transition state of this ‘flipping’ (Fig. 19).

![Fig. 19. The ‘flipping’ of the DAD$^{2-}$ double bond in complexes [Cp$_2$(R,R’–DAD)M] (M = Ti, Zr, Hf) [12].](image)

With respect to the definition of two possible isomers for a folded R,R’–DAD$^{2-}$ ligand in cyclopentadienyl half-sandwich complexes it is tenable to use it also in the presence of the isolobal RN$^{2-}$ ligand.
Applying this terminology the ‘flipping’ of the DAD\(^2–\) double bond is the converting of the supine into the prone isomer and vice versa (Fig. 18). It is obvious that in common case supine and prone isomers are magnetically and energetically non-equivalent and should exhibit different NMR spectra. Furthermore, being in equilibrium, supine and prone isomers should have different populations because of different energy, which correlates with their signal intensities in NMR spectra.

Thus characteristic signals for two different molecules of type A (Fig. 18), namely, supine and prone isomers, are expected in the limiting NMR spectra at low temperature, if ‘flipping’ or rotation occurs.

These two mechanisms of molecular rearrangement may also operate in tetrahedral complexes of type B (Fig. 18), however the DNMR technique offers no possibility to detect it: the NMR spectra of [(DAD)M(N\(^t\)Bu)(X)], M = Nb and Ta, with X = Cp, Ind, acac, O\(^t\)Bu [14], and Bz (7 and 8) are temperature independent. This is consistent with either the rapid supine–prone rearrangement, which cannot be localised on the NMR time scale, or with the presence of only one isomer in solution.

The room temperature \(^1\)H-NMR spectra of [(DAD)M(N\(^t\)Bu)(Cl)(py)], M = Nb (1) and Ta (2), show a broadening of the signals belonging to the DAD\(^2–\) moiety. The full picture of the dynamic behaviour can be obtained from the spectra in the range of 200-400 K. At high temperatures the DAD\(^2–\) ligand shows one singlet for the \(^t\)Bu group and one for methine protons. The methine protons split into two doublets of an AA’ spin system with \(J_{HH}\) of approx. 3 Hz and \(^t\)Bu groups split into two singlets at low temperatures (Fig. 3 – Fig. 6). As expected the behaviour of niobium complex 1 and tantalum complex 2 are very similar, the largest difference being the coalescence temperature, which is about 10 K lower for tantalum complex 2. Only one set of signals was found in the limiting low temperature NMR spectra of 1, while supine and prone isomers in proportion 0.82:0.18 are present in the solid state (Fig. 1). As it was considered for tetrahedral complexes of the type [(DAD)M(N\(^t\)Bu)(X)] there are two possible explanations for this phenomenon: either the rapid supine–prone rearrangement takes place or only one isomer (supine or prone) is present in the solution.

Initially this dynamic phenomenon was ascribed to the ‘flipping’ of the double bond of the DAD\(^2–\) ligand, which was observed for complexes with different substituted R,R’–DAD\(^2–\) ligands [Cp\(_2\)(R,R’–DAD)M] (M = Ti, Zr, Hf) [12]. This is in accordance with the crystal structure of 1 (Fig. 1), which revealed that both supine and prone isomers are present with
different populations. But further NMR experiments and in particular the isolation of the dimeric chloro compounds 3 and 4 and derivatives with benzyl substituent 5-8 have shown that the real reason for dynamic behaviour in solution is dissociation/association process of the weakly bonded pyridine ligand.

There are several experimental facts, which support the dissociation exchange mechanism:

1) According to the intensity of the split DAD$^{2-}$ signals (1:1) the low temperature limiting spectra are consistent with either one molecule with DAD$^{2-}$ unit in the asymmetrical environment or with two molecules of the same energy, which contain DAD$^{2-}$ ligands in the symmetrical environment. The last case is less probable, especially, for the supine and prone isomers, which should have close but different energy and as a consequence different populations.

2) Two different $^t$Bu imido signals are expected at low temperatures if the ‘flipping’ of the double bond or rotation of the DAD$^{2-}$ ligand occurs, but similar to tetrahedral complexes of the type [(DAD)M(N$^t$Bu)(X)] only one signal unchangeable with temperature was observed in the spectra of 1 and 2.

3) In the $^1$H-NMR spectra of 1 and 2 at 200 K the CH signals of the DAD$^{2-}$ ligand appear as two doublets. This is only possible in the case of a DAD$^{2-}$ ligand in asymmetrical environment.

4) As it is shown in Fig. 20 and Fig. 21 the $^1$H- and $^{13}$C-NMR spectra of 2 with additional amounts of pyridine show only one set of signals for pyridine protons at room temperature. Furthermore, the line shape of the signals assigned to the DAD$^{2-}$ ligand shows some broadening with increasing pyridine concentration. The sharper a signal is beyond the coalescence point, the faster the dynamics is in solution. Thus adding pyridine slows down the exchange reaction rate. This observation is consistent with a dissociation mechanism of ligand exchange and not with an intramolecular pseudo-rotation.
5) The existence of the dimeric chloro complexes without pyridine 3 and 4 and their formation from the chloro pyridine derivative 1 and 2 by sublimation underlines the possibility of dissociation of 1 and 2 in solution.

6) The $^1$H-NMR spectra of a mixture containing $[\text{(DAD)Nb(N}^t\text{Bu)(Cl)(py)}]$ 1 and $[\text{(DAD)Nb(N}^t\text{Bu)(μ-Cl)}]_2$ 3 show only one set of signals for the DAD$^{2-}$ ligand and the $^t\text{Bu}$ imido
group at room temperature (Fig. 22 and Fig. 23), while peaks for both compounds can be independently observed at low temperature (Fig. 24 and Fig. 25). This is in accordance with a rapid pyridine exchange between these complexes.

![Diagram](image)

**Fig. 22.** The $^1$H-NMR spectrum of a mixture containing **1** and **3** at 300 K (500 MHz, $d^8$-toluene, aliphatic range).

![Diagram](image)

**Fig. 23.** The $^1$H-NMR spectrum of a mixture containing **1** and **3** at 300 K (500 MHz, $d^8$-toluene, aromatic range).
Chapter V

1.0 1.2 1.4 1.6 1.8 2.0

mixture of 1 and 3

d8 - toluene

Fig. 24. The $^1$H-NMR spectrum of the mixture containing 1 and 3 at 200 K (500 MHz, d$_8$-toluene, aliphatic range).

5.8 6.2 6.6 7.0 7.4 7.8 8.2

Mixture of 1 and 3

Fig. 25. The $^1$H-NMR spectrum of the mixture containing 1 and 3 at 200 K (500 MHz, d$_8$-toluene, aromatic range).
7) Coordinated pyridine ligand as well as free pyridine can be observed in the NMR spectra of \([(\text{DAD})\text{Nb}(\text{N}^t\text{Bu})(\text{Bz})(\text{py})]\) 5 with pyridine excess (Fig. 26) at low temperatures. In contrast only one set of pyridine signals was observed at temperatures higher than 250 K demonstrating rapid exchange between molecules in solution and in complex.

8) A phenomenon similar to that for complexes 1 and 2 was observed in the NMR spectra of benzyl compounds 5 and 6 (Fig. 13 – Fig. 16), while their derivatives without pyridine 7 and 8 seem to be monomers with tetrahedral coordination spheres and do not show any dynamic behaviour in solution.

![Fig. 26. The $^1$H-NMR spectrum of 5 in the presence of pyridine excess at different temperatures (500 MHz, d$^8$-toluene).](image)

There are several important differences in the DNMR spectra of \([(\text{DAD})\text{M}(\text{N}^t\text{Bu})(\mu-\text{Cl})]\), M = Nb (3) and Ta (4) compared to the pyridine chloro complexes \([(\text{DAD})\text{M}(\text{N}^t\text{Bu})(\text{Cl})(\text{py})]\), M = Nb (1) and Ta (2):

1) The signal of the $^t\text{Bu}$ group of the imido ligand also splits into two singlets at low temperatures, while only one singlet was observed in the spectra of 1 and 2.

2) $^\text{CH}$ signals of the DAD$^{2-}$ ligand are singlets in the low temperature NMR spectra of 3 and 4 in contrast to 1 and 2, for which two doublets were observed.
3) The intensities of the split signals for the DAD\(^{2-}\) and imido ligands have almost unchangeable proportion 2:3 below the coalescence point.

4) In contrast to 3 and 4 the corresponding Dip imido complexes \([(DAD)M(NDip)(\mu-Cl)]_2\), M = Nb (9) and Ta (10), do not show similar changes in their NMR spectra at different temperatures.

In accordance with these experimental data two different species with the DAD\(^{2-}\) units in symmetrical environments exist at low temperatures in the case of chloro complexes 3 and 4. One of them has to be assigned to a dinuclear anti (supine-supine) structure with inversion symmetry, which is present in the solid state of 4 (Fig. 7). The second one can neither be a monomeric species nor a ‘flipping’ isomer of the DAD\(^{2-}\) ligand double bond: in the first case the populations or intensities of the signals of the dimeric and monomeric forms have to depend strongly on the temperature in equilibrium [21] and would not be constant as it was observed for 3 and 4. In the second case at least three isomers should be observed in solution: supine-supine, supine-prone and prone-prone, but only two species were observed in the NMR spectra. Additionally, such dynamic behaviour was not observed for the tetragonal pyramidal complexes \([(DAD)W(NR)Cl_2]\) [22], R = Ph and Cy, that impugns the ‘flipping’ mechanism.

The most probable explanation is the existence of an energetically slightly higher syn (supine-supine) isomer with symmetry plane, which makes both DAD\(^{2-}\) ligands and both imido groups magnetically equivalent. This isomer can be in equilibrium with anti (supine-supine) isomer via a monomeric form. This assumption correlates with exchange experiments, where a mixture of 3 and 1 was investigated by \(^1\)H-NMR at different temperatures (Fig. 22 – Fig. 25). A dissociative mechanism allows complexes 1 and 3 to exchange the pyridine ligand. This leads to the observation of one signal set at room temperature.
A similar dependence upon temperature was observed in the $^1$H-NMR spectra of [Cp(DAD)TiCl] [11b]. For this complex a monomeric structure was proposed and the ‘flipping’ mechanism of the DAD$^{2-}$ double bond was considered. Taking into account that the fragment [(DAD)M(N$^i$Bu)Cl] (M = Nb, Ta) is isolobal to [Cp(DAD)TiCl], the observed two signals of Cp ligand may be due to the presence of syn and anti isomers of a dinuclear chloro-bridged titanium species.

It is interesting that 2,6-di-isopropylphenylimido complexes 9 and 10 do not show any similar dynamic behaviour in solution. Although they have a dimeric anti (supine-supine) structure according to X-ray studies of 10 (Fig. 17), the repulsion between bulky 2,6-di-isopropylphenyl substituents seems to prevent the formation of the syn (supine-supine) isomer and only one set of signals for the DAD$^{2-}$ and Dip ligands was observed in the NMR spectra at different temperatures.
In order to calculate the thermodynamic parameters for the dissociation barrier in 1-6 a Band-Shape Analysis [18] and the Win-Dyna 32 program [23] were applied. The values of the rate constants $k$ were obtained from the $^1$H-NMR spectra at different temperatures $T$, the coalescence of the $^1$Bu signals of the DAD$^{2-}$ ligands was used for pyridine complexes 1-2 and 5-6. For the chloro complexes 3 and 4 the data were obtained independently for all coalescing signals (CH-DAD, $^1$Bu-DAD and $^1$Bu-imido) and afterwards were combined in one set in supposition that the dynamic observations have the same origin. This dependence, $k$ versus $T$, was fitted to the standard Eyring equation [18] to determine thermodynamic parameters of activation entropy $\Delta S^\neq$ and enthalpy $\Delta H^\neq$:

$$ k = \frac{\sigma k_B T}{h} e^{-\frac{\Delta H^\neq - T \Delta S^\neq}{RT}} $$

where $k_B$ represents Boltzmann’s constant, $T$ is absolute temperature, $h$ is Planck’s constant and $R$ is the universal gas constant. The transmission coefficient $\sigma$ was taken equal to one for this type of barrier. The logarithmic variant [24] allows calculating $\Delta H^\neq$ and $\Delta S^\neq$ values from the experimental data set of the rate constants $k$ depending on the temperature $T$. By plotting the experimental data in a half-logarithmic diagram $\Delta H^\neq$ and $\Delta S^\neq$ values can be obtained from a linear fit.

$$ \lg(k/T) = 10.32 - \frac{\Delta H^\neq}{19.13} \left( \frac{1}{T} \right) + \frac{\Delta S^\neq}{19.13} $$

The experimental data for the pyridine complexes 1-2 and 5-6 are presented in Fig. 27 and for the dimeric chloro complexes 3 and 4 in Fig. 28.
Fig. 27. Eyring plot for complexes 1, 2, 5 and 6.

Fig. 28. Eyring plot for complexes 3 and 4.

For linear fitting the PFIT45W program was applied [25]. A temperature uncertainty of 0.5 K and a relative uncertainty of 20% for the rate constants were taken to estimate the error of...
the fitted parameters. The calculated values of activation entropy $\Delta S^\neq$ and enthalpy $\Delta H^\neq$ for the first-order dissociation reactions are listed in Table 2 [26].

### Table 2. Activation entropy and enthalpy values calculated from the DNMR experiments.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$T_{coal}, K$</th>
<th>$\Delta G_{298}^\neq$, kJ·mol$^{-1}$</th>
<th>$\Delta H^\neq$, kJ·mol$^{-1}$</th>
<th>$\Delta S^\neq$, J·mol$^{-1}·K^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>280*</td>
<td>52 ± 3</td>
<td>74 ± 2</td>
<td>75 ± 5</td>
</tr>
<tr>
<td>2</td>
<td>295*</td>
<td>56 ± 3</td>
<td>77 ± 2</td>
<td>70 ± 6</td>
</tr>
<tr>
<td>3</td>
<td>285**</td>
<td>58 ± 5</td>
<td>72 ± 2</td>
<td>49 ± 8</td>
</tr>
<tr>
<td>4</td>
<td>280**</td>
<td>56 ± 5</td>
<td>73 ± 2</td>
<td>59 ± 8</td>
</tr>
<tr>
<td>5</td>
<td>260*</td>
<td>48 ± 4</td>
<td>63 ± 2</td>
<td>50 ± 7</td>
</tr>
<tr>
<td>6</td>
<td>265*</td>
<td>49 ± 3</td>
<td>65 ± 1</td>
<td>55 ± 6</td>
</tr>
</tbody>
</table>

* coalescence temperature of $^1$Bu-DAD signals
** coalescence temperature of CH-DAD and $^1$Bu imido signals

All calculated activation entropies $\Delta S^\neq$ for 1-6 are significantly positive supporting a dissociative mechanism of exchange, while a value close to zero is characteristic for the ‘flipping’ mechanism [13,14, 27]. For the pseudo–rotation isomerisation a negative or close to zero value is also expected. For example, in five-coordinated cyclopentadienyl phosphine complexes of the type [CpMo(CO)$_2$(PR)$_3$(X)] [19b], where X = H, Me, Bz or halogen, the activation entropy $\Delta S^\neq$ was found to be in the range from $-30$ to $+5$ J·mol$^{-1}·K^{-1}$ and in the gaseous SF$_4$ a value of $-12 \pm 2$ J·mol$^{-1}·K^{-1}$ was obtained, which is in good accordance with theoretical computations [28]. In contrast to these data the wide range of entropies from $-50$ to $+50$ J·mol$^{-1}·K^{-1}$ was observed for dynamics in tetrakis(isocynano)cobalt and rhodium complexes of the type [M(RNC)$_4$]{η$^2$-(CN)$_2$C=C(CN)$_2$}][X]$^-$, M = Co, Rh; X = PF$_6$, BPh$_4$, ClO$_4$ [19c]. Indeed, the authors consider three different intra molecular processes and contribution of each mechanism was not estimated quantitatively. Consequently, the measured entropy values cannot be regarded only to the pseudo-rotation process.

There is no clear trend of dependence of thermodynamic parameters with respect to the nature of the metal centre. Calculated values are very close to each other and often lie in the error range. The activation enthalpy $\Delta H^\neq$ for dissociation of the benzyl complexes 5 and 6 is lower than that for chloro complexes 1-4, showing that [(DAD)M(N$^1$Bu)Cl] particle is a stronger Lewis acid than the alkyl derivatives, because of the electron withdrawing chloro ligand.
Conclusions

The dimeric chloro complexes \([(DAD)M(N^tBu)(\mu-Cl)]_2, M = Nb (3) and Ta (4), and their mononuclear pyridine adducts \([(DAD)M(N^tBu)(Cl)(py)], M = Nb (1) and Ta (2), were prepared. Complexes 1 and 2 react with BzMgCl to produce benzyl pyridine complexes \([(DAD)M(N^tBu)(Bz)(py)], M = Nb (5) and Ta (6), while reaction of 3 and 4 with BzMgCl affords pyridine free complexes \([(DAD)M(N^tBu)(Bz)], M = Nb (7) and Ta (8), which are liquids at room temperature. Complexes \([(DAD)Ta(N^tBu)(\mu-Cl)]]_2 and \([(DAD)M(NDip)(\mu-Cl)]_2, M = Nb (9) and Ta (10), were obtained by reduction of \([M(NR)Cl_3(dad)]\) with C\(_6\)K.

According to the molecular structures of 2, 4, 6 and 10, imido DAD\(^{2-}\) complexes have a tendency to form the supine conformation. Although 1 exhibits both supine and prone isomers in a ratio of 0.82:0.18 in a solid state, only one is present in solution. The latter seems to have supine conformation with respect to similarity of the NMR observations for 1 and 2.

The dynamic behaviour observed in solution for pyridine complexes 1-2 and their benzyl analogues 5-6 should be regarded as inter molecular exchange of pyridine ligand based on the dissociation mechanism. According to this mechanism the mononuclear species \([(DAD)M(N^tBu)(Cl)]\) have to be formed in solution. This is also in accordance with dynamic investigations in solution on dimeric complexes 3 and 4, for which syn and anti isomers are proposed to be in equilibrium through monomeric species \([(DAD)M(N^tBu)(Cl)]\).

Experimental Part

General: All reactions and manipulations were carried out under argon using standard Schlenk tube techniques. Solvents and liquid starting materials were refluxed in the presence of an appropriate drying agent and distilled: C\(_6\)D\(_6\) and hexane (Na/K alloy); THF and Et\(_2\)O (Na/benzophenone); toluene (Na); amines, CH\(_2\)Cl\(_2\), CDCl\(_3\) and \(^{1}\)BuOH (CaH\(_2\)). Literature methods were employed for the synthesis of starting materials and 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene (DAD) [29a], Li\(_2\)DAD [6, 29b], [M(NtBu)Cl\(_3\)(py)\(_2\)] [7], [M(N^tBu)(NH^tBu)Cl\(_2\)(NH\(_2\)^tBu)\(_2\)] [29c], [M(N^tBu)(NH^tBu)Cl\(_2\)(py)\(_2\)] [29d], [M(NR)Cl\(_3\)(dad)] [3], M = Nb and Ta, R = \(^{1}\)Bu and Dip. Lithium salts of CpH and IndH were obtained by reaction with n-BuLi in n-hexane and acacNa by reaction of acacH with NaH in THF. Melting points were measured with a Büchi MP B-540 (uncorrected). C, H and N analyses were carried out with a Heraeus CHN-Rapid analyser. Mass spectra were taken on a Varian MAT CH-7a (EI, 70 eV).
\(^1\)H- and \(^{13}\)C\(^{(1)}\)H\)-NMR spectra were recorded with Bruker AMX300, AMX400 and DRX500; chemical shifts were referenced (in ppm) to the \(^1\)H (\(\delta 7.15\)) and \(^{13}\)C (\(\delta 128.0\)) residual signals of the C\(_6\)D\(_6\), \(^1\)H (\(\delta 7.24\)) and \(^{13}\)C (\(\delta 77.0\)) residual signals of the CDCl\(_3\), \(^1\)H (\(\delta 2.03\)) and \(^{13}\)C (\(\delta 20.3\)) residual signals of the methyl group of d\(^8\)-toluene. Infrared spectra were recorded with Bruker IFS 88 FT; samples (if not specified) as Nujol mulls between KBr plates.

**Preparation of [(DAD)Nb(N\(^{tb}\)Bu)(Cl)(py)] 1.**

**Method A.** A solution of Li\(_2\)DAD 2.1 g (11.7 mmol) in 20 mL THF was added dropwise at –80°C to a solution of 5.0 g (11.7 mmol) [Nb(N\(^{tb}\)Bu)Cl\(_3\)py\(_2\)] in 20 mL THF. After approx. 30 min of stirring at low temperature the colour changed to dark-brown and the resulting mixture was stirred for 10h at room temperature. The volatiles were completely removed in vacuum and the residue was extracted with 2 x 10 mL Et\(_2\)O. Removing the solvent and washing the yellow residue with 20 mL hexane produced a yellow microcrystalline solid. A second crop was obtained by crystallisation of the hexane fraction at –80°C. Yield: 3.76 g (72%).

**Method B.** This compound was obtained in quantitative yield from the reaction of 50 mg (68 \(\mu\)mol) [(DAD)Nb(N\(^{tb}\)Bu)(µ-Cl)]\(_2\) (3) with 11 \(\mu\)L (136 \(\mu\)mol) of pyridine in ether. T\(_{\text{m.p.}}\) 115.4°C. Anal. Calcd for C\(_{19}\)H\(_{34}\)N\(_4\)ClNb (\(M = 446.87\) g mol\(^{-1}\)): C 51.07, H 7.67, N 12.54. Found: C 49.26, H 7.64, N 11.84. MS-EI: 367 (M\(^+\) – Py, 30%), 352 (M\(^+\) – Py – Me, 46%), 296 (M\(^+\) – Py – Me\(_2\)C=CH\(_2\) – Me, 3%), 240 (M\(^+\) – Py – 2 Me\(_2\)C=CH\(_2\) – Me, 2%), 199 (M\(^+\) – Py – 3·Me\(_2\)C=CH\(_2\), 13%), 57 (100%). \(^1\)H-NMR (C\(_6\)D\(_6\), 300 MHz, 300 K): 8.53 (d, \(3\)\(^{\text{JHH}}\) = 3.6 Hz, 2H, o-py), 6.79 (t, \(3\)\(^{\text{JHH}}\) = 7.6 Hz, 1H, p-py), 6.47 (pseudo-t, \(3\)\(^{\text{JHH}}\) = 6.3 Hz, 2H, m-py), 6.17 (bs, 2H, CH-DAD), 1.52 (s, 9H, N\(^{tb}\)Bu), 1.35 (bs, 18H, \(t\)Bu-DAD). \(^{13}\)C\(^{(1)}\)H-NMR (C\(_6\)D\(_6\), 75 MHz, 300 K): 150.6, 136.9 and 123.7 (py), 57.3 (CMe\(_3\)-DAD), 32.9 (NCMe\(_3\)), 30.7 (CMe\(_3\)-DAD). IR (KBr, cm\(^{-1}\)): 3020(w), 1602(w), 1480(w), 1365(w), 1295(w), 1217(s), 1155(w), 1138(w), 1057(w), 1045(w), 1012(w), 875(m), 814(m), 775(m), 761(m), 723(w), 700(m), 634(w).
Preparation of \[(\text{DAD})\text{Ta(N}^t\text{Bu})(\text{Cl})(\text{py})\] 2.

**Method A.** A solution of Li$_2$DAD 3.6 g (19.8 mmol) in 20 mL THF was added dropwise at −80°C to a solution of 10.2 g (19.6 mmol) [Ta(N$^t$Bu)Cl$_3$py$_2$] in 20 mL THF. After approx. 30 min of stirring at low temperature the colour changed to dark brown and the resulting mixture was stirred for 10h at room temperature. The volatiles were completely removed in vacuum and the residue was extracted with 2 x 10 mL Et$_2$O. Removing the solvent and washing the yellow residue with 20 mL hexane produced a yellow microcrystalline solid. A second crop was obtained by crystallisation of the hexane fraction at −80°C. Yield: 8.73 g (83%).

**Method B.** This compound was also obtained with quantitative yield from the reaction of 50 mg (55 µmol) [(DAD)Ta(N$^t$Bu)(µ-Cl)]$_2$ (4) with 9 µL (111 µmol) of pyridine in ether. T$_{\text{m.p.}}$ 142.8°C. Anal. Calcd for C$_{19}$H$_{34}$N$_4$ClTa (M = 534.91 g mol$^{-1}$): C 42.66, H 6.41, N 10.47. Found: C 42.27, H 5.97, N 10.19. MS-EI: 455 (M$^+$ – Py, 15%), 440 (M$^+$ – Py – Me, 39%), 399 (M$^+$ – Py – Me$_2$C=CH$_2$, 1%), 328 (M$^+$ – Py – 2·Me$_2$C=CH$_2$ – Me, 7%), 328 (M$^+$ – Py – 2·Me$_2$C=CH$_2$ – Me, 7%), 287 (M$^+$ – Py – 3·Me$_2$C=CH$_2$), 79 (Py$^+$, 100%).

[1H-NMR (C$_6$D$_6$, 300 MHz, 300 K): 8.57 (d, $^3$J$_{HH} = 4.9$ Hz, 2H, o-py), 6.77 (t, $^3$J$_{HH} = 7.7$ Hz, 1H, p-py), 6.45 (pseudo-t, $^3$J$_{HH} = 6.7$ Hz, 2H, m-py), 6.17 (bs, 2H, C$_{H}$-DAD), 1.55 (s, 9H, N$^t$Bu), 1.34 (bs, 18H, t$_{Bu}$-DAD).] $^{13}$C{$_1$H}-NMR (C$_6$D$_6$, 75 MHz, 300 K): 150.7, 137.5 and 124.0 (py), 65.5 (CMe$_3$N), 56.6 (CMe$_3$-DAD), 34.2 (NCMe$_3$), 30.9 (CMe$_3$-DAD). $^{13}$C{$_1$H}-NMR (d$_8$-toluene, 100 MHz, 230 K): 152.9, 139.9 and 126.8 (py), 150.7, 137.5 and 124.0 (py), 65.5 (CMe$_3$N), 56.6 (CMe$_3$-DAD), 34.2 (NCMe$_3$), 30.9 (CMe$_3$-DAD). $^{13}$C{$_1$H}-NMR (d$_8$-toluene, 100 MHz, 230 K): 152.9, 139.9 and 126.8 (py), 111.8 and 101.4 (CH-DAD), 68.1 (NCMe$_3$), 59.0 and 58.8 (CMe$_3$-DAD), 36.7 (NCMe$_3$), 33.5 and 33.0 (CMe$_3$-DAD).

Preparation of \[(\text{DAD})\text{Nb(N}^t\text{Bu})(\mu-\text{Cl})]_2\) 3.

**Method A.** Sublimation of 500 mg [(DAD)Nb(N$^t$Bu)(µ-Cl)]$_2$ (1) at 150°C/10$^{-4}$ mbar produced 230 mg (56%) of a yellow solid.

**Method B.** 1BuNH$_2$ (58.0 mL, 555.1 mmol) was added dropwise to a stirred suspension of 50.0 g NbCl$_5$ (185.1 mmol) in 300 mL CH$_2$Cl$_2$ at 0°C. The mixture was warmed to room temperature and stirred for 3h. Then DAD (31.1 g, 185.1 mmol) was added and the resulting
suspension was stirred for 8h. After this 150 mL of hexane was added and the solution was filtered off. The volatiles were removed in vacuum and the residue dissolved in 200 mL of THF. Two equivalents of Li (2% Na) powder (2.6 g, 370.2 mmol) were slowly added to this under ice cooling; the colour being changed immediately to dark brown. After 8h THF was evaporated and the compound was extracted with 2 x 150 mL ether. The solvent was removed in vacuum and the product was sublimed (160°C/10⁻⁴ mbar). Yield 32.0 g (47%). Tm.p. 188.4°C. Anal. Calcd for monomer C₁₄H₂₉N₃ClNb (M = 367.77 g mol⁻¹): C 45.72, H 7.95, N 11.43. Found: C 45.88, H 8.04, N 11.41. MS-EI: 367 (M⁺, 1%), 352 (M⁺ – Me, 1%), 296 (M⁺ – Me₂C=CH₂ – Me, 1%), 58 (100%). ¹H-NMR (C₆D₆, 300 MHz, 300 K): 6.08 (bs, 2H, CH-DAD), 1.45 (s, 9H, NᵗBu), 1.38 (s, 18H, NᵗBu-DAD). ¹H-NMR (d₈-toluene, 400 MHz, 230 K): anti isomer: 6.00 (s, 3H, CH-DAD), 1.36 (s, 27H, NᵗBu-DAD), 1.35 (s, 13.5H, NᵗBu), syn isomer: 5.75 (s, 2H, CH-DAD), 1.58 (s, 9H, NᵗBu), 1.31 (s, 18H, NᵗBu-DAD). ¹³C{¹H}-NMR (C₆D₆, 75 MHz, 300 K): 106.0 (CH-DAD), 57.7 (CMe₃-DAD), 32.4 (NCMe₃), 30.8 (CMe₃-DAD). IR (KBr, cm⁻¹): 3032(w), 1491(w), 1456(s), 1393(w), 1360(m), 1263(w), 1246(w), 1215(s), 1155(w), 1144(w), 1092(w), 1061(w), 1036(w), 1026(w), 1017(w), 951(w), 870(m), 810(m), 774(s), 723(w), 698(w), 669(w), 584(w), 569(m), 540(w), 515(w).

**Preparation of [(DAD)Ta(NᵗBu)(µ-Cl)]₂ 4.**

**Method A.** [Ta(NᵗBu)Cl₃(dad)] (1.17 g, 2.23 mmol) was dissolved in 20 mL THF. To the solution 0.60 g (0.96 mmol) of CsK were added. After 8h at room temperature the dark brown solution was filtered off and the solvent was evaporated. Further sublimation at 160°C/10⁻⁴ mbar yielded 0.72 g (71%) of the analytical pure compound as a pale yellow solid.

**Method B.** NᵗBuNH₂ (43.8 mL, 418.7 mmol) was added dropwise to a stirred suspension of 50.0 g TaCl₅ (139.6 mmol) in 300 mL CH₂Cl₂ at 0°C. The mixture was warmed to room temperature and stirred for 3h. Then DAD (23.5 g, 139.6 mmol) was added and the resulting suspension was stirred for 8h at room temperature. After this time 150 mL of hexane was added and the solution was filtered. The volatiles were removed in vacuum and the residue dissolved in 200 mL of THF. 2 eq of Li (2% Na) powder (2.0 g, 288.2 mmol) were slowly added under ice cooling. The colour changed immediately to dark-brown. After 8h, THF was evaporated and the compound was extracted with 2 x 150 mL ether. The solvent was removed in vacuum and the product was sublimed (160°C/10⁻⁴ mbar). Yield 38.8 g (61%).

**Method C.** As an alternative reducing agent CsK can be used instead of Li in method B. In this case yield was 59% in the 1g-reaction scale.
Method D. [(DAD)Ta(N\text{t}Bu)(Cl)(py)] (2) (1.00 g) was sublimed at 150°C/10⁻⁴ mbar. Yield: 500 mg (59%). Anal. Calcd for monomer C₁₄H₂₉N₃Ta (M = 455.81 g mol⁻¹): C 36.89, H 6.41, N 9.22. Found: C 36.39, H 6.37, N 9.18. MS-EI: 455 (M⁺, 9%), 440 (M⁺ – Me, 21%), 399 (M⁺ – Me₂C=CH₂, 7%), 384 (M⁺ – Me₂C=CH₂ – Me, 5%), 328 (M⁺ – 2·Me₂C=CH₂ – Me, 5%), 58(100%). ¹H-NMR (C₆D₆, 300 MHz, 300 K): 6.07 (bs, 2H, CH-DAD), 1.47 (s, 9H, N\text{t}Bu), 1.35 (s, 18H, N\text{t}Bu-DAD).

Preparation of [(DAD)Nb(N\text{t}Bu)(Bz)(py)] 5.
Method A. [(DAD)Nb(N\text{t}Bu)(Cl)(py)] (1) (1.00 g, 2.2 mmol) was dissolved in 10 mL Et₂O. A suspension of 0.50 g [BzMgCl*thf] [30] (2.2 mmol) in 10 mL Et₂O was added at –80°C. After 10 min the colour had changed to orange and reaction mixture was stirred for 5h at room temperature. The yellow precipitate was filtered off and washed with 5 mL of Et₂O. Evaporation of the solvent and recrystallisation from hexane produced the pure product as orange crystals in 39% yield (0.43 g).

Method B. This compound can be also obtained in quantitative yield from the reaction of 50 mg (118 µmol) [(DAD)Nb(N\text{t}Bu)(Bz)] (7) with 10 µL (123 µmol) of pyridine in hexane. Tₘp. 110.9°C. Anal. Calcd for C₂₆H₄₁N₄Nb (M = 502.55 g mol⁻¹): C 62.14, H 8.22, N 11.15. Found: C 62.14, H 8.22, N 11.15. MS-EI: 423 (M⁺ – Py, 38%), 408 (M⁺ – Py – Me, 3%), 367 (M⁺ – Py – Me₂C=CH₂, 2%), 332 (M⁺ – Bz – Py, 100%), 275 (M⁺ – Bz – Py – Me₂C=CH₂ – H, 50%). ¹H-NMR (C₆D₆, 300 MHz, 300 K): 8.15 (bs, 2H, o-py), 6.90 (pseudo-t, JHH = 7.6 Hz, 2H, m-Bz), 6.74–6.63 (m, 4H, o- and p-Bz overlapped with p-py), 6.33 (pseudo-t, JHH = 6.7 Hz, 2H, m-py), 6.02 (s, 2H, CH-DAD), 2.34 (bs, 2H, CH₂-Bz), 1.55 (s, 9H, N\text{t}Bu), 1.26 (bs, 18H, N\text{t}Bu-DAD).
¹³C{¹H}-NMR (C₆D₆, 75 MHz, 300 K): 150.0 (o-py), 136.6 (p-py), 127.6 (m-Bz), 126.0 (o-Bz), 123.6 (m-py), 119.1 (p-Bz), 106.2 (CH-DAD) 66.5 (NCMe₃) 56.6 (CMe₃-DAD), 45.4 (CH₂-Bz), 33.7 (NCMe₃), 31.0 (CMe₃-DAD). IR (KBr, cm⁻¹): 3057(w), 3021(w), 1603(w), 1589(m), 1497(w), 1480(w), 1456(s), 1445(w), 1360(m), 1258(s), 1242(w), 1213(s), 1173(w), 1148(m), 1138(w), 1096(w), 1071(w), 1055(w), 1042(w), 1028(w), 1013(w), 963(m), 949(w), 870(m), 810(m), 770(s), 723(w), 567(w), 544(w), 511(w), 453(w).
Preparation of [(DAD)Ta(N'Bu)(Bz)(py)] 6.

**Method A.** 500 mg of [(DAD)Ta(N'Bu)(Cl)(py)] (2) (0.94 mmol) were dissolved in 10 mL Et₂O. A suspension of 210 mg [BzMgCl*thf] (0.94 mmol) in 10 mL Et₂O was added at –80°C. After 10 min the colour had changed to orange and the reaction mixture was stirred for 5h at room temperature. The yellow precipitate was filtered and washed with 5 mL of Et₂O. Evaporation of the combined extracts and recrystallisation from hexane produced pure product as orange crystals in 38% yield (210 mg).

**Method B.** This compound was obtained in quantitative yield from the reaction of 50 mg (98 µmol) [(DAD)Ta(N'Bu)(Bz)] (8) with 8 µL (99 µmol) of pyridine in hexane. Tₘ.p. 117.7°C. Anal. Calcd for C₂₆H₄₁N₄Ta (M = 590.59 g mol⁻¹): C 52.88, H 7.00, N 9.49. Found: C 47.31, H 7.03, N 8.45. MS-EI: 511 (M⁺ – Py, 3%), 52(100%).

1H-NMR (C₆D₆, 300 MHz, 300 K): 8.21 (pseudo-d, 3Jₜₜ = 3.1 Hz, 2H, o-py), 6.91 (pseudo-t, 3Jₜₜ = 7.6 Hz, 2H, m-Bz), 6.72–6.62 (m, 4H, o- and p-Bz overlapped with p-py), 6.30 (pseudo-t, 3Jₜₜ = 6.7 Hz, 2H, m-py), 6.06 (s, 2H, CH-DAD), 2.10 (bs, 2H, CH₂-Bz), 1.58 (s, 9H, N'tBu), 1.26 (bs, 18H, tBu-DAD).

13C{¹H}-NMR (C₆D₆, 75 MHz, 300 K): 153.8 (Ci-Bz), 150.2 (o-py), 136.7 (p-py), 127.2 (m-Bz), 126.5 (o-Bz), 123.8 (m-py), 119.5 (p-Bz), 104.8 (CH-DAD) 65.5 (NCMe₃), 56.3 (CMe₃-DAD), 53.6 (CH₂-Bz), 34.8 (NCMe₃), 31.2 (CMe₃-DAD). IR (KBr, cm⁻¹): 3057(w), 1602(w), 1591(w), 1361(w), 1276(m), 1262(w), 1218(m), 1172(w), 1152(w), 1137(w), 1094(w), 1071(w), 1058(w), 1040(w), 1028(w), 1014(m), 986(w), 960(w), 867(w), 805(m), 764(w), 747(w), 723(w), 693(w), 631(w), 592(w), 557(w), 538(w), 503(w).

Preparation of [(DAD)Nb(N'Bu)(Bz)] 7. A mixture of 1.00 g (1.36 mmol) [(DAD)Nb(N'Bu)(µ-Cl)]₂ (3) and 0.60 g (2.72 mmol) [BzMgCl*thf] was dissolved in 20 mL THF. The obtained solution was stirred for 12h. THF was removed in vacuum and the resulting oil was extracted with 20 mL hexane. Hexane was evaporated and the product was purified by distillation (150°C/10⁻⁴ mbar). Yield: 0.66 g (57%) of slightly yellow liquid. Tₘ.p. between –30°C and 25°C. Anal. Calcd C₂₁H₃₆N₃Nb (M = 423.45 g mol⁻¹): C 59.57, H 8.57, N 9.92. Found: C 57.69, H 8.60, N 9.65. MS-EI: 423 (M⁺, 26%), 332 (M⁺ – Bz, 100%), 275 (M⁺ – Bz – Me₂C=CH₂ – H, 16%). ¹H-NMR (C₆D₆, 500 MHz, 300 K): 7.02 (pseudo-t, 3Jₜₜ = 7.7 Hz, 2H, m-Bz), 6.88 (d, 3Jₜₜ = 7.3 Hz, 2H, o-Bz), 6.82 (t, 3Jₜₜ = 7.3 Hz, 1H, p-Bz), 5.63 (s, 2H, CH-DAD), 2.19 (s, 2H, CH₂-Bz), 1.50 (s, 9H, N'Bu), 1.13 (s, 18H, tBu-DAD). ¹³C{¹H}-NMR (C₆D₆, 125
MHz, 300 K): 129.4 (m-Bz), 126.5 (o-Bz), 122.5 (p-Bz), 104.1 (CH-DAD), 66.7 (NCMe₃), 57.1 (CMe₃-DAD), 48.6 (CH₂-Bz), 33.7 (NCMe₃), 31.3 (CMe₃-DAD). IR (KBr, pure, cm⁻¹): 3067(w), 3021(w), 2965(s), 2922(s), 2897(s), 2865(m), 1591(m), 1495(w), 1480(s), 1454(m), 1447(w), 1389(m), 1362(s), 1258(s), 1221(s), 1177(w), 1146(s), 1138(w), 1105(w), 1084(w), 1065(w), 1028(m), 999(w), 976(w), 951(m), 911(w), 791(w), 774(s), 747(s), 694(s), 606(w), 561(m), 531(m), 519(w), 451(m).

Preparation of [(DAD)Ta(N₄Bu)(Bz)] 8. 1.00 g (1.10 mmol) of [(DAD)Ta(N₄Bu)(μ-Cl)]₂ and 0.49 g (2.19 mmol) of [BzMgCl ∗ thf] were mixed. The mixture of solids was dissolved in 20 mL THF and the obtained solution was stirred for 12h. THF was removed in vacuum and the resulting oil was extracted with 20 mL hexane. Hexane was evaporated and the product was purified by distillation (150°C/10⁻⁴ mbar). Yield: 0.83 g (74%) of pale yellow liquid. T m.p. over -30°C and below 20°C. Anal. Calcd C₂₁H₃₆N₃Ta (M = 511.49 g mol⁻¹): C 49.31, H 7.09, N 8.22. Found: C 45.78, H 6.41, N 8.27. MS-EI: 511 (M⁺, 23%), 496 (M⁺ – Me, 32%), 420 (M⁺ – Bz, 5%), 363 ([DAD]TaN⁺, 13%), 57 (100%).

1H-NMR (C₆D₆, 200 MHz, 300 K): 7.22–7.00 (m, 5H, Bz), 5.66 (s, 2H, CH-DAD), 2.01 (s, 2H, CH₂-Bz), 1.62 (s, 9H, N₄Bu), 1.18 (s, 18H, t-Bu-DAD). 13C{¹H}-NMR (C₆D₆, 50 MHz, 300 K): 143.2 (C₉-Bz), 128.4 (m-Bz), 127.4 (o-Bz), 122.4 (p-Bz), 103.1 (CH-DAD), 65.4 (NCMe₃), 57.6 (CH₂-Bz), 57.1 (CMe₃-DAD), 35.0 (NCMe₃), 31.3 (CMe₃-DAD). IR (KBr, pure, cm⁻¹): 3071(w), 3051(w), 3015(m), 2965(s), 2924(s), 2940(s), 2897(s), 2866(m), 1593(s), 1483(s), 1470(m), 1456(m), 1402(w), 1391(m), 1375(m), 1363(s), 1283(s), 1221(s), 1179(w), 1138(s), 1107(w), 1076(w), 1030(m), 1018(m), 993(w), 963(m), 872(s), 820(m), 808(w), 787(w), 777(s), 747(s), 694(s), 625(w), 565(m), 523(s), 451(m).

Preparation of [(DAD)Nb(NDip)(μ-Cl)]₂ 9. [Nb(NDip)Cl₃(dad)] (2.3 g, 4.3 mmol) was dissolved in 20 mL THF. To the solution 1.2 g (4.6 mmol) of C₈K were added. After 8h at room temperature the dark brown solution was filtered off and the solvent was evaporated. Further sublimation at 160°C/10⁻⁴ mbar yielded 0.5 g (25%) of the analytical pure compound as a yellow solid. T m.p. 170°C(dec.). Anal. Calcd for monomer C₂₂H₃₇N₃ClNb (M = 471.92 g mol⁻¹): C 55.99, H 7.90, N 8.90. Found: C 54.60, H 8.31, N 8.87. MS-EI: 471 (M⁺, 92%), 456 (M⁺ – Me, 16%), 415 (M⁺ – Me₂C=CH₂, 5%), 400 (M⁺ – Me₂C=CH₂ – Me, 14%), 296 (M⁺ – Dip – Me + H, 5%), 240 (M⁺ – Me₂C=CH₂ – Dip – Me + H, 5%). ¹H-NMR (C₆D₆, 500 MHz, 300 K): 7.13 (d, 2H, ³JHH = 7.8 Hz, m-NDip), 7.00 (t, 1H, ³JHH = 7.8 Hz, p-NDip), 6.38 (s, 2H, CH-DAD), 3.96 (sept, ³JHH = 6.6 Hz, CH-NDip), 1.34 (s, 18H, t-Bu-DAD), 1.33 (d, 12H, ³JHH = 6.6 Hz, CH₃-
13C{1H}-NMR (C₆D₆, 125 MHz, 300 K): 143.2 (o-NDip), 123.4 (p-NDip), 123.1 (m-NDip), 105.4 (CH-DAD), 59.7 (CMe₃-DAD), 30.3 (CMe₂-DAD), 27.5 (CH₃-NDip). IR (KBr, cm⁻¹): 3053(w), 3034(w), 1491(w), 1456(s), 1433(w), 1397(w), 1366(w), 1358(w), 1348(s), 1292(m), 1250(w), 1211(s), 1159(w), 1111(w), 1101(w), 1063(w), 1055(w), 1044(w), 1016(w), 988(m), 947(w), 932(w), 876(m), 808(m), 799(w), 774(s), 754(s), 721(w), 696(w), 608(w), 571(w).

Preparation of [(DAD)Ta(NDip)(µ-Cl)]₂ 10. 300 mg (0.48 mmol) of [TaCl₃(NDip)(dadt)] were dissolved in 20 mL THF. To this 130 mg (0.96 mmol) of C₈K were added. The next day the dark brown solution was filtered off and the solvent was evaporated. Further sublimation at 160°C/10⁻⁴ mbar yielded 30 mg of the analytical pure compound (11%).

Tₘ.p. 244°C(dec.). Anal. Calcd for monomer C₂₂H₃₇N₃ClTa (M = 559.96 g mol⁻¹): C 47.19, H 6.66, N 7.50. Found: C 46.68, H 6.52, N 7.53. MS-EI: 559 (M⁺, 61%), 162 (100%).

1H-NMR (d₈-toluene, 500 MHz, 300 K): 7.08 (d, 2H, 3JHH = 7.8 Hz, m-NDip), 6.86 (t, 1H, 3JHH = 7.8 Hz, p-NDip), 6.28 (s, 2H, CH-DAD), 3.84 (sept, 3JHH = 6.7 Hz, CH₃-NDip), 1.26 (d, 12H, 3JHH = 6.7 Hz, CH₃-NDip), 1.24 (s, 18H, tBu-DAD).

References


[3] see Chapter I.


[5] see Chapter VII.


[14] see Chapter VI.


[22] see Chapter II.


[24]

\[
\ln(k) = \ln\left(\frac{\sigma k_B T}{h}\right) + \ln(T) + \left(-\frac{\Delta H^* - T\Delta S^*}{RT}\right)
\]

\[
\ln(k) - \ln(T) = \ln\left(\frac{\sigma k_B T}{h}\right) - \frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R}
\]

\[
\log\left(\frac{k}{T}\right) = 10.32 - \frac{\Delta H^*}{19.13} \left(\frac{1}{T}\right) + \frac{\Delta S^*}{19.13}; \sigma = 1
\]


[26] $\Delta G^e_{298} = \Delta H^* - 298 \cdot \Delta S^*$
[27] see Chapter IV.


[29] (a) Kliegman, J. M.; Barners, R. K., *Tetrahedron* 1970, 26, 2555-2560; (b) see Results and Discussion for detailed information; (c) P. A. Bates, A. J. Nielson, J. M. Waters, *Polyhedron* 1985, 4(8), 1391-1401; (d) A. Merkoulov, S. Schmidt, K. Harms, J. Sundermeyer, in press, see Chapter IX.

[30] A THF solution of BzMgCl was prepared from BzCl and Mg. The volatiles were removed in vacuum and a white residue was dried at 25°C/10⁻⁴ mbar for 12h. The constitution of the solid was found to be [BzMgCl*thf] by titration with aqueous HCl.
Chapter VI

Chemical Reactivity of DAD Niobium and Tantalum Complexes of the Type [(DAD)M(NtBu)(Cl)(L)]

Introduction

Metal nitrides of the formula M\textsubscript{1.0}N\textsubscript{1.0}, where M is a group IV or V element, are in the focus of attention, because of their use in microelectronics. They possess a wide range of useful properties, especially, hardness and good electrical conductivity. This explains their application as barrier materials between copper and silicon layers, which prevents the copper atoms from diffusing into silicon substrates at high fabrication temperatures [1].

Well investigated deposited TiN films exhibit a columnar grain boundary structure and create fast diffusion paths for copper atoms, while TaN films have a disordered grain boundary structure and make the diffusion of copper atoms ineffective [1]. Tested nitrogen containing metalorganic compounds, [Ta(NEt\textsubscript{3})\textsubscript{3}], [Ta(NtBu)(NEt\textsubscript{2})\textsubscript{3}] and dimer [Ta(NtBu)(NH\textsubscript{2}Bu)Cl\textsubscript{2}(NH\textsubscript{2}Bu)]\textsubscript{2}, produce either Ta\textsubscript{3}N\textsubscript{5} (isolator) or carbon enriched films with large resistivity [1, 2]. Applicable films were only obtained by using plasma assisted CVD with TaBr\textsubscript{5} and from the substance isolated after reaction of TaCl\textsubscript{5} with Me\textsubscript{2}NNH\textsubscript{2} excess, which was claimed to be [Ta(NNMe\textsubscript{2})(NNHMe\textsubscript{2})Cl\textsubscript{2}(NH\textsubscript{2}NMe\textsubscript{2})]n [2]. The latter compound possesses a low volatility and that is why the development of new precursors for CVD of TaN is a challenge and a topic in applied coordination chemistry.

Complexes on the basis of the 1,4-diaza-1,3-diene (R,R’–DAD) ligand backbone have been the focus of attention for many years. Due to several possible coordination modes and their red-ox activity, R,R’–DAD ligands can stabilize metals in a wide range of formal oxidation states [3]. While neutral R,R’–DAD is a strong π–acceptor, stabilizing low-valent metal centres, the 2-electron reduced R,R’–DAD\textsuperscript{2–} ligand, which is best described as an ene-diamid functionality, can be envisaged as a strong π–donor, stabilizing high-valent metal centres.
From the wide spectrum of the described R,R’–DAD ligands we chose 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene (tBu,H–DAD or simply DAD). This derivative has several advantages, namely, it is very simple to synthesise on large scale and it possesses a high vapour pressure [4] and therefore can be easily sublimed or even distilled under reduced pressure. It is interesting that its metalorganic derivatives also show high volatility and most of them can be purified by sublimation.

The earlier reported [5] imido complexes [(DAD)M(N\textsuperscript{t}Bu)(\mu-Cl)]\textsubscript{2} and [(DAD)M(N\textsuperscript{t}Bu)(Cl)(py)], M = Nb and Ta, possess a chemically ‘active’ chloro ligand and provide the possibility of obtaining precursors with new chemical and physical properties, such as volatility, reductive decomposition pathways etc., by their chemical transformations. In this chapter the chemical reactivity of [(DAD)M(N\textsuperscript{t}Bu)(\mu-Cl)]\textsubscript{2} and [(DAD)M(N\textsuperscript{t}Bu)(Cl)(py)] in nucleophilic substitution, reduction and metathesis reactions is reported.

**Results and discussion**

**Synthetic studies**

*Nucleophilic substitution of chloride ligand*

The chloro pyridine complexes [(DAD)M(N\textsuperscript{t}Bu)(Cl)(py)], M = Nb and Ta, react with π–basic nucleophiles forming pyridine free compounds. All reactions were carried out in THF as a solvent at –80°C. After removing the solvent, products were extracted with hexane and sublimed for purification if needed. The obtained complexes are presented in Fig. 1 and yields are listed in Table 1.
Fig. 1. Reactions of 1 and 2 with different nucleophiles.

Table 1. Yields for the reaction of 1 and 2 with π–donor ligands.

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Nb</th>
<th>Yield</th>
<th>Ta</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpLi</td>
<td>(1)</td>
<td>28%</td>
<td>(2)</td>
<td>48%</td>
</tr>
<tr>
<td>IndLi</td>
<td>(3)</td>
<td>78%</td>
<td>(4)</td>
<td>45%</td>
</tr>
<tr>
<td>allMgCl</td>
<td>(5)</td>
<td>48%</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>acacNa</td>
<td>(7)</td>
<td>67%</td>
<td>(8)</td>
<td>60%</td>
</tr>
<tr>
<td>tBuOK</td>
<td>(9)</td>
<td>66%</td>
<td>(10)</td>
<td>52%</td>
</tr>
</tbody>
</table>

*obtained from [(DAD)Ta(N'tBu)(µ-Cl)]$_2$.
Principally, compounds 1-10 can be also obtained from dimeric complexes \([(\text{DAD})M(N^t\text{Bu})(\mu-\text{Cl})]_2, \text{M} = \text{Nb and Ta},\) using the same reactants and reaction conditions. This method was successfully applied for large-scale synthesis of \([(\text{DAD})\text{Ta}(N^t\text{Bu})(\eta^3-C_3\text{H}_5)]\) (6), which was tested in CVD process of TaN films [4].

All synthesised compounds 1-10 are air-sensitive solids, which are very well soluble in hexane, and can be sublimed or distilled for purification.

\[\text{[Cp(DAD)M(N}^t\text{Bu})]} \text{ M} = \text{Nb (1) and Ta (2)}\]

The $^1\text{H}$-NMR and $^{13}\text{C}$-NMR spectra of the cyclopentadienyl derivatives 1 and 2 exhibit a sharp singlet for the Cp$^-$ ligand. This observation is temperature independent in the region of 180–400 K in accordance with a symmetrical $\eta^5$ coordination mode of the ligand or extremely rapid hapticity change even at 180 K. The EI mass spectra of 1 and 2 show apart from the insensitive molecular ions \([\text{Cp(DAD)M(N}^t\text{Bu})]\) also fragments after abstraction of a methyl radical and isobutylene molecules. Surprisingly, according to the mass spectra of 1 and 2 the abstraction of the stable Cp radical does not take place under these conditions.

Cyclopentadienyl complexes 1 and 2 can be also obtained by reaction of \([\text{CpM(N}^t\text{Bu)Cl}_2]\) [6], \text{M} = \text{Nb and Ta}, with Li$_2$DAD. The yield in this reaction in the case of niobium is better than in reaction of \([(\text{DAD})\text{Nb}(N^t\text{Bu})(\text{Cl})(\text{py})]\) with CpLi. However, in the case of tantalum it produced lower yields than the reaction of \([(\text{DAD})\text{Ta}(N^t\text{Bu})(\text{Cl})(\text{py})]\) with CpLi.
In the $^1$H-NMR spectra of the indenyl complexes 3 and 4 two signals, namely, a triplet for the proton 2 and a doublet for the protons 1 and 3, were observed. These data are consistent with symmetrical either $\eta^5$ or $\eta^3$ coordination modes for indenyl ligand. In order to gain further insight into the coordination mode of the title complexes 3 and 4 the molecular structure of 4 was determined by X-ray analysis (Fig. 2). A suitable crystal was obtained by cooling a concentrated hexane solution of 4 to –30°C.

**Fig. 2.** ORTEP plot of $[(\eta^5\text{-Ind})(\text{DAD})\text{Ta(N}^t\text{Bu})]_4$ with thermal ellipsoids at 30% probability. Space group P n m a, $Z = 4$. Selected bond length [Å] and angles [°]: Ta(01)–N(1) 2.009(2), Ta(01)–N(2) 1.761(3), Ta(01)–C(1) 2.403(4), Ta(01)–C(2) 2.466(3), Ta(01)–C(3) 2.707(3), N(1)–C(6) 1.378(3), C(6)–C(6_8) 1.369(4), C(1)–C(2) 1.399(5), C(2)–C(3) 1.431(4), C(3)–C(3_8) 1.426(4), Ta(01)–N(2)–C(11) 177.8(4).
The coordination polyhedron of the tantalum atom in 4 is a distorted tetrahedron formed by the centroid of the indenyl five ring, nitrogen atoms of the DAD$^{2-}$ and imido ligands. The molecule contains a mirror plane defined by atoms C(1), Ta(01), N(2) and centroid of the DAD$^{2-}$ double bond C(6)–C(6_8).

In the structurally characterised indenyl complexes of tantalum found in literature [7] the $\eta^5$ coordination mode was observed. The Ta–C bond distances were found to be in the range of 2.35–2.59 Å, the bond lengths to the indenyl bridging carbon atoms being slightly longer.

The difference between the bridging carbon atoms C(3) and C(3_8) and allylic atom C(1) increases insignificantly in 8. The bond lengths Ta(01)–C(3) and Ta(01)–C(3_8) are equal 2.707(3) Å, Ta(01)–C(2) and Ta(01)–C(2_8) 2.466(3) Å, and Ta(01)–C(1) 2.403(4) Å.

Indeed, the small $\Delta$(M–C) value of 0.262(6) Å, which corresponds to the difference between the average metal–carbon bond distances to the two bridging quaternary carbon atoms C(3) and C(3_8) and to the allylic atoms C(2), C(2_8) and C(1), is in accordance with an asymmetrical $\eta^5$ coordination mode of the indenyl ligand [8]. Furthermore, the dihedral angle between the plane defined by the three allylic carbon atoms C(1), C(2) and C(2_8) and that formed by C(2), C(2_8), C(3) and C(3_8) of 7.7(4)$^\circ$ indicates a small trend to distortion in the indenyl ligand that again should be referred to the $\eta^5$-bonded indenyl ligand and not to $\eta^3$ [8].

The DAD$^2$–M metallacycle exhibits a folded conformation in solid state. The metal centre is not located in the plane formed by the N$_2$C$_2$ atoms of the DAD$^2$ moiety. It has a metal–to–plane distance of 1.0662(1) Å. In comparison with the free DAD ligand [9] and its donor–acceptor complex with d$^9$ niobium [Nb(NC$_6$H$_5$Cl)$_3$(dad)] [10] a decrease in C–C bond distance and an increase in C–N bond distances are observed. The same tendencies were found in other structurally characterised R,R’–DAD$^2$–d$^9$ complexes of niobium and tantalum [11], in which the MC$_2$N$_2$ backbone exhibits very close structural parameters. For illustration, the selected parameters for the DAD$^2$– ligand in reference complex [Cp(DAD)NbCl$_3$] [11f] are presented in Table 2.
Table 2. Selected structural parameters (distances in Å and angles in °) of DAD$^{2-}$ and imido ligands in complex 4 and reference complexes [Cp(DAD)NbCl$_2$] [11f] and [Nb(NC$_6$H$_2$Cl$_3$)Cl$_3$(dad)] [10].

<table>
<thead>
<tr>
<th>Complex</th>
<th>DAD$^{2-}$</th>
<th>imido</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.369(4)</td>
<td>1.378(3)</td>
</tr>
<tr>
<td>ref. [11f]</td>
<td>1.402(6)</td>
<td>1.354(6)</td>
</tr>
<tr>
<td>DAD [9]</td>
<td>1.468(2)</td>
<td>1.267(2)</td>
</tr>
<tr>
<td>ref. [10]</td>
<td>1.471(3)</td>
<td>1.270(3)</td>
</tr>
</tbody>
</table>

With respect to the definition of *prone* and *supine* conformers [11h, 12, 13] for the folded R,R’–DAD$^{2-}$ ligand applied in cyclopentadienyl complexes we can suggest using it also in the presence of the isolobal RN$^{2-}$ ligand. In the molecular structure of tantalum complex 4 the *supine* isomer is present. In spite of the short distances of approx. 2.5 Å between the metal centre and carbon atoms of the double bond in 1 and 2 the latest computations [11b, 14] suggest that there is no considerable chemical interaction. In contrast, the short M–N bond distances of around 2 Å indicate strong metal–nitrogen interaction with the DAD$^{2-}$ moiety. For example, these M–N distances in [Nb(NC$_6$H$_2$Cl$_3$)Cl$_3$(dad)], where the DAD ligand is a neutral σ–donor, are 2.301(2) and 2.460(2) Å, respectively. Therefore, the reduced DAD$^{2-}$ moiety has to be considered as an ene-diamido ligand.

Similar to cyclopentadienyl complexes 1 and 2 the indenyl derivatives 3 and 4 exhibit a temperature independent NMR spectra in the region of 180–400 K. Again, the abstraction of a methyl radical and isobutylene was found to be the major fragmentation of the molecules in the EI mass spectra.
[(DAD)M(N^t-Bu)(\eta^3-C_3H_5)] M = Nb (5) and Ta (6)

In contrast to complexes 1-4 allyl derivatives 5 and 6 show broad signals in the $^1$H- and $^{13}$C-NMR spectra for the allyl moiety indicating dynamic behaviour of molecules in solution, while DAD$^{2-}$ signals are sharp singlets in the range of 180–400 K. In order to cast light on this phenomenon a crystal of 5 suitable for X-ray analysis was obtained by cooling a concentrated solution in hexane to –30$^\circ$C. The molecular structure of 5 is presented in Fig. 3.

![Molecular structure of [(DAD)Nb(N^t-Bu)(\eta^3-C_3H_5)] 5](image)

**Fig. 3.** The molecular structure of [(DAD)Nb(N^t-Bu)(\eta^3-C_3H_5)] 5 with thermal ellipsoids at 10% probability. The site occupation factor of positions C(2), C(3), N(1) and N(4) is 0.89; C(2a), C(3a), N(1a) and N(16a) 0.11; C(14) and C(15) 0.67; C(14a) and C(15a) 0.33. Space group P b c a, Z = 8. Selected bond length [Å] and angles [°]: Nb(1)–N(1) 2.034(4), Nb(1)–N(1a) 1.93(2), Nb(1)–N(4) 2.022(4), Nb(1)–N(16) 1.776(3), Nb(1)–N(16a) 2.01(3), Nb(1)–C(2) 2.561(5), Nb(1)–C(2a) 2.40(3), Nb(1)–C(3) 2.547(5), Nb(1)–C(3a) 2.32(3), Nb(1)–C(13) 2.400(5), Nb(1)–C(14) 2.4034, Nb(1)–C(14a) 2.44(5), Nb(1)–C(15) 2.393(6), Nb(1)–C(15a) 2.53(6), Nb(1)–N(16)–C(17) 177.1(3), Nb(1)–N(16a)–C(9) 157(3)

The coordination sphere of the metal centre in allyl complex 5 (Fig. 8) as well as in indenyl derivative 4 is a tetrahedron formed by the three nitrogen atoms of the imido and DAD$^{2-}$ ligands; and the forth position is occupied by the centroid of the allylic system. A very unusual disorder with site occupation factors 0.89:0.11 is observed in the molecular structure of 5. The
imido group atoms N(16), C(17) and so on as well as the 'Bu group of the DAD$^{2-}$ ligand with tertiary carbon atoms C(5) change their position so that C(5) is part of the imido moiety and N(16) and C(17) along with the residual atoms of this 'Bu group form a fragment of the DAD$^{2-}$.

The second independent disorder of the allyl group with an occupancy of 0.67:0.33 demonstrates flexibility of the allyl ligand in the η$^3$ fashion around metal–to–centroid axis.

The structural parameter of the imido and DAD$^{2-}$ moieties in the positions with 0.89 occupancy are similar to those found in the indenyl complex of tantalum 4, while the bonding parameters for the second disordered positions with the lower occupancy cannot be adequately discussed because of the large standard deviation. The molecule exhibits supine conformation with respect to the DAD$^{2-}$ and imido ligands for both disordered fragments.

We have not found any example of a structurally characterised d$^0$ niobium complex with allyl ligand in η$^3$ fashion [15]. In the d$^2$ complex [(η$^5$-C$_5$H$_4$CH$_3$)$_2$Nb(η$^3$-C$_3$H$_5$)] [16] the distance of 1.7448(11) Å between Nb and the plane of the allyl ligand is extremely short. For comparison, the distances to the methylcyclopentadienyl rings are 2.061(2) and 2.090(2) Å in the molecule. This can be explained by strong back-donation from the d$^2$ metal centre. However, a reference example can be found in tantalum chemistry: the distance between Ta and the plane of the η$^3$-allyl ligand is 1.9244(3) Å in d$^0$ tantalum complex [(η$^5$-C$_5$Me$_5$)Ta(NSiMe$_3$)(η$^3$-C$_3$H$_5$)(η$^1$-C$_3$H$_5$)] [17], which correlates to the value of 1.9410(3) Å in 5. The M–C distances to the η$^3$-allyl carbon atoms are in the range of 2.39–2.53 Å in 5 and in the range of 2.31–2.49 Å in reference complex [(η$^5$-C$_5$Me$_5$)Ta(NSiMe$_3$)(η$^3$-C$_3$H$_5$)(η$^1$-C$_3$H$_5$)] [17].

In the EI mass spectra of 5 and 6 peaks representing molecular ions were observed. Surprisingly, abstraction of the allyl ligand but no isobutylene fragmentation was found for 5 and 6, making these complexes favourable for testing them in the CVD of MN films.

The $^1$H-NMR spectra of the η$^3$-allyl complexes 5 and 6 show temperature dependence as was mentioned above. This dependence is presented in Fig. 4 for 5 and in Fig. 5 for 6. Below 220 K three well-resolved signals of a A$_2$M$_2$X spin system were observed. The signal strongly shifted to low field at 6.5 ppm for the H$^X$ proton appears as a triplet of triplet with two spin-spin coupling constants of approximately 8 Hz (J$_{XM}$) and 14 Hz (J$_{XA}$) leading to seven lines with relative intensities of 1:2:3:4:3:2:1. At high temperatures this signal transforms to a quintet of a B$_4$X spin system with a coupling constant of around 11 Hz. Two doublets, which can be observed at low temperatures at approx. 3.8 ppm (H$^X$) and 0.5 ppm (H$^A$), show coalescence and
give one signal at high temperatures, which resolves over 350 K for 6 as a doublet with the same coupling constant of around 11 Hz as in the quintet.

**Fig. 4.** The $^1$H-DNMR spectra of 5 (500 MHz, d$_8$-toluene).

**Fig. 5.** The $^1$H-DNMR spectra of 6 (500 MHz, d$_8$-toluene).
The described phenomenon can be explained by an allyl $\eta^3-\eta^1-\eta^3$ rearrangement, which was also found in other allyl complexes with earlier transition metals [17, 18]. The existence of an allyl ligand in the $\eta^1$ fashion was confirmed by X-ray analysis of the complex $[(\eta^5-C_5(CH_3)_{3})(Me_3SiN)Ta(\eta^3-C_3H_5)(\eta^1-C_3H_5)]$ [17], where both $\eta^1$ and $\eta^3$ fashions of allyl ligand were detected. In our case the intermediate $\eta^1$ species was not observed in the NMR experiments, probably, because of its short lifetime and low concentration. But this time is long enough for rotation around the M–C $\sigma$-bond. This $\sigma,\pi$–rearrangement renders the terminal protons $H^M$ and $H^A$ magnetically equivalent changing the $A_2M_2X$ spin system into a $B_4X$ system.

In order to calculate the thermodynamic parameters ($\Delta S^\neq$ and $\Delta H^\neq$) for the barrier of the $\sigma,\pi$–rearrangement Band-Shape Analysis [19] and the Win-Dyna 32 program [20] were applied. The experimental data of the rate constants ($k$) were obtained at different temperatures ($T$). The fitting to the Eyring equation allows estimating the activation parameters for the rearrangement barrier in 5-6.

$$k = \frac{\sigma k_B T}{h} e^{\frac{-\Delta H^* - T\Delta S^*}{RT}}$$

where $k_B$ is Boltzmann’s constant, $T$ is absolute temperature, $h$ is Planck’s constant and $R$ is the universal gas constant. The transmission coefficient $\sigma$ was taken equal to one. The logarithmic variant [21] allows calculating the $\Delta H^\neq$ and $\Delta S^\neq$ values from a linear fit. The plot $1/T$ versus $\lg(k/T)$ is presented in Fig. 6.
\[
\log (k/T) = 10.32 - \frac{\Delta H^\neq}{19.13} \left( \frac{1}{T} \right) + \frac{\Delta S^\neq}{19.13}
\]

![Graph](image)

**Fig. 6.** Eyring equation plot for complexes 5 and 6.

For linear fitting the *PFIT45W* program was applied [22]. Temperature uncertainty of 0.5 K and a relative uncertainty of 20% of the rate constants were taken to estimate the error of the fitted parameters. The calculated values of activation entropy \(\Delta S^\neq\) and enthalpy \(\Delta H^\neq\) are listed in Table 3.

**Table 3.** Activation entropy and enthalpy values for complexes 5 and 6 calculated from the DNMR experiments.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(T_{\text{coal}}, K)</th>
<th>(\Delta G_{298}^\neq, \text{kJ/mol}) [23]</th>
<th>(\Delta H^\neq, \text{kJ/mol}^{-1})</th>
<th>(\Delta S^\neq, \text{J/mol}^{-1}\cdot\text{K}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>340</td>
<td>62 ± 4</td>
<td>73 ± 2</td>
<td>36 ± 7</td>
</tr>
<tr>
<td>6</td>
<td>275</td>
<td>48 ± 4</td>
<td>60 ± 2</td>
<td>43 ± 7</td>
</tr>
</tbody>
</table>

The activation enthalpy \(\Delta H^\neq\) for niobium complex 5 (73 ± 2 kJ/mol\(^{-1}\)) is higher than that for tantalum complex 6 (60 ± 2 kJ/mol\(^{-1}\)) and correlates to the activation enthalpy of 50 ± 4 kJ/mol\(^{-1}\) found for \([\text{Cp}_2\text{Zr(η}^3\text{-C}_3\text{H}_4\text{Me})^+\text{Me–B(C}_6\text{F}_5)_3^-]\) [18c]. The positive activation entropy
values can be considered equal for 5 \((36 \pm 7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})\) and 6 \((43 \pm 7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})\) in the range of standard deviation. Surprisingly, \(\Delta S^*\) differs considerably from that found in complex \([\text{Cp}_2\text{Zr}(\eta^3-C_3\text{H}_4\text{Me})^+\{\text{Me–B(C}_6\text{F}_5)_3\}^-]\), for which a \(\eta^3–\eta^1–\eta^3\) rearrangement mechanism was suggested as well and the \(\Delta S^*\) was claimed to be \(-56 \pm 5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\). The negative activation entropy \(\Delta S^*\) may be explained by an associative mechanism in the case of \([\text{Cp}_2\text{Zr}(\eta^3-C_3\text{H}_4\text{Me})^+\{\text{Me–B(C}_6\text{F}_5)_3\}^-]\), in which a solvent molecule coordinates in the first step of the reaction and induces formation of the \(\eta^1\)-bonded intermediate species [24].

The positive value for \(\Delta S^*\) in the case of 5 and 6 is in accordance with an increase of degree of freedom in the intermediate \(\eta^1\) form compared to the \(\eta^3\) ground state, which is consistent with the flexibility of \(\sigma\)-bonded allyl chain. For example, the DFT calculation on the system \([\text{M}(\eta^3-C_3\text{H}_5)_3]\), \(\text{M} = \text{Rh, Ir}\), gives an entropy difference of approx. 16 \(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\) for Rh and approx. 28 \(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\) for Ir between \([\text{M}(\eta^3-C_3\text{H}_5)_2(\eta^1-C_3\text{H}_5)]\) and \([\text{M}(\eta^3-C_3\text{H}_5)_3]\) ground states [25].

The value of activation enthalpy determines the difference in the activation energies (approx. 15 \(\text{kJ} \cdot \text{mol}^{-1}\) at 298 K) and coalescence temperatures (approx. 65 K) for niobium and tantalum complexes. According to this data the rearrangement between \(\eta^3\) and \(\eta^1\) coordination modes takes place more slowly in niobium complex 5 than in tantalum complex 6.

\[
[(\text{DAD})\text{M}(N^t\text{Bu})(\text{acac})]\text{ }\text{M} = \text{Nb (7) and Ta (8)}
\]

Two singlets with relative intensities of 1:6 with \(\delta_\text{H}\) around 5.1 ppm and 1.6 ppm were observed in the \(^1\text{H}\)-NMR spectra for the acetylacetonate ligand in \([(\text{DAD})\text{M}(N^t\text{Bu})(\text{acac})]\), \(\text{M} = \text{Nb (7) and Ta (8)}\). Additionally, only three signals were located for this ligand in the \(^{13}\text{C}\)-NMR spectra. The DAD\(^2\text{–}\) signals were observed as two sharp singlets in \(^1\text{H}\)-NMR and as three peaks in \(^{13}\text{C}\)-NMR. This is consistent with symmetrical surroundings of DAD\(^2\text{–}\) and \(\kappa^2\)-acetylacetonate ligands. A single crystal of 7 suitable for X-ray analysis was obtained by cooling a saturated hexane solution to \(-30^\circ\text{C}\).
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Fig. 7. The molecular structure of \(\text{[(DAD)Nb(N}^\text{t} \text{Bu)(acac)]} \) \(\text{7} \) with thermal ellipsoids at 40\% probability. Space group \(\text{P } 2_1/n\), \(Z = 4\). Selected bond length [\(\text{Å}\)] and angles [\(^\circ\)]: \(\text{Nb(1)}–\text{N(1)} 2.020(1), \text{Nb(1)}–\text{N(2)} 2.016(1), \text{Nb(1)}–\text{N(3)} 1.763(2), \text{Nb(1)}–\text{O(1)} 2.161(1), \text{Nb(1)}–\text{O(2)} 2.154(1), \text{Nb(1)}–\text{C(6)} 2.530(2), \text{Nb(1)}–\text{C(7)} 2.531(2), \text{C(6)}–\text{C(7)} 1.376(2), \text{N(1)}–\text{C(6)} 1.385(2), \text{N(2)}–\text{C(7)} 1.383(2), \text{O(1)}–\text{C(1)} 1.272(2), \text{O(2)}–\text{C(3)} 1.277(2), \text{C(1)}–\text{C(2)} 1.395(3), \text{C(2)}–\text{C(3)} 1.381(3), \text{Nb(1)}–\text{N(3)}–\text{C(16)} 175.88(13), \text{N(1)}–\text{Nb(1)}–\text{N(2)} 85.18(5), \text{O(1)}–\text{Nb(1)}–\text{O(2)} 78.39(5), \text{N(3)}–\text{Nb(1)}–\text{N(1)} 112.66(6), \text{N(3)}–\text{Nb(1)}–\text{N(2)} 111.83(6), \text{N(3)}–\text{Nb(1)}–\text{O(1)} 99.74(6), \text{N(3)}–\text{Nb(1)}–\text{O(2)} 104.17(6).

The molecular structure of acetylacetonate derivative \(\text{11} \) is presented in Fig. 7. The coordination polyhedron at the niobium atom can be described as a tetragonal pyramid. The oxygen atoms \(\text{O(1)} \) and \(\text{O(2)} \) of the acetylacetonate ligand and the nitrogen atoms \(\text{N(1)} \) and \(\text{N(2)} \) of the \(\text{DAD}^2– \) ligand form the base plane and the nitrogen atom \(\text{N(3)} \) of the imido ligand occupies the apical position. The \(\text{N(3)}–\text{Nb(1)}–X \) angles, where \(X = \text{N(1)}, \text{N(2)}, \text{O(1)} \) and \(\text{O(2)} \), are in the range of 99.7–112.7\(^\circ\) and the metal–to–base plane distance is 0.6200(1) \(\text{Å}\).

Although there is no symmetry plane containing atoms \(\text{C(2)}, \text{N(3)}, \text{Nb(1)} \) and the centroid of the \(\text{C(6)}–\text{C(7)} \) bond, the bond lengths \(\text{Nb(1)}–\text{N(1)} \) and \(\text{Nb(1)}–\text{N(2)} \) of 2.016(1) and 2.020(1) \(\text{Å}\), respectively, and \(\text{Nb(1)}–\text{O(1)} 2.161(1) \) and \(\text{Nb(1)}–\text{O(2)} 2.154(1) \) \(\text{Å}\) are very similar. This mirror plane should exist in solution, because characteristic signals for the \(\text{DAD}^2– \) and acetylacetonate ligands in symmetrical surroundings were observed in the \(^1\text{H}\)- and \(^{13}\text{C}\)-NMR spectra. The \(\text{Nb–O} \) bond lengths in \(\text{11} \) are in good agreement with the range of 1.98–2.28 \(\text{Å}\) found in the acetylacetonate complex \(\text{[Nb(acac)\(_2\)(μ–S)]}_2} \) [26].
The metallacycle containing acetylacetonate ligand is not perfectly flat with a distance of 0.47287(12) Å between the metal centre and the ligand plane. This deviation is not abnormal for acetylacetonate complexes with early transition metals [15]. For example, this metal–to–plane distance in vanadium d$^0$ complex [V(acac)$_2$(O)(O$^i$Pr)] [27], where two independent molecules were located, ranges from 0.071(2) to 0.556(2) Å.

The DAD$^2$-Nb metallacycle has folded *supine* conformation with respect to the imido ligand. The metal–DAD$^2$– distance is 1.1510(1) Å. The short M–N distances of 2.020(1) and 2.016(1) Å, the short C–C distance of 1.376(2) Å and the long C–N distances of 1.385(2) and 1.383(2) Å in the metallacycle are in good agreement with those found in tantalum complex 4 and niobium complex 5 and indicate that the DAD ligand is bonded in its ene-diamido form.

\[(DAD)M(N^tBu)(O^tBu)] M = Nb (9) and Ta (10)\]

The $^1$H-NMR spectra of \([(DAD)M(N^tBu)(O^tBu)], M = Nb (9) and Ta (10),\] consist of a sharp singlet in low-field approx. 5.8 ppm with relative intensity of 2 (CH protons of the DAD$^2$- ligand) and three sharp singlets for $^t$Bu groups in high-field on a ration of 9:18:9. This is consistent with symmetrical surroundings of the DAD$^2$- ligand in tetrahedral coordination sphere of the metal centre.

In the EI mass spectra of the acetylacetonate and O$t$Bu derivatives 7-10 the peaks representing molecular ions are present and the abstraction of methyl groups and isobutylene was found to be the most prominent decomposition pathway for these molecules.

\([(DAD)M(N^tBu)(\eta^2-BH_4)] M = Nb (11) and Ta (12)\]

Surprisingly, the reaction of \([(DAD)M(N^tBu)(\mu-Cl)]_2, M = Nb and Ta, with NaBH_4 in THF at room temperature leads to boranate complexes 11 and 12. The room temperature non-decoupled $^{11}$B-NMR spectra of 11 and 12 exhibit quintets at –20 ppm. This is consistent with a rapid exchange of hydrogen atoms in the BH$_4^-$ anion. Unfortunately, single crystal X-ray diffraction experiments with crystals obtained from the gas phase did not solve the molecular structure of these compounds because of the extremely high extent of disorder of all light atoms.
Although all to date known structurally characterised boranate (BH₄⁻) complexes of niobium and tantalum [15], have κ² coordination mode [28], on the basis of IR, Raman and temperature dependent ¹H-NMR spectra the coordination mode of the boranate ligand in 11 and 12 is more likely to be κ³ [29]. Four possible bonding modes of the M–BH₄ unit are discussed in the paper of Marks et al. [29b] with respect to the spectroscopic properties (IR and Raman). The characteristic IR and Raman spectral region for 11 and 12 lies between 2600 and 2000 cm⁻¹ (the B–H valence vibrations), while there are other signals derived from the DAD₂⁻ and imido ligands in the symmetric bridge stretching (approx. 1400–1500 cm⁻¹) and the deformation (approx. 1100–1200 cm⁻¹) regions of M–BH₄ moiety.

The high solubility of 11 and 12 in hexane and activity in the Raman spectra (Fig. 8) rule out an ionic bonding description D in these complexes. The comparison of the IR spectra of [M(κ³-BH₄)_₄] (M = Zr, Hf) [29a, 29b], in which κ³ mode was confirmed by X-ray analysis, and those of 11 and 12 is presented in Fig. 8. The sharp singlet at 2507 cm⁻¹ for 11 and 2519 cm⁻¹ for 12 (a doublet in this region would be in accordance with the κ² mode B or κ¹ mode C) and similarity of other bands in this region, which are all also Raman active, correlates to κ³ coordination mode A.
Fig. 8. The IR and Raman spectra of 11 and 12 in comparison with \([M(\kappa^3-BH_4)_4]\) [29b].

The similarity of the \(^1\)H-NMR spectra of 20 and \([Zr(\eta^3-BH_4)_4]\) [29a] in their temperature dependency (Fig. 9) additionally assures that both complexes possess an identical coordination mode for the BH\(_4^-\) ligand.

* The fourth BH\(_4^-\) signal overlaps with the 'Bu imido group and is omitted for clarity

Fig. 9. Temperature dependence of BH\(_4^-\) signals in \(^1\)H-NMR for 12 and \([Zr(\eta^3-BH_4)_4]\) [29a].
Both complexes 11 and 12 are extremely soluble in hexane and decompose slowly in solution. Actually, they can be sublimed under mild conditions without a great loss of the product. This property is essential for CVD experiments, in which complex 12 was tested as a precursor for TaN films [4].

![Graph showing decomposition of complex 12 at different temperatures.](image)

**Fig. 10.** Decomposition of 12 at different temperatures. Loss of $^1$H-NMR signal intensity in C$_6$D$_6$.

In order to gain insight into the thermal stability of 11 and 12 the decomposition experiments of 12 were carried out in an NMR-tube with a Teflon valve at different temperatures in C$_6$D$_6$. On the basis of the $^1$H-NMR spectra the relative concentration of 12 was measured by integration of the CH signal of the DAD$^{2-}$ ligand at 5.91 ppm using Me$_4$Si as the internal standard. The dependency of the concentration on time is presented in Fig. 10. Unfortunately, all the curves cannot be well fitted to the exponential first-order reaction rate equation $C = C_0 \cdot e^{-kt}$, where $k$ is the rate constant, $t$ is time, and $C_0$ is the starting concentration [30]. In Fig. 11 the dependency of $k$ values upon temperature $T$ is presented. The application of Arrhenius or Eyring equations on the obtained array of $(k,T)$ failed. This means that the decomposition process is more complicated than a simple first-order reaction or that the products formed have influence on the reaction rate.
According to the $^1$H-NMR spectra the decomposition proceeds unselectively and affords several species containing DAD$_2$ ligand, while only one major product was observed in the $^{11}$B$^1$H- NMR spectra with a chemical shift of approx. +20 ppm.

If the decomposition was examined in the presence of pyridine, a selective formation of two DAD$_2$ species was observed. Unfortunately, we were not able to identify them on the basis of the NMR spectra.

![Graph](image_url)

**Fig. 11.** Rate constants for decomposition of 12.

**Reduction of [(DAD)M(N^tBu)(µ-Cl)]$_2$ and [(DAD)M(N^tBu)(Cl)(py)], M = Nb and Ta**

This work continues investigation in the sphere of reductive generation and dimerisation of highly π–loaded 4d$^1$ and 5d$^1$ radicals of group V metals. As it was previously shown [31] reduction of [Cp$_2$M(N$^t$Bu)Cl], M = Nb and Ta, leads to formation of dimeric species [Cp$_2$M(µ-N$^t$Bu)]. Consequently the coordinatively and electronically more unsaturated moiety [(DAD)M(N$^t$Bu)Cl] is expected to produce dimeric compounds [(DAD)M(µ-N$^t$Bu)]$_2$ after reduction. In order to prove this assumption reductive studies on compounds [(DAD)M(N$^t$Bu)(µ-Cl)]$_2$ and [(DAD)M(N$^t$Bu)(Cl)(py)], M = Nb and Ta, were carried out.
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\[
[(DAD)M(\mu-N^tBu)]_2, \ M = Nb \ (13) \ and \ Ta \ (14)
\]

The latter compounds can be reduced with \( \text{C}_8\text{K} \) or Na amalgam in toluene applying ultrasound for activation to form diamagnetic products 13 and 14, which are soluble in hot hexane and toluene. The best results were obtained by reaction of \([(DAD)\text{Nb}(N^t\text{Bu})(\text{Cl})(\text{py})] \) and \([(DAD)\text{Ta}(N^t\text{Bu})(\mu-\text{Cl})]_2 \) applying \( \text{C}_8\text{K} \) as the reducing agent. The use of Li produces no reduction in toluene and the reaction in THF was found to be extremely unselective, so that the target complexes could not be purified by crystallisation.

Complexes 13 and 14 exhibit sharp signals in the \(^1\text{H}-\) and \(^{13}\text{C}-\)NMR spectra typical for diamagnetic species. Furthermore, only two different \(^t\text{Bu} \) groups and one methine group are present in the spectra of 13 and 14. Additionally, the NMR spectra of 13 and 14 are temperature independent in the region of 180–400 K. All these data are consistent with a dimeric structure containing bridging imido ligands, which possesses an inversion centre or mirror plane.

Single crystals of 13 and 14 suitable for X-ray analysis were obtained by cooling concentrated at 60°C hexane solutions to room temperature. The molecular structures of 13 and 14 are presented in Fig. 12 and Fig. 13, respectively.
Fig. 12. ORTEP plot of [(DAD)Nb(µ-NtBu)]2 13 with thermal ellipsoids at 50% probability. Space group P 21/n, Z = 2. Selected bond length [Å] and angles [°]: Nb(1)–N(3) 1.981(2), Nb(1)–N(3_3) 2.016(2), Nb(1)–N(1) 2.018(2), Nb(1)–N(2) 2.027(2), Nb(1)–C(1) 2.440(3), Nb(1)–C(2) 2.437(3), Nb(1)–Nb(1_3) 2.7144(5), C(1)–C(2) 1.367(5), C(1)–N(1) 1.395(4), C(2)–N(2) 1.393(4), N(1)–Nb(1)–N(2) 89.36(9), N(1)–Nb(1)–N(3_3) 120.9(1), N(2)–Nb(1)–N(3) 116.24(9), N(3)–Nb(1)–N(3_3) 94.46(9), Nb(1)–N(3)–Nb(1_3) 85.54(9).

Fig. 13. The molecular structure of [(DAD)Ta(µ-NtBu)]2 14 with thermal ellipsoids at 60% probability. Space group P 21/n, Z = 2. Selected bond length [Å] and angles [°]: Ta(1)–N(1) 2.004(3), Ta(1)–N(2) 2.010(3), Ta(1)–N(3) 1.974(3), Ta(1)–N(3_3) 2.019(3), Ta(1)–C(1) 2.456(3), Ta(1)–C(2) 2.452(3), Ta(1)–Ta(1_3) 2.7402(4), N(1)–Ta(1)–N(2) 89.4(1), N(1)–Ta(1)–N(3) 117.2(1), N(2)–Ta(1)–N(3_3) 121.8(1), N(3)–Ta(1)–N(3_3) 93.4(1), Ta(1)–N(3_3)–C(11_3) 135.8(2), Ta(1)–N(3)–C(11) 137.6(2), Ta(1)–N(3)–Ta(1_3) 86.7(1).
The molecular structures of niobium and tantalum complexes show very large similarity as expected and crystallise in the same monoclinic space group P 2\(_1\)/n. The molecules consist of two tetrahedral d\(^1\) MN\(_4\) moieties, which share a common edge. The crystallographic centre of inversion found in 13 and 14 also explains the behaviour in the DNMR solution spectra. Even at 180 K only 2 signals for 'Bu groups were observed – one for the DAD\(^2\)– ligand and one for the imido one, due to the geometrical and magnetic equivalence.

The M–M distances of 2.7144(5) Å in 13 and 2.7402(4) Å in 14 and N–M–M angles of 85.5(1)° in 13 and 86.7(1)° in 14 correlate to those found for other dimeric bridging imido complexes of niobium and tantalum [31, 32]. For example, in complex [C\(_2\)P\(_2\)Ta(\(\mu\)-N'Bu)]\(_2\) the Ta–Ta distance was found to be 2.8382(8) Å and the Ta–N–Ta angles 88.7(2)° and 88.3(2)° [31]. These data indicate a direct metal–metal interaction [31, 32, 33] and explain the diamagnetic properties of 13 and 14.

Due to the inversion unit, the central M\(_2\)N\(_2\) core is absolutely planar and slightly asymmetrical, the M–N distances being 1.981(2) and 2.016(2) Å in 13 and 1.974(3) and 2.019(3) Å in 14.

The DAD\(^2\)–M metallacycles exhibit folded conformations similar to those found in 4, 5 and 7. The metal centres lie at 1.1594(3) Å in 13 and 1.1330(1) Å in 14 out of the C\(_2\)N\(_2\) plane of the DAD\(^2\)– ligand. Other structural features of the DAD\(^2\)–M metallacycles are similar to those found in the molecular structures of 4, 5 and 7 and are in accordance with an ene-diamido description of the bonding situation.

**Metathesis reaction**

Other N–substituted imido chloro complexes of niobium and tantalum carrying the DAD\(^2\)– ligand can be obtained from corresponding organo imido trichloride complexes with neutral DAD ligand. Reduction of aryl imido complexes [M(NDip)Cl\(_3\)(dad)], M = Nb and Ta [10], with C\(_8\)K in THF leads to the formation of DAD\(^2\)– complexes [(DAD)M(NDip)(\(\mu\)-Cl)]\(_2\) [5]. One drawback of this strategy is the fact that yields in this reaction are pretty small and that the preparation of the starting complexes is time consuming.
The second problem results from the fact that some imido trichloride compounds of the type [M(NR)Cl$_3$L$_2$], M = Nb and Ta [34], cannot be directly synthesised from MCl$_5$. For example, neutral monohydrazido$^{2-}$ (R$_2$NN$^{2-}$) trichloride complexes are not known for niobium and tantalum. Thus we wanted to find a new synthetic pathway to DAD$^{2-}$ complexes having substituents other than tBu at the imido nitrogen.

$$[(DAD)Ta(NDip)(\mu-Cl)]_2$$ [5] (15)

The other possible synthetic method is the well-known amine metathesis reaction. According to NMR experiments the dimeric complex $$[(DAD)Ta(N^tBu)(\mu-Cl)]_2$$ reacts with excess of DipNH$_2$ or its salt DipNH$_3^+$Cl$^-$ at $110^\circ$C to form an amine adduct of the desired product IM$_1$. The same intermediate product was observed in the NMR reaction of $$[(DAD)Ta(N^tBu)(NH^tBu)]$$ with DipNH$_3^+$Cl$^-$ [5]. The desired product $$[(DAD)Ta(NDip)(\mu-Cl)]_2$$ (15) can be obtained after sublimation, as IM$_1$ loses amine at $160^\circ$C/$10^{-4}$ mbar.

In this metathesis reaction the more acidic aromatic amine DipNH$_2$ substitutes the tBuN$_2^-$ group kicking out the more basic amine tBuNH$_2$ or its salt tBuNH$_3$Cl. The driving force of such equilibrium reactions is the formation of an amine or its ammonium salt with lower
acidity and an increase in M–N bonding energy by incorporation of an imido ligand of higher group electronegativity.

Unfortunately, this reaction with Me$_2$NNH$_2$ as well as with Me$_2$NH$^+\text{NNH}_2\text{Cl}^-$ leads to decomposition with liberation of the free DAD ligand. Thus this method is not applicable for the synthesis of DAD$^{2-}$ complexes with hydrazido$^{2-}$ ($R^2\text{NN}^{2-}$) ligands from 1'Bu imido derivatives [(DAD)M(N'Bu)(µ-Cl)]$_2$, M = Nb and Ta.

**MS Studies**

Because of the high volatility for all complexes 1-14 electron impact ionisation mass spectroscopy provides good results. Peaks representing molecular ions were detected in all cases. In contrast to the spectra of the d$^0$ complexes with neutral DAD ligand [10], where ions without the intact DAD moiety were observed, the abstraction of isobutylene from the DAD$^{2-}$ unit was found to be the specific pathway of fragmentation for most complexes. First of all, it means that the DAD$^{2-}$ ligand is strongly bonded to the metal and that the desired reductive abstraction of neutral DAD with formation of reduced M(III) species does not take place. Actually, if this decomposition pathway is the most essential one in CVD experiments, then the presence of carbon in the TaN films [4] may arise from the fragment of the DAD$^{2-}$ ligand.
IR Studies

There are several important conclusions, which can be made from the comparison of the IR spectra of DAD\(^{2-}\) complexes and neutral DAD ligand. First of all, the very intense absorption at 1631 cm\(^{-1}\), which refers to the stretching mode of the C=N double bond of the free ligand, is not present in the spectra of 1-14. Two other strong absorptions at around 1361 cm\(^{-1}\) and around 1211 cm\(^{-1}\) can be found in all complexes somewhat shifted to shorter wavelengths compared to the DAD ligand. Other two medium absorptions at approx. 870 cm\(^{-1}\) and 760 cm\(^{-1}\) seem to originate from the DAD ligand, but here assignment is more complicated because other organic groups are present in the molecules. The wave numbers for the methine C–H vibration mode in the DAD\(^{2-}\) complexes are found in the range of 3050-3010 cm\(^{-1}\) demonstrating a considerable weakening of the C–H bond in comparison with the free ligand (3266 cm\(^{-1}\)) caused by large changes in electron density distribution in the reduced moiety.

NMR studies

All complexes 1-14 are diamagnetic substances. The non-reduced DAD ligand and its complexes with d\(^0\) metal centres exhibit signals for CH-groups in the \(^1\)H-NMR spectra at low field approx. 8.0 ppm and in the \(^13\)C-NMR spectra in the region around 150 ppm [10]. In contrast to this for the reduced DAD\(^{2-}\) moiety all signals are shifted to high field: \(\delta_{(CH)}\) of about 5-7 ppm in \(^1\)H-NMR and 90-100 ppm in \(^13\)C-NMR spectra. The influence on the signals of \(^t\)Bu-groups is considerably smaller: signals are shifted to low field compared to signals of the free DAD approx. 0.2 ppm in \(^1\)H-NMR and approx. 2 ppm in \(^13\)C-NMR.

Conclusions

The dimeric chloro [(DAD)M(N\(^t\)Bu)(\(\mu\)-Cl)]\(^2\) and monomeric chloro pyridine [(DAD)M(N\(^t\)Bu)(Cl)(py)] complexes of niobium and tantalum react with a large spectrum of nucleophiles to produce new DAD\(^{2-}\) imido derivatives of the type [(DAD)M(N\(^t\)Bu)(X)], X = Cp, Ind, allyl, acac, O\(^t\)Bu. The molecular structure of [(\(\eta^5\)-Ind)(DAD)Ta(N\(^t\)Bu)] (4), [(DAD)Nb(N\(^t\)Bu)(\(\eta^3\)-C\(_3\)H\(_5\))] (5) and [(DAD)Nb(N\(^t\)Bu)(\(\eta^3\)-C\(_3\)H\(_5\))] (7) reveal that these imido DAD\(^{2-}\) complexes prefer supine conformation in solid state with respect to the imido ligand. The
allyl complexes \([\text{DAD}M(\text{N}^\text{t-Bu})(\eta^3-\text{C}_3\text{H}_5)], \ M = \text{Nb} \ (5) \ \text{and} \ \text{Ta} \ (6)\), exhibit dynamic behaviour in solution referred to the \(\eta^3-\eta^1-\eta^3\) rearrangement, for which activation parameters \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\) were estimated.

The reduction of complexes \([\text{DAD}M(\text{N}^\text{t-Bu})(\mu-\text{Cl})]_2\) and \([\text{DAD}M(\text{N}^\text{t-Bu})(\text{Cl})(\text{py})]\) with C\(_8\)K in toluene leads to the formation of d\(^1\)-d\(^1\) dinuclear compounds \([\text{DAD}M(\mu-\text{N}^\text{t-Bu})]_2\), \(M = \text{Nb} \ (13) \ \text{and} \ \text{Ta} \ (14)\). The molecular structures of 13 and 14 confirm the dinuclear nature of the complexes with bridging imido ligands, which explains their diamagnetic behaviour in solution.

The metathesis reaction of \([\text{DAD}\text{Ta}(\text{N}^\text{t-Bu})(\mu-\text{Cl})]_2\) with DipNH\(_2\) followed by sublimation leads to the formation of \([\text{DAD}\text{Ta}(\text{NDip})(\mu-\text{Cl})]_2\) (15). According to the NMR monitoring, the intermediate product in this reaction seems to be mononuclear complex \([\text{DAD}M(\text{Cl})(\text{DipNH}_2)]\).

**Experimental Part**

**General:** All reactions and manipulations were carried out under argon using standard Schlenk tube techniques. Solvents and liquid starting materials were refluxed in the presence of an appropriate drying agent and distilled: C\(_6\)D\(_6\) and hexane (Na/K alloy); THF and Et\(_2\)O (Na/benzophenone); toluene (Na); amines, CH\(_2\)Cl\(_2\), CDCl\(_3\) and \(\text{t-BuOH} \ (\text{CaH}_2)\). Literature methods were employed for the synthesis of starting materials and 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene (DAD) \([35a]\), Li\(_2\)DAD \([35b]\), \([\text{M}(\text{N}^\text{t-Bu})\text{Cl}_2\text{py}_2]\) \([34a]\), \([\text{CpM}(\text{N}^\text{t-Bu})\text{Cl}_2]\) \([6]\), \([\text{DAD}M(\text{N}^\text{t-Bu})(\text{Cl})(\text{py})]\) and \([\text{DAD}M(\text{N}^\text{t-Bu})(\mu-\text{Cl})]_2\) \([5]\), \(M = \text{Nb} \ \text{and} \ \text{Ta}\). Lithium salts of CpH and IndH were obtained by reaction with n-BuLi in n-hexane and acacNa by reaction of acacH with NaH in THF. Melting points were measured with a Büchi MP B-540 (uncorrected). C, H and N analyses were carried out with a Heraeus CHN-Rapid analyser. Mass spectra were taken on a Varian MAT CH-7a (EI, 70 eV). \(^1\)H- and \(^13\)C\({_1\})-NMR spectra were recorded with Bruker AMX300, AMX400 and DRX500; chemical shifts were referenced (in ppm) to the \(^1\)H (\(\delta \ 7.15\)) and \(^13\)C (\(\delta \ 128.0\)) residual signals of the C\(_6\)D\(_6\), \(^1\)H (\(\delta \ 7.24\)) and \(^13\)C (\(\delta \ 77.0\)) residual signals of the CDCl\(_3\), \(^1\)H (\(\delta \ 2.03\)) and \(^13\)C (\(\delta \ 20.3\)) residual signals of the methyl group of d\(^8\)-toluene. Infrared spectra were recorded with Bruker IFS 88 FT; samples (if not specified) as Nujol mulls between KBr plates.
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Preparation of \([\text{Cp(DAD)Nb(N}^\text{tBu})] \) 1.

**Method A.** \([\text{[(DAD)Nb(N}^\text{tBu})(\text{Cl})(\text{py})]} \) (500 mg, 1.1 mmol) was dissolved in 10 mL THF and a solution of 1 eq CpLi (81 mg, 1.1 mmol) in 10 mL THF was added dropwise at –80°C. After addition the mixture was warmed to room temperature and stirred for 3h. Then the THF was removed and the resulting dark oil was extracted with 2·15 mL hexane. Analytically pure compound was obtained by recrystallisation from hexane at –80°C. Yield: 120 mg (28%).

**Method B.** A solution of 1 eq Li\(_2\)DAD (0.61 mg, 3.3 mmol) in 10 mL THF was added dropwise at –80°C to a stirred solution of 1.00 g \([\text{CpNb(N}^\text{tBu})\text{Cl}_2]\) (3.3 mmol) in 15 mL THF. After addition the mixture was warmed to room temperature and stirred for 3h. Then the THF was removed in vacuum and the resulting dark oil was extracted with 2·15 mL pentane. The solvent was reduced to 5 mL and recrystallisation at –30°C produced 0.68 g (52%) of yellow crystals. T\(_{\text{m.p.}}\) 79.6°C. Anal. Calcd for C\(_{19}\)H\(_{34}\)N\(_3\)Nb (M = 397.41 g mol\(^{-1}\)): C 57.42, H 8.62, N 10.57. Found: C 57.12, H 9.22, N 10.36. MS-EI: 397 (M\(^+\), 52%), 382 (M\(^+\)– Me, 100%), 326 (M\(^+\)– Me\(_2\)C=CH\(_2\)– Me, 9%), 214 (M\(^+\)– 3·Me\(_2\)C=CH\(_2\)– Me, 3%). \(^1\)H-NMR (C\(_6\)D\(_6\), 300 MHz, 300 K): 5.69 (s, 2H, C\(_H\)-DAD), 5.66 (s, 5H, C\(_5\)H\(_5\)), 1.27 (s, 9H, N\(_^t\)Bu), 1.25 (s, 18H, tBu-DAD).

\(^{13}\)C\({}^{1}\)H\(_N\)-NMR (C\(_6\)D\(_6\), 75 MHz, 300 K): 110.4 (CH-DAD), 100.7 (C\(_3\)H\(_3\)), 55.7 (CMe\(_3\)-DAD), 32.9 (NCMe\(_3\)), 31.7 (CMe\(_3\)-DAD). IR (KBr, cm\(^{-1}\)): 3016(w), 1494(w), 1459(s), 1404(w), 1358(m), 1257(s), 214 (M\(^+\)– 3·Me\(_2\)C=CH\(_2\)– Me, 3%).

Preparation of \([\text{Cp(DAD)Ta(N}^\text{tBu})] \) 2.

**Method A.** 300 mg of \([\text{[(DAD)Ta(N}^\text{tBu})(\text{Cl})(\text{py})]} \) (0.56 mmol) was dissolved in 5 mL THF and a solution of 1 eq CpLi (40 mg, 0.56 mmol) in 5 mL THF was added dropwise at –80°C. After addition the mixture was warmed to room temperature and stirred for 3h. Then the THF was removed in vacuum and the resulting dark oil was extracted with 2·15 mL hexane. Analytically pure compound was obtained by recrystallisation from hexane and sublimation (90°C, 10\(^{-2}\) mbar). Yield: 130 mg (48%) of a yellow solid.

**Method B.** This compound was also obtained in 20% yield from the Li\(_2\)DAD and \([\text{CpTa(N}^\text{tBu})\text{Cl}_2]\) in THF using the procedure for isolation and purification described in method B for 5. T\(_{\text{m.p.}}\) 65.3°C. Anal. Calcd for C\(_{19}\)H\(_{34}\)N\(_3\)Ta (M = 485.45 g mol\(^{-1}\)): C 47.01, H 7.06, N 8.66. Found: C 45.03, H 7.06, N 7.93. MS-EI: 485 (M\(^+\), 55%), 470 (M\(^+\)– Me, 100%), 429 (M\(^+\)– Me\(_2\)C=CH\(_2\), 2%), 414 (M – Me\(_2\)C=CH\(_2\) – Me, 16%), 373 (M\(^+\) – 2·Me\(_2\)C=CH\(_2\), 2%), 358 (M\(^+\) – 2·Me\(_2\)C=CH\(_2\) – Me, 8%), 317 (M\(^+\) – 3·Me\(_2\)C=CH\(_2\), 10%), 302 (M\(^+\) – 3·Me\(_2\)C=CH\(_2\) – Me, 3%). \(^1\)H-NMR (C\(_6\)D\(_6\), 300 MHz, 300 K): 5.67 (s, 2H, CH-DAD), 5.66 (s, 5H, C\(_3\)H\(_3\)), 1.30 (s, 9H, C\(_3\)H\(_3\)).

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Preparation of [(η^5-Ind)(DAD)Nb(N^t-Bu)] 3. [(DAD)Nb(N^t-Bu)(Cl)(py)] (1.00 g, 2.2 mmol) was dissolved in 10 mL THF. A solution of IndLi (0.27 g, 0.93 mmol) in 10 ml THF was added at –80°C and the mixture was stirred for 8h at room temperature. The THF was removed in vacuum and the complex was extracted with 2·15 mL. Removing hexane in vacuum yielded 0.77 g (78%) of an analytically pure yellow solid. T_m.p. 138.5°C. Anal. Calcd for C_{23}H_{36}N_3Nb (M = 447.47 g mol⁻¹): C 61.74, H 8.11, N 9.39. Found: C 60.37, H 8.09, N 8.97. MS-EI: 447 (M⁺, 49%), 432 (M⁺ – Me, 17%), 464 (M⁺ – Me₂C=CH₂ – Me, 2%), 376 (M⁺ – 3·Me₂C=CH₂, 4%), 332 (M⁺ – Ind, 5%), 115 (Ind⁺, 27%), 58 (100%). ¹H-NMR (C₆D₆, 300 MHz, 300 K): 7.18 (overlapped with residual protons of C₆D₆, 4,7-Ind), 6.97 (t, 1H, 3_J_H-H = 3.2 Hz, 2-Ind), 6.64 (dd, 2H, 5,6-Ind), 6.18 (d, 2H, 3_J_H-H = 3.2 Hz, 1,3-Ind), 5.18 (s, 2H, CH-DAD), 1.30 (s, 18H, N^t-Bu-DAD), 1.25 (s, 9H, N^t-Bu).
³C{¹H}-NMR (C₆D₆, 75 MHz, 300 K): 123.1 (4,7-Ind), 122.2 (5,6-Ind), 110.5 (2-Ind), 110.1 (CH-DAD), 85.4 (1,3-Ind), 59.9 (NCMe₃), 56.0 (CMe₃-DAD), 32.9 (NCMe₃), 31.7 (CMe₃-DAD). IR (KBr, cm⁻¹): 3074(w), 3047(w), 3036(w), 1491(m), 1406(w), 1358(s), 1329(m), 1258(s), 1244(s), 1221(s), 1169(w), 1148(w), 1134(w), 1115(w), 1098(w), 1059(w), 1038(m), 1026(w), 1015(w), 1007(w), 931(w), 880(m), 868(w), 816(s), 804(w), 774(s), 741(m), 733(s), 660(w), 602(w), 561(w).

Preparation of [(η^5-Ind)(DAD)Ta(N^t-Bu)] 4. [(DAD)Ta(N^t-Bu)(Cl)(py)] (500 mg, 0.93 mmol) was dissolved in 10 mL THF. A solution of IndLi (114 mg, 0.93 mmol) in 10 ml THF was added at –80°C and the mixture was stirred for 8h at room temperature. The THF was removed in vacuum and the complex was extracted with 2·15 mL. Removing hexane in vacuum yielded 300 mg (60%) of the product as a yellow solid. T_m.p. 147.3°C. Anal. Calcd for C_{23}H_{36}N_3Ta (M = 535.51 g mol⁻¹): C 51.59, H 6.78, N 7.85. Found: C 50.39, H 6.79, N 7.56. MS-EI: 535 (M⁺, 44%), 520 (M⁺ – Me, 87%), 464 (M⁺ – Me₂C=CH₂ – Me, 7%), 367 (M⁺ – 3·Me₂C=CH₂, 4%), 352 (M⁺ – 3·Me₂C=CH₂ – Me, 3%), 116 (IndH⁺,73%), 57 (100%). ¹H-NMR (C₆D₆, 300 MHz, 300 K): 7.17 (overlapped with residual protons of C₆D₆, 4,7-Ind), 6.92 (t, 1H, 3_J_H-H = 3.2 Hz, 2-Ind), 6.66 (dd, 2H, 5,6-Ind), 6.14 (d, 2H, 3_J_H-H = 3.2 Hz, 1,3-Ind), 5.11 (s, 2H, CH-DAD), 1.28 (s, 27H, N^t-Bu overlapped with ¹Bu-DAD). ³C{¹H}-NMR (C₆D₆, 75 MHz, 300 K): 123.1 (4,7-Ind), 122.8 (5,6-Ind), 110.6 (2-Ind), 107.4 (CH-DAD), 84.8 (1,3-Ind), 64.5
Preparation of [(DAD)Nb(N\textit{t}Bu)(\eta^3-C_3H_5)] 5. A mixture of 1.00 g of [(DAD)Nb(N\textit{t}Bu)(Cl)(py)] (2.2 mmol) and 0.6 g [allMgBr*\textit{thf}]* (2.2 mmol) was dissolved in 20 mL THF and stirred at room temperature for 12h. After this the solvent was removed in vacuum leaving a yellow solid, which was extracted with two portions of 10 mL hexane. After removing the solvent, the residue was sublimed at 80°C/10^{-4} mbar and produced 0.40 g (49%) of a pale yellow solid. T\textit{mp.} 75.5°C. Anal. Calcd for C_{17}H_{34}N_{3}Nb (M = 373.39 g mol^{-1}): C 54.69, H 9.18, N 11.25. Found: C 54.28, H 8.84, N 11.28. MS-EI: 373 (M^{+}, 1%), 332 (M^{+} – C_3H_5, 22%), 57 (100%). \textit{^1}H-NMR (C_6D_6, 500 MHz, 300 K): 6.37 (quin, 1H, 2-C_3H_5), 5.58 (s, 2H, CH-DAD), 3.87 (bs, 2H, cis-1,3-C_3H_5), 1.39 (s, 18H, tBu-DAD), 1.23 (s, 9H, N\textit{t}Bu). \textit{^13}C{\{^1}H\}NMR (C_6D_6, 125 MHz, 300 K): 130.5 (2-C_3H_5), 105.5 (CH-DAD), 68.5 (1,3-C_3H_5), 56.3 (CMe_3-DAD), 33.4 (NCMe_3), 31.7 (CMe_3-DAD). IR (KBr, cm^{-1}): 3065(w), 3016(w), 1509(m), 1490(w), 1457(s), 1400(w), 1359(s), 1259(s), 1245(w), 1219(s), 1159(w), 1138(w), 1109(w), 1056(w), 1016(w), 1002(m), 946(w), 922(w), 869(m), 831(s), 808(s), 769(s), 757(w), 740(w), 686(w), 629(w), 599(w), 564(m), 536(w), 523(w), 504(w), 461(m).

Preparation of [(DAD)Ta(N\textit{t}Bu)(\eta^3-C_3H_5)] 6. A mixture of 1.00 g of [(DAD)Ta(N\textit{t}Bu)(\mu-Cl)]_2 (1.1 mmol) and 0.50 g [allMgBr*\textit{thf}]* (2.2 mmol) was dissolved in 20 mL THF and stirred at room temperature for 12h. After this the solvent was removed in vacuum leaving a yellow solid, which was extracted with two portions of 10 mL hexane. After removing the solvent, the residue was sublimed at 80°C/10^{-4} mbar and produced 0.74 g (73%) of a pale yellow solid. T\textit{mp.} 61.9°C. Anal. Calcd for C_{17}H_{34}N_{3}Ta (M = 461.43 g mol^{-1}): C 44.25, H 7.43, N 9.11. Found: C 43.81, H 7.37, N 9.04. MS-EI: 461 (M^{+}, 53%), 446 (M^{+} – Me, 25%), 420 (M^{+} – C_3H_5, 22%), 363 ([[DAD]TaN]^+), 21%), 57 (100%). \textit{^1}H-NMR (C_6D_6, 300 MHz, 300 K): 6.44 (quin, 1H, 3J_{HH} = 11.4 Hz, 2-C_3H_5), 5.50 (s, 2H, CH-DAD), 2.31 (bs, 4H, 1,3-C_3H_5), 1.36 (s, 18H, \textit{t}Bu-DAD), 1.26 (s, 9H, N\textit{t}Bu). \textit{^13}C{\{^1}H\}NMR (d_8-toluene, 500 MHz, 200 K): 6.44 (tt, 1H, 2-C_3H_5, trans-J_{HH} = 14.6 Hz, cis-J_{HH} = 8.1 Hz), 5.40 (s, 2H, CH-DAD), 3.88 (d, 2H, cis-J_{HH} = 8.1 Hz, cis-1,3-C_3H_5), 1.35 (s, 18H, \textit{t}Bu-DAD), 1.23 (s, 9H, N\textit{t}Bu), 0.52 (d, 2H, trans-J_{HH} = 14.6 Hz, trans-1,3-C_3H_5).
C\textsubscript{3}H\textsubscript{5}, \textit{trans}-\textsuperscript{3}J\textsubscript{HH} = 14.4 Hz, \textit{cis}-\textsuperscript{3}J\textsubscript{HH} = 7.8 Hz, \textit{cis}-1,3-C\textsubscript{3}H\textsubscript{5}), 1.34 (s, 18H, \textit{t}-Bu-DAD), 1.33 (s, 9H, N\textsubscript{t}-Bu), 0.52 (d, 2H, \textit{trans}-\textsuperscript{3}J\textsubscript{HH} = 14.4 Hz, \textit{trans}-1,3-C\textsubscript{3}H\textsubscript{5}).

\textsuperscript{13}C\textsubscript{1}H{-}\text{NMR (C\textsubscript{6}D\textsubscript{6}, 75 MHz, 300 K)}: 132.8 (2-C\textsubscript{3}H\textsubscript{5}), 102.3 (CH-DAD), 68.8 (1,3-C\textsubscript{3}H\textsubscript{5}), 65.4 (NCMe\textsubscript{3}), 56.2 (CMe\textsubscript{3}-DAD), 34.3 (NCMe\textsubscript{3}), 31.5 (CMe\textsubscript{3}-DAD). IR (KBr, cm\textsuperscript{-1}): 3065(w), 3027(m), 1628(w), 1501(m), 1456(s), 1389(m), 1360(s), 1281(s), 1248(w), 1221(s), 1150(m), 1109(w), 1063(w), 1016(w), 1003(m), 961(w), 866(m), 841(s), 808(m), 768(s), 723(w), 694(w), 629(w), 563(w).

\textbf{Preparation of [(DAD)Nb(N\textsubscript{t}-Bu)(acac)] 7.} A suspension of 0.27 g (2.2 mmol) acacNa in 10 mL THF was added at –80°C to a solution of 1.00 g (2.2 mmol) [(DAD)Nb(N\textsubscript{t}-Bu)(Cl)(py)] in 15 mL THF. After 10h of stirring at room temperature the solvent was removed, leaving a brown oily substance. Extraction and further recrystallisation from hexane produced 0.64 g (67%) of orange crystals. T\textsubscript{m.p.} 97.9°C. Anal. Calcld for C\textsubscript{19}H\textsubscript{36}N\textsubscript{3}O\textsubscript{2}Nb (M = 431.42 g mol\textsuperscript{-1}): C 52.90, H 8.41, N 9.74. Found: C 51.34, H 8.31, N 9.32. MS-EI: 431 (M\textsuperscript{+}, 10%), 58 (100%). \textsuperscript{1}H-NMR (C\textsubscript{6}D\textsubscript{6}, 300 MHz, 300 K): 6.08 (s, 2H, CH-DAD), 5.14 (s, 1H, CH-acac), 1.65 (s, 6H, C\textsubscript{6}H\textsubscript{3}-acac), 1.56 (s, 18H, \textit{t}-Bu-DAD), 1.44 (s, 9H, N\textsubscript{t}-Bu). 

\textsuperscript{13}C\textsubscript{1}H{-}\text{NMR (C\textsubscript{6}D\textsubscript{6}, 75 MHz, 300 K)}: 191.4 (CO-acac), 105.3 (CH-DAD), 102.5 (CH-acac), 56.4 (CMe\textsubscript{3}-DAD), 32.9 (NCMe\textsubscript{3}), 31.2 (CMe\textsubscript{3}-DAD), 26.4 (CH\textsubscript{3}-acac). IR (KBr, cm\textsuperscript{-1}): 3030(w), 1589(s), 1557(w), 1526(s), 1497(w), 1456(s), 1358(w), 1281(w), 1262(s), 1246(w), 1221(s), 1150(m), 1111(w), 1062(w), 1024(m), 951(w), 928(w), 868(m), 806(m), 783(m), 770(s), 721(w), 694(w), 664(w), 656(w), 569(m), 546(w), 536(w), 511(w), 428(w), 411(w).

\textbf{Preparation of [(DAD)Ta(N\textsubscript{t}-Bu)(acac)] 8.} 0.64 g (1.2 mmol) of [(DAD)Ta(N\textsubscript{t}-Bu)(Cl)(py)] were dissolved in 15 mL THF. To this a suspension of 0.15 g (1.2 mmol) acacNa in 10 mL THF was added at –80°C. After 10h of stirring at room temperature the solvent was removed, leaving a brown oily substance. Extraction and further recrystallisation from hexane produced 0.28 g (45%) of orange crystals. T\textsubscript{m.p.} 99.1°C. Anal. Calcld for C\textsubscript{19}H\textsubscript{36}N\textsubscript{3}O\textsubscript{2}Ta (M = 519.47 g mol\textsuperscript{-1}): C 43.93, H 6.99, N 8.09. Found: C 40.89, H 6.88, N 7.36. MS-EI: 519 (M\textsuperscript{+}, 74%), 504 (M\textsuperscript{+} – Me, 43%), 448 (M\textsuperscript{+} – Me\textsubscript{2}C=CH\textsubscript{2}, 3%), 57 (100%). \textsuperscript{1}H-NMR (C\textsubscript{6}D\textsubscript{6}, 300 MHz, 300 K): 6.04 (s, 2H, CH-DAD), 5.06 (s, 1H, CH-acac), 1.60 (s, 6H, CH\textsubscript{2}-acac), 1.56 (s, 18H, \textit{t}-Bu-DAD), 1.47 (s, 9H, N\textsubscript{t}-Bu). 

\textsuperscript{13}C\textsubscript{1}H{-}\text{NMR (C\textsubscript{6}D\textsubscript{6}, 75 MHz, 300 K)}: 191.7 (CO-acac), 103.6 (CH-acac) 103.4 (CH-DAD), 55.7 (CMe\textsubscript{3}-DAD), 34.3 (NCMe\textsubscript{3}), 31.5 (CMe\textsubscript{3}-DAD), 26.1 (CH\textsubscript{3}-acac). IR (KBr, cm\textsuperscript{-1}): 1590(m), 1530(m), 1281(m), 1262(w), 1223(m), 1137(w), 1093(w), 1026(w), 968(w), 933(w), 861(w), 804(w), 762(w), 722(w), 665(w), 566(w), 534(w), 432(w).
Preparation of \([\text{DAD}]\text{Nb} (\text{N}^\text{Bu})(\text{O}^\text{Bu})\] 9. A solution of 112 mg (1.11 mmol) \(\text{tBuOK}\) in 10 mL THF was added at \(-80^\circ C\) to a solution of 500 mg \([\text{DAD}]\text{Nb}(\text{N}^\text{Bu})(\text{Cl})(\text{py})\] (1.11 mmol) in the same amount of THF. After 5h of stirring at room temperature the solvent was removed, leaving a brown oily substance. After purification by sublimation (100°C, 10\(^{-2}\) mbar) 300 mg of a yellow solid (66% yield) were isolated. \(T_{\text{m.p.}}\) 68.4°C. Anal. Calcd for C\(_{18}\)H\(_{39}\)N\(_3\)ONb (\(M = 405.43\) g mol\(^{-1}\)): C 53.33, H 9.45, N 10.36. Found: C 52.97, H 10.10, N 9.86. MS-EI: 405 (M\(^+\), 4%), 349 (M\(^+\) – Me\(_2\)C=CH\(_2\), 2%), 334 (M\(^+\) – Me\(_2\)C=CH\(_2\) – Me, 6%), 57 (100%). \(^1\)H-NMR (d\(_8\)-toluene, 400 MHz, 300 K): 5.76 (s, 2H, C\(_H\)-DAD), 1.43 (s, 9H, N\(_t\)Bu), 1.26 (s, 18H, tBu-DAD), 1.25 (s, 9H, O\(_t\)Bu). \(^{13}\)C\{\(^1\)H\}-NMR (d\(_8\)-toluene, 100 MHz, 300 K): 105.6 (C\(_H\)-DAD), 56.0 (CMe\(_3\)-DAD), 33.9 (NCMe\(_3\)), 33.3 (OCMe\(_3\)), 31.7 (CMe\(_3\)-DAD). IR: (KBr, cm\(^{-1}\)) 3027(w), 1498(w), 1389(w), 1359(s), 1263(s), 1244(w), 1223(s), 1186(s), 1150(w), 1138(w), 1109(w), 1065(w), 1024(w), 993(s), 872(m), 816(w), 808(w), 785(w), 774(m), 723(w), 569(m), 552(w), 513(w), 469(w).

Preparation of \([\text{DAD}]\text{Ta} (\text{N}^\text{Bu})(\text{O}^\text{Bu})\] 10. 200 mg \([\text{DAD}]\text{Ta}(\text{N}^\text{Bu})(\text{Cl})(\text{py})\] (0.37 mmol) were dissolved in 10 mL THF. A solution of 42 mg (0.37 mmol) \(\text{tBuOK}\) in the same amount of THF was added at \(-80^\circ C\). After 5h of stirring at room temperature the solvent was removed, leaving a brown oily substance. After purification by sublimation (100°C, 10\(^{-2}\) mbar) 95 mg of a pale yellow solid (52% yield) was isolated. \(T_{\text{m.p.}}\) 79.2°C. Anal. Calcd for C\(_{18}\)H\(_{39}\)N\(_3\)OTa (\(M = 493.47\) g mol\(^{-1}\)): C 43.81, H 7.76, N 8.52. Found: C 42.89, H 7.88, N 8.29. MS-EI: 493 (M\(^+\), 44%), 478 (M\(^+\) – Me, 21%), 437 (M\(^+\) – Me\(_2\)C=CH\(_2\), 5%), 422 (M\(^+\) – Me\(_2\)C=CH\(_2\) – Me, 100%), 381 (M\(^+\) – 2·Me\(_2\)C=CH\(_2\), 60%), 366 (M\(^+\) – 2·Me\(_2\)C=CH\(_2\) – Me, 5%), 310 (M\(^+\) – 3·Me\(_2\)C=CH\(_2\) – Me, 2%). \(^1\)H-NMR (C\(_6\)D\(_6\), 300 MHz, 300 K): 5.82 (s, 2H, C\(_H\)-DAD), 1.54 (s, 9H, N\(_t\)Bu), 1.33 (s, 9H, O\(_t\)Bu), 1.32 (s, 18H, \(\text{Bu}-\text{DAD}\)). \(^{13}\)C\{\(^1\)H\}-NMR (C\(_6\)D\(_6\), 75 MHz, 300 K): 104.4 (C\(_H\)-DAD), 55.9 (CMe\(_3\)-DAD), 35.3 (s, NCMe\(_3\)), 33.3 (OCMe\(_3\)), 32.0 (CMe\(_3\)-DAD). IR: (KBr, cm\(^{-1}\)) 3034(w), 1586(w), 1361(s), 1286(s), 1223(s), 1188(s), 1142(m), 1072(w), 1008(s), 959(w), 920(w), 869(m), 806(m), 789(m), 779(m), 772(m), 722(w), 563(w), 529(w), 514(w), 471(w).

Preparation of \([\text{DAD}]\text{Nb} (\text{N}^\text{Bu})(\text{O}^\text{Bu})(\eta^3\text{-BH}_4)\] 11. 1.5 g (2.0 mmol) of \([\text{DAD}]\text{Nb}(\text{N}^\text{Bu})(\mu\text{-Cl})_2\] and 0.15 g (4.0 mmol) of NaBH\(_4\) were suspended in 50 mL THF and stirred at room temperature for 12h. The slightly orange solution was filtered off and the solvent removed in vacuum leaving a red oil. Further sublimation at 60°C/10\(^{-4}\) mbar produced 0.85 g (67%) of a pale yellow solid. \(T_{\text{m.p.}}\) 65.4°C. Anal. Calcd for C\(_{14}\)H\(_{33}\)BN\(_3\)Nb (\(M = 347.16\) g mol\(^{-1}\)): C 48.44, H 9.58, N 12.10. Found: C 47.88, H 9.56, N 12.11. MS-EI: 347 (M\(^+\), 100%), 332 (M\(^+\) –
Me, 8%), 318 (M̅ – Me – BH₃, 13%), 276 (M̅ – Me₂C=CH₂ – Me, 42%). ¹H-NMR (d₈-toluene, 500 MHz, 300 K): 5.87 (s, 2H, CH-DAD), 1.31 (s, 9H, NᵗBu), 1.19 (s, 18H, ¹Bu-DAD), 0.04 (q, 4H, ¹JₙB₄ = 85 Hz, BH₄). ¹³C{¹H}-NMR (C₆D₆, 75 MHz, 300 K): 107.8 (CH-DAD), 33.1 (NCMe₂), 31.6 (CMe₃-DAD). ¹¹B-NMR (d₈-toluene, 160 MHz, 300 K): -21.3 (quin, ¹JₙB₄ = 85 Hz, BH₄). IR (KBr, cm⁻¹): 3032(w), 2507(s), 2319(w), 2274(w), 2099(w), 2037(s), 1495(w), 1456(s), 1390(w), 1364(s), 1302(w), 1258(s), 1217(s), 1157(s), 1140(w), 1111(w), 1061(w), 1026(w), 1017(w), 947(w), 876(s), 816(s), 777(s), 723(w), 567(w), 516(w), 494(w), 449(w).

Preparation of [(DAD)Ta(NᵗBu)(η³-BH₄)] 12. 2.0 g of [(DAD)Ta(NᵗBu)(µ-Cl)]₂ (2.2 mmol) and 0.17 g NaBH₄ (4.4 mmol) were suspended in 50 mL THF and stirred at room temperature for 12h. The slightly orange solution was filtered off and the solvent removed in vacuum leaving a red oil. Further sublimation at 60°C/10⁻⁴ mbar produced 1.64 g (86%) of a pale yellow solid. Tₘ.p. 69.5°C. Anal. Calcd for C₁₄H₃₃BN₃Ta (M = 435.20 g mol⁻¹): C 38.64, H 7.64, N 9.66. Found: C 38.86, H 7.71, N 9.47. MS-EI: 435 (M⁺, 11%), 420 (M⁺ – Me, 7%), 406 (M⁺ – Me – BH₃, 13%), 378 (M⁺ – Me₂C=CH₂ – H, 5%), 365 (M⁺ – Me₂C=CH₂ – BH₃, 2%), 58 (100%). ¹H-NMR (C₆D₆, 500 MHz, 300 K): 5.91 (s, 2H, CH-DAD), 1.73 (q, 4H, ¹JₙB₄ = 85 Hz, BH₄), 1.41 (s, 9H, NᵗBu), 1.24 (s, 18H, ¹Bu-DAD). ¹³C{¹H}-NMR (C₆D₆, 125 MHz, 300 K): 105.8 (CH-DAD), 65.8 (NCMe₃), 57.0 (CMe₃-DAD), 34.5 (NCMe₃), 31.8 (CMe₃-DAD). ¹¹B-NMR (d₈-toluene, 160 MHz, 300 K): -20.2 (quin, ¹JₙB₄ = 85 Hz, BH₄). IR (KBr, cm⁻¹): 3041(w), 2519(s), 2319(w), 2274(w), 2099(w), 2037(s), 1495(w), 1456(s), 1390(w), 1364(s), 1302(w), 1258(s), 1217(s), 1157(s), 1140(w), 1111(w), 1061(w), 1026(w), 1017(w), 947(w), 876(s), 816(s), 777(s), 723(w), 567(w), 516(w), 494(w), 449(w).

Preparation of [(DAD)Nb(NᵗBu)(µ-Cl)]₂ 13. 1.00 g of [(DAD)Nb(NᵗBu)(Cl)(py)] (1.36 mmol) and 0.50 g of CsK (3.70 mmol) were mixed. Then 30 mL of toluene were added and stirred for 5d at room temperature. To initiate reaction ultrasound was applied for 1h. The formed graphite was filtered off and the solvent removed under reduced pressure. Further extraction with 5 portions of 20 mL of hot hexane followed by recrystallisation at -30°C produced pure product as red crystals. Yield: 0.60 g (66%). Tₘ.p. 310°C(dec.). Anal. Calcd C₂₈H₅₈N₆Nb₂ (M = 664.63 g mol⁻¹): C 50.60, H 8.80, N 12.64. Found: C 49.46, H 8.87, N 12.22. MS-EI: 664 (M⁺, 13%), 607 (M⁺ – Me₂C=CH₂ – H, 100%). ¹H-NMR (d₈-toluene, 500 MHz, 300 K): 6.25 (s, 2H, CH-DAD), 1.26 (s, 9H, NᵗBu), 1.05 (s, 18H, ¹Bu-DAD). ¹³C{¹H}-NMR (d₈-toluene, 125 MHz, 300
Chapter VI

K): 102.2 (CH-DAD), 72.7 (NCMe₃), 54.9 (CMe₃-DAD), 34.9 (NCMe₃), 32.2 (CMe₃-DAD). IR (KBr, cm⁻¹): 3021(w), 1502(w), 1458(s), 1359(m), 1304(w), 1242(w), 1216(s), 1189(s), 1138(m), 1097(w), 1055(w), 1032(w), 1015(m), 935(w), 876(m), 811(w), 790(w), 772(m), 723(w), 669(w), 635(w), 563(w).

Preparation of [(DAD)Ta(µ-N⁴Bu)]₂ 14. 500 mg of [(DAD)Ta(N⁴Bu)(µ-Cl)]₂ (0.55 mmol) and 300 mg of C₈K (2.20 mmol) were mixed. 30 mL of toluene were added and stirred for 2d at room temperature. To initiate reaction ultrasound was applied for 1h. The formed graphite was filtered off and the solvent removed under reduced pressure. Further extraction with 4 portions of 25 mL of hot hexane followed by recrystallisation at –30°C produced pure product as dark yellow crystals. Tₘ.p. 295°C(dec.) Yield: 150 mg (32%). Anal. Calcd C₂₈H₅₈N₆Ta₂ (M = 840.71 g mol⁻¹): C 40.00, H 6.95, N 10.00. Found: C 37.63, H 6.97, N 8.91. MS-EI: 840 (M⁺, 10%), 783 (M⁺ – Me₂C=CH₂ – H, 100%). ¹H-NMR (d₈-toluene, 500 MHz, 300 K): 6.25 (s, 2H, CH-DAD), 1.29 (s, 9H, N⁴Bu), 1.06 (s, 18H, tBu-DAD). ¹³C{¹H}-NMR (d₈-toluene, 125 MHz, 300 K): 99.9 (C₄H-DAD), 54.7 (CMe₃-DAD), 35.5 (NCMe₃), 32.3 (CMe₃-DAD). IR (KBr, cm⁻¹): 3040(w), 1508(w), 1360(m), 1314(w), 1262(w), 1244(w), 1219(s), 1190(w), 1130(m), 1098(w), 1018(w), 945(w), 874(m), 804(m), 772(m), 723(w), 669(w), 635(w), 563(w).

Preparation of [(DAD)Ta(NDip)(µ-Cl)]₂ 15. Excess of DipNH₂ (1.0 mL, 5 eq.) was added to a solution of 0.50 mg (0.55 mmol) [(DAD)Ta(N⁴Bu)(µ-Cl)]₂ in 20 mL toluene. After heating at 110°C for 12h the solvent was removed in vacuum and the residue sublimed at 160°C/10⁻⁴ mbar. Yield: 0.28 g (46%). For the spectroscopic data see ref. [5].

Reaction of [(DAD)Ta(N⁴Bu)(µ-Cl)]₂ with DipNH₂. DipNH₂ (11.7 mg, 66 µmol) and [(DAD)Ta(N⁴Bu)(µ-Cl)]₂ (10.0 mg, 11 µmol) were placed in an NMR tube and suspended in 1 mL C₆D₆. The mixture was heated for 2h at 110°C and the ¹H-NMR spectra were recorded at various times. ¹H-NMR (500 MHz, C₆D₆) of the proposed mononuclear complex [(DAD)Ta(NDip)(Cl)(H₂NR)] (IM₁): ¹H-NMR (C₆D₆, 500 MHz, 300 K): 7.20 (d, 2H, ³J_HH = 7.6 Hz, m-NDip), 6.95 (t, 1H, ³J_HH = 7.6 Hz, p-NDip), 6.06 (s, 2H, CH-DAD), 4.47 (sept, ³J_HH = 6.9 Hz, CH₃-Dip), 1.40 (d, 12H, ³J_HH = 6.9 Hz, CH₃-Dip), 1.30 (s, 18H, ¹Bu-DAD).

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References


[4] see Chapter VIII.

[5] see Chapter V.


[10] see Chapter I.


[21]

\[
k = \frac{\sigma k_B T}{h} e^{-\frac{\Delta H^* - T \Delta S^*}{RT}}
\]

\[
\ln(k) = \ln\left(\frac{\sigma k_B}{h}\right) + \ln(T) + \left(-\frac{\Delta H^* - T \Delta S^*}{RT}\right)
\]

\[
\ln(k) - \ln(T) = \ln\left(\frac{\sigma k_B}{h}\right) - \frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R}
\]

\[
\log\left(k / T\right) = 10.32 - \frac{\Delta H^*}{19.13}\left(\frac{1}{T}\right) + \frac{\Delta S^*}{19.13}; \sigma = 1
\]


[23] $\Delta G_{298}^* = \Delta H^* - 298 \cdot \Delta S^*$


\[
\frac{dA}{dt} = \frac{\partial C_A(t)}{\partial t} = k \cdot C_A(t)
\]

\[
\Rightarrow \quad C_A(t) = C_0 \cdot e^{-kt}
\]


[35] (a) J. M. Kliegman, R. K. Barners, Tertahedron 1970, 26, 2555-2560; (b) see Chapter V Results and Discussion for detailed information; (c) P. A. Bates, A. J. Nielson, J. M. Waters, Polyhedron 1985, 4(8), 1391-1401; (d) A. Merkoulov, S. Schmidt, K. Harms, J. Sundermeyer, in press, see Chapter IX.

[36] A THF solution of allMgBr was prepared from allBr and Mg. The volatiles were removed in vacuum and a white residue dried at 25°C/10⁻⁴ mbar for 12h. The constitution of the solid was found to be [allMgBr*(thf)₁,₁] with M = 230.77 g mol⁻¹ by titration with aqueous HCl.
Chapter VII

Chemical Reactivity of DAD Imido Amido Complexes of Niobium and Tantalum

Introduction

Imido amido complexes having redox active 1,4-diaza-1,3-diene ligands (R,R’–DAD) were considered to be promising candidates for the deposition of TaN films. These films possess a wide range of useful properties. For example, their hardness and good electrical conductivity allow using them as barrier materials between cooper and silicon in microelectronics [1].

In our approach we focused on N–tBu substituted imido/amido 1,4-diaza-1,3-diene complexes in order to increase the volatility of precursors of the lowest possible molecular weight.

In order to test our complexes in Chemical Vapour Deposition (CVD) experiments, at least 20 g of purest grade compound was needed to guarantee a constant flow rate of precursor from the bubbler.

Amido and imido complexes are perfect precursors in metathesis reactions. This allows modifying them and obtaining new derivatives, which are possibly difficult to synthesise in other
ways. In this chapter the synthetic aspects of the complexes $[(\text{DAD})\text{M}(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})]$, $\text{M} = \text{Nb}$ and Ta, DAD = 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene, and their chemical activity in metathesis reactions with amines, organic acids and lithium alkyls are discussed. The synthesised complexes display a molecular dynamic rearrangement, which was also investigated by NMR spectroscopy.

## Results and discussion

### Synthetic studies

The complexes $[(\text{DAD})\text{M}(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})]$, $\text{M} = \text{Nb}$ (1) and Ta (2), can be obtained from readily available precursors $[\text{M}(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})\text{Cl}_2\text{py}_2]$ [2] or $[\text{M}(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})(\text{Cl})(\mu\text{-Cl})(\text{NH}_2^t\text{Bu})]_2$ [3] by reaction with $\text{Li}_2\text{DAD}$ or by \textit{in situ} reduction with Mg in the presence of the DAD ligand.

The best synthetic strategy for large-scale syntheses of 1 and 2 is a combination of the literature known reaction between $\text{MCl}_5$ and excess of $^t\text{BuNH}_2$ [3] followed by \textit{in situ} reduction of the obtained dimer with Mg in the presence of DAD in THF. The intermediate dimeric compound $[\text{M}(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})\text{Cl}_2(\text{NH}_2^t\text{Bu})]_2$ should be separated from the ammonium salt $^t\text{BuNH}_3\text{Cl}$, which can react with the product (see below). The reaction with Mg proceeds well in
polar THF, however no product was isolated from the reaction in toluene. It seems that the formation of the by-product MgCl$_2$(thf)$_n$ serves as a driving force in this transformation. All attempts to improve the efficiency or to simplify the operations, such as changing the solvents (toluene) or reducing agents (C$_3$K, Li), failed. An overall yield of more than 40% starting from MCl$_5$ after two synthetic steps and two sublimations of the final product 1 or 2 can be considered acceptable.

\[
\begin{align*}
\text{MCl}_5 & \xrightarrow{ \text{tBuNH}_2 \text{exe} \text{, toluene}} \xrightarrow{\text{- 3 tBuNH}_3\text{Cl} \text{, filtration}} 1 \\
& \xrightarrow{\text{DAD , Mg , THF}} \xrightarrow{\text{- MgCl}_2 \text{, hexane extraction}} 2
\end{align*}
\]

1 and 2 are pale yellow solids with low melting points and high volatilities, which are extremely well soluble in hexane. They do not exhibit any Lewis acidity towards pyridine, amines or phosphines. This is in contrast to the dimeric complexes [(DAD)M(N^tBu)(µ–Cl)]$_2$ and mononuclear complexes [(DAD)M(N^tBu)(Bz)], which react with pyridine forming adducts [(DAD)M(N^tBu)(X)(py)], M = Nb and Ta; X = Cl and Bz [4]. It is well known that the amido ligand is a strong 4e$^-$ donor and makes the metal centre more electron rich in 1 and 2 compared to the latter compounds. This fact, together with a bulky tBu group, prevents the complexes from forming a Lewis acid–base adduct.

A crystal of 2 suitable for X-ray analysis was obtained by cooling a concentrated hexane solution to –80°C. The molecular structure of 2 is presented in Fig. 1. The coordination polyhedron of the tantalum atom is a distorted tetrahedron, in which nitrogen atoms of imido amido and DAD$^{2-}$ ligands occupy all four positions.

The imido moiety exhibits standard parameters [5] for its 6e$^-$ mode, a short M–N bond distance of 1.761(7) Å and a nearly linear M–N–C angle of 176.9(6)$^\circ$. The metal–amido bonding situation correlates with the parameters for 4e$^-$ mode [5], the Ta(1)–N(4) bond length being 1.992(7) Å and the Ta(1)–N(4)–C(15) angle being 142.9(6)$^\circ$. 

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Fig. 1. The molecular structure of [(DAD)Ta(N^tBu)(NH^tBu)] 2 with thermal ellipsoids at 30% probability (the hydrogen atoms are omitted). Space group P 2_1 2_1 2_1, Z = 4. Selected bond length [Å] and angles [°]: Ta(1)–N(1) 1.997(6), Ta(1)–N(2) 1.995(6), Ta(1)–N(3) 1.761(7), Ta(1)–N(4) 1.992(7), Ta(1)–C(1) 2.494(9), Ta(1)–C(2) 2.47(1), N(1)–C(1) 1.39(1), N(2)–C(2) 1.37(1), C(1)–C(2) 1.39(1), N(3)–Ta(1)–N(4) 112.9(3), N(3)–Ta(1)–N(1) 114.3(3), N(3)–Ta(1)–N(2) 114.8(3), N(1)–Ta(1)–N(2) 89.4(3), Ta(1)–N(3)–C(11) 176.9(6), Ta(1)–N(4)–C(15) 142.9(6).

The DAD^2− M metallacycle exhibits a folded conformation in solid state. The metal centre is not located in the plane formed by the N_2C_2 atoms of the DAD^2− moiety with metal–to–plane distances of 1.0478(3) Å. With respect to the definition of *prone* and *supine* conformers [6, 7] for the folded R,R’–DAD^2− ligand in cyclopentadienyl complexes of early transition metals it is suggested to use this definition for the isolobal RN^2− ligand as well. In the molecular structure of 2 the *supine* isomer is present.

In comparison with the free DAD ligand [8] and its d^6 niobium donor–acceptor complex [Nb(NC_4H_2Cl_3)Cl_3(dad)] [9] a decrease in C–C bond distance and an increase in C–N bond distances are observed in 2 (Table 1). The same tendencies were found in other structurally characterised R,R’–DAD^2− d^6 complexes with niobium and tantalum [6d, 10, 11], in
which the \( \text{MC}_2\text{N}_2 \) backbone exhibits very similar structural parameters. For example, the selected parameters for the \( \text{DAD}^{2−} \) ligand in reference complex \([\text{Cp(DAD)}\text{NbCl}_2] \) [11] are presented in Table 1.

\textbf{Table 1.} Selected distances [Å] and angles [°] of \( \text{DAD}^{2−} \) and imido ligands in 2 and reference complexes \([\text{Cp(DAD)}\text{NbCl}_2] \) [11] and \([\text{Nb(NC}_6\text{H}_2\text{Cl}_3)\text{Cl}_3(\text{dad})] \) [9].

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \text{DAD}^{2−} )</th>
<th>imido</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{C – C} )</td>
<td>( \text{N – C} )</td>
</tr>
<tr>
<td>2</td>
<td>1.388(13)</td>
<td>1.371(12)</td>
</tr>
<tr>
<td>ref. [11]</td>
<td>1.402(6)</td>
<td>1.354(6)</td>
</tr>
<tr>
<td>DAD [8]</td>
<td>1.468(2)</td>
<td>1.267(2)</td>
</tr>
<tr>
<td>ref. [9]</td>
<td>1.471(3)</td>
<td>1.270(3)</td>
</tr>
</tbody>
</table>

In spite of the short distances of approx. 2.5 Å between the metal centre and carbon atoms of the double bond in 2, recent computations [10f, 12] suggest that there is no considerable bonding M–C interaction. In contrast, the short M–N bond distances of around 2 Å indicate strong metal–nitrogen interaction with \( \text{DAD}^{2−} \) moiety. For example, these M–N distances in \([\text{Nb(NC}_6\text{H}_2\text{Cl}_3)\text{Cl}_3(\text{dad})] \), where the DAD ligand is a neutral \( \sigma− \)donor, are 2.301(2) and 2.460(2) Å. Therefore the reduced \( \text{DAD}^{2−} \) moiety has to be considered as an ene-diamido ligand.

The \( ^1\text{H} \)- and \( ^1\text{C} \)-NMR spectra of 1 and 2 exhibit sharp signals at 300 K and are temperature independent in the range of 180–400 K. The \( \text{CH} \) signals of the \( \text{DAD}^{2−} \) ligand are shifted to high field (singlets with \( \delta_H \sim 5.7 \) ppm and \( \delta_C \sim 102 \) ppm) compared to these signals in the ligand (\( \delta_H \sim 8.1 \) ppm and \( \delta_C \sim 158 \) ppm) and its donor–acceptor complex \([\text{M(NR)}\text{Cl}_3(\text{dad})] \) (\( \delta_H \sim 8.2 \) ppm and \( \delta_C \sim 155 \) ppm), where \( \text{M} = \text{Nb} \) and \( \text{Ta} \), \( \text{R} = ^1\text{Bu} \) and Dip [9]. This is the common trend for complexes with \( \text{R,} \text{H} – \text{DAD}^{2−} \) ligands, in which methine \( \text{CH} \) carbon and proton signals are found to be shifted to high field compared to free ligands [4, 6b, 6d, 7, 10a-e]. In the aliphatic region of the \( ^1\text{H} \)-NMR spectra three signals with intensities 9:18:9 were observed. These signals are assigned to imido, \( \text{DAD}^{2−} \) and amido \( ^1\text{Bu} \) groups. The \( \text{NH} \) signals appear as slightly broadened singlets at \( \sim 4 \) ppm in \( ^1\text{H} \)-NMR. Four \( ^1\text{Bu} \) groups exhibit three sets of signals.
in the $^{13}$C-NMR spectra of 1 and 2. These NMR data are consistent with a DAD$^{2-}$ unit in symmetrical surrounding.

In the EI mass spectra of 1 and 2 the peaks representing molecular ions were detected. In contrast to the spectra of the d$^0$ complexes with neutral DAD ligand of the type [M(NR)Cl$_3$(dad)] [9], where ions without the intact DAD moiety were observed, the abstraction of isobutylene from imido group and DAD$^{2-}$ unit was found to be the specific pathway of fragmentation in the case of 1 and 2. First of all, it means that DAD$^{2-}$ ligand is strongly bonded to the metal and the desired reductive abstraction of neutral DAD accompanied by the formation of reduced M(III) species does not take place. Actually, if this decomposition pathway is the most essential one in CVD experiments, then the presence of carbon in the TaN films can arise from the rest of the DAD$^{2-}$ ligand.

### Reactions of 1 and 2 with amines and hydrazines

Two aromatic amines, namely 2,6-di-isopropylaniline (DipNH$_2$) and pentafluoroaniline (C$_6$F$_5$NH$_2$) as well as 1,2-dimethylhydrazine (Me$_2$NNH$_2$) were used in order to check the reactivity of 1 and 2 in metathesis reactions with amines.

The reaction of 2 with DipNH$_2$ proceeds in several steps and was intensively investigated by $^1$H-NMR spectroscopy. The intermediate products can only be observed in an NMR monitoring experiment. The large-scale reaction in a Schlenk tube produces either the product of double substitution 3 and 4 or a mixture of starting material and product depending on the amount of DipNH$_2$ used.

The proposed intermediates and a suggested reaction mechanism are presented in the Scheme 1. The corresponding $^1$H-NMR spectra are displayed in Fig. 2. The first step of the reaction cannot be prevented even at 180 K and formation of IM$_1$ as well as $^1$BuNH$_2$ can be observed immediately. The next intra molecular acid–base reaction is rather slow and the reaction mixture should be slightly warmed in order to form the further products with the desirable reaction rate.
Scheme 1. Reaction of 2 with DipNH2.

Fig. 2. The $^1$H-NMR spectra of the NMR reaction of 2 with DipNH2 (1:2) at 350 K (500 MHz, $d^8$-toluene, only $CH$-DAD, $CH$-Dip and $NH$ signals are shown).

The thermodynamically most stable Ta containing products in the reaction of 2 with two equivalents of DipNH2 seem to be IM$_2$ and complex 4. Only these two compounds were
observed in the NMR spectra after several days standing at room temperature. The \(^{t}\)Bu amido ligand has a larger basicity compared to aryl amido thus explaining the absence of IM\(_1\) and 2.

Additionally, 4 rapidly reacts with large \(^{t}\)BuNH\(_2\) excess (10 eq.) in a NMR tube at room temperature to form IM\(_2\). After several days standing at room temperature the mixture consists of IM\(_2\) and 2 without traces of 4 or IM\(_1\). These observations again are in good agreement with the mechanism of the formation of 4, in which two intermediate amido imido complexes IM\(_1\) and IM\(_2\) take part.

The pure complexes 3 and 4 were obtained in approx. 45% yield as crystals suitable for X-ray analysis by the reaction of 1 and 2 with 2 equivalents of DipNH\(_2\) in hexane after 2 days standing at room temperature. The molecular structures of 3 and 4 are presented in Fig. 3 and Fig. 4.
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[Å] and angles [°]: Nb(1)–N(4) 1.999(4), Nb(1)–N(1) 1.996(4), Nb(1)–N(13) 1.793(4), Nb(1)–N(26) 2.012(2), Nb(1)–C(3) 2.487(2), Nb(1)–C(2) 2.482(2), Nb(1)–σ(DAD2–) 1.1310(2), N(4)–C(3) 1.387(2), N(1)–C(2) 1.386(2), C(2)–C(3) 1.372(2), N(26)–C(27) 1.420(2), N(13)–C(14) 1.387(2), Nb(1)–N(13)–C(14) 176.9(2), Nb(1)–N(26)–C(27) 141.5(1), N(13)–Nb(1)–N(26) 112.86(6), N(13)–Nb(1)–N(1) 115.00(6), N(13)–Nb(1)–N(4) 115.44(6), N(1)–Nb(1)–N(4) 87.22(6).

Fig. 4. The molecular structure of [(DAD)Ta(NDip)(NHDip)] 4 with thermal ellipsoids at 30% probability (non NH hydrogen atoms are omitted). Space group P 1, Z = 2. Selected bond length [Å] and angles [°]: Ta(1)–N(1) 1.979(2), Ta(1)–N(2) 1.983(2), Ta(1)–N(3) 1.992(2), Ta(1)–N(4) 1.796(2), Ta(1)–C(3) 2.494(2), Ta(1)–C(4) 2.493(2), Ta(1)–σ(DAD2–) 1.09102(9), N(1)–C(3) 1.398(2), N(2)–C(4) 1.388(3), C(3)–C(4) 1.375(3), N(3)–C(13) 1.429(3), N(4)–C(25) 1.392(2), Ta(1)–N(3)–C(13) 140.2(1), Ta(1)–N(4)–C(25) 176.1(1), N(4)–Ta(1)–N(1) 115.44(7), N(4)–Ta(1)–N(2) 115.55(7), N(4)–Ta(1)–N(3) 113.04(8), N(2)–Ta(1)–N(1) 87.72(6).

As expected, the molecular structures of niobium complex 3 and tantalum complex 4 exhibit large similarity. The metal centres are tetrahedrally coordinated by four nitrogen atoms. The imido groups exhibit short metal–nitrogen bonds of 1.793(4) Å in 3 and 1.796(2) Å in 4. Together with the nearly linear M–N–C angles of 176.9(2)° in 3 and 176.1(1)° in 4 a 6e− bonding mode for these imido groups is indicated [5]. The amido M–N bond length of 2.012(2) Å in 3 and 1.992(2) Å in 4 are considerably longer and the metal–nitrogen–carbon angles of ~140° are
smaller compared to those of imido ligands. This is consistent with the 4e\textsuperscript{−} donor situation for the DipNH\textsuperscript{−} ligands.

3 and 4 possess supine conformation in the crystal with respect to DAD\textsuperscript{2−} and the imido group. The parameters of DAD\textsuperscript{2−}M metallacycles in 3 and 4 are very similar to those found in [(DAD)Ta(N\textsuperscript{t}Bu)(NH\textsuperscript{t}Bu)]\textsubscript{2} discussed above.

![Chemical structure of 3 and 4](image)

**Fig. 5.** Two projections of 4 in crystal. All methyl groups and hydrogen atoms are omitted for clarity.

The aromatic rings of the Dip amido and imido ligands are twisted forming interplanar ring–ring angles of 65.63(9)\degree in 3 and 65.11(11)\degree in 4 (Fig. 5) so that the repulsion of \textsuperscript{1}Pr groups is minimised. Although there is no mirror plane containing atoms Nb(1)–N(13)–C(14)–N(26)–C(27)–DAD\textsuperscript{2−}_\text{centroid} in 3 or Ta(1)–N(4)–C(25)–N(3)–C(13)–DAD\textsuperscript{2−}_\text{centroid} in 4, the latter should exist in solution, because signals for the DAD\textsuperscript{2−} ligand in symmetrical surrounding were observed in \textsuperscript{1}H- and \textsuperscript{13}C-NMR in the temperature range of 180–400 K. This plane also leads to magnetic equivalence of the \textsuperscript{1}Pr groups in the amido moiety even in the low temperature limiting spectrum at 180 K.

Two sets of signals for Dip moieties with magnetically equivalent \textsuperscript{1}Pr groups within each set were observed in the NMR spectra of 3 and 4 at room temperature. These signals are assigned to the DipN\textsuperscript{2−} and DipNH\textsuperscript{−} ligands. Surprisingly, the coalescence of CH-\textsuperscript{1}Pr and CH\textsubscript{3}-\textsuperscript{1}Pr Dip signals for one of the two sets of Dip signals was observed in 4 at 190 K (Fig. 6). Two non-equivalent CH-\textsuperscript{1}Pr signals for a Dip group can arise from the freezing of rotation around the
nitrogen–carbon bond. In this case only the imido CH–iPr signal is expected to be split having different surroundings (Fig. 5), while the amido Dip group as well as the DAD\(^2^–\) ligand maintain their local symmetry discussed above. As a consequence two iPr groups of the imido ligand are non-equivalent and give two signals at low temperature in the DNMR spectra.

**Fig. 6.** The coalescence of the CH–iPr signal in 4 (500 MHz, d\(^8\)-toluene)

The assumption that the imido and not the amido Dip group defines the dynamics, is in good agreement with the observations made for the dimeric chloro complex \([(\text{DAD})\text{Ta}(\text{NDip})(\mu-\text{Cl})]_2\) [4]. This compound exhibits the same temperature dependence in the NMR spectra. Furthermore, the activation energy calculated from the coalescence point [13] for 4 (\(\Delta G^{188\text{K}} = 36 \pm 2\ kJ/mol\)) correlates with the \(\Delta G^{190\text{K}}\) value of 37 \(\pm\) 2 kJ/mol for \([(\text{DAD})\text{Ta}(\text{NDip})(\mu-\text{Cl})]_2\) (the absolute statistical deviation of 2 K for the temperature and relative error of 100% for the rate constant were taken to calculate the accuracy).
The reaction between [(DAD)M(N\textsuperscript{t}Bu)(NH\textsuperscript{t}Bu)], M = Nb (1) and Ta (2), and C\textsubscript{6}F\textsubscript{5}NH\textsubscript{2} proceeds rapidly at room temperature; the NMR signals of the starting complexes disappear immediately after adding 2 eq. C\textsubscript{6}F\textsubscript{5}NH\textsubscript{2}. Unfortunately, the result is a mixture of products containing the DAD\textsuperscript{2–} ligand, which cannot be identified on the basis of the \textsuperscript{1}H-, \textsuperscript{13}C- and \textsuperscript{19}F-NMR spectra. All efforts to isolate the products separately by recrystallisation failed. Surprisingly, the reaction of the dimeric chlorido complex [(DAD)Nb(N\textsuperscript{t}Bu)(\mu-Cl)]\textsubscript{2} [4] with lithium salt C\textsubscript{6}F\textsubscript{5}NHLi produced the same mixture as the metathesis reaction of 1 with C\textsubscript{6}F\textsubscript{5}NH\textsubscript{2}. The intermediate compounds might be more stable in the reaction of 1 and 2 with C\textsubscript{6}F\textsubscript{5}NH\textsubscript{2} than in the reaction with DipNH\textsubscript{2}. Indeed, the increase of the intermediates’ stability suggested performing the reaction at high temperatures or even subliming the resulting mixture after the amine metathesis reaction at room temperature. Amazingly, a simple sublimation produces very good results. In the case of tantalum complex 2 only one DAD\textsuperscript{2–} compound 7 was isolated after sublimation at 160\textdegree C/10\textsuperscript{-4} mbar, while two DAD\textsuperscript{2–} compounds 5 and 6 were observed in the NMR spectra for the reaction of niobium complex 1 with C\textsubscript{6}F\textsubscript{5}NH\textsubscript{2}. Complexes 5 and 6 can be separated by fractional crystallisation from hexane, because complex 5 is more soluble, possibly, due to the \textsuperscript{t}Bu imido group.

\begin{align*}
\textbf{1} & \quad \text{sublimation} \\
\text{C}_6\text{F}_5\text{NHLi} & \quad \text{B} \\
\textbf{2} \quad \text{A} & \quad 4 \text{C}_6\text{F}_5\text{NH}_2 \\
\textbf{5} & \quad \text{B} \\
\textbf{6} & \quad \text{B} \\
\text{5 : 6} = 2 : 1 & \\
\text{overall yield ca. 60\% (A)} & \\
\text{ca. 40\% (B)} & \\
\end{align*}

\begin{align*}
\textbf{2} & \quad \text{sublimation} \\
\text{C}_6\text{F}_5\text{NHLi} & \quad \text{sublimation} \\
\textbf{2} \quad \text{B} & \quad > 3 \text{C}_6\text{F}_5\text{NH}_2 \\
\textbf{7} (87\%) & \\
\end{align*}
The dinuclear nature of complexes 5-7 was confirmed by EI mass spectroscopy, where peaks representing molecular ions were detected, and by an X-ray analysis of 5 and 7. A single crystal suitable for X-ray analysis was obtained by cooling a concentrated hexane solution in the case of 5 and a concentrated toluene solution in the case of 7 to −30°C. The molecular structure of 5 is presented in Fig. 7.

![Fig. 7. The molecular structure of [(DAD)$_2$Nb$_2$(NAr$_F$)$_2$(N$^t$Bu)] 5 with thermal ellipsoids at 20% probability (hydrogen and fluoro atoms are omitted for clarity). Space group P 2$_1$, Z = 2. Selected bond length [Å] and angles [°]: Nb(1)–N(1) 1.99(1), Nb(1)–N(2) 2.00(1), Nb(1)–N(3) 1.76(1), Nb(1)–N(6) 2.29(1), Nb(1)–N(7) 2.40(2), Nb(1)–C(1) 2.56(2), Nb(1)–C(2) 2.53(3), Nb(1)–Nb(2) 3.131(1), Nb(2)–N(4) 1.986(9), Nb(2)–N(5) 2.013(9), Nb(2)–N(6) 1.89(1), Nb(2)–N(7) 1.84(2), N(1)–C(1) 1.51(3), N(2)–C(2) 1.42(3), C(1)–C(2) 1.35(4), N(4)–C(15) 1.45(2), N(5)–C(16) 1.40(1), C(15)–C(16) 1.36(2), Nb(2)–C(15) 2.50(1), Nb(2)–C(16) 2.47(1), Nb(1)–N(3)–C(11) 175(1), N(3)–Nb(1)–N(2) 110.1(4), N(3)–Nb(1)–N(1) 109.3(5), N(3)–Nb(1)–N(6) 113.9(4), N(3)–Nb(1)–N(7) 105.7(5), N(6)–Nb(2)–N(7) 95.7(6), N(6)–Nb(2)–N(4) 117.0(4), N(6)–Nb(2)–N(5) 117.5(4), Nb(2)–N(6)–Nb(1) 96.6(4), Nb(2)–N(7)–Nb(1) 94.4(7), Nb(2)–N(6)–C(25) 139(1), Nb(2)–N(7)–C(31) 147(1).

Surprisingly, two different (DAD$^{5−}$)Nb cores are found in the molecular structure 5, which are bonded by two asymmetrical C$_6$F$_5$ imido ligand bridges. The Nb(1) core contains a $^t$Bu imido ligand and is best considered as a tetragonal pyramid, in which atoms N(1), N(2), N(6) and N(7) atoms form the base plane and N(3) occupies the apex. The metal–to–base plane distance is 0.7238(8) Å. This core exhibits supine conformation with respect to the DAD$^{5−}$ and
1BuN$^{2-}$ groups and the typical bonding parameter for these ligands discussed above. The metal–nitrogen bond distances to the bridging nitrogen atoms are Nb(1)–N(6) 2.288(11) Å and Nb(1)–N(7) 2.395(16) Å. These long M–N bond lengths are in the range of the weak donor–acceptor interaction of the d$^0$ niobium with amines [14] and this value, for example, is 2.309(2) Å in the pyridine complex [(DAD)Nb(N$^t$Bu)Cl(py)] [4].

In the second core the central atom Nb(2) has a tetrahedral coordination sphere, where two positions are occupied by DAD$^{2-}$ ligand and two by C$_6$F$_5$ imido groups. Actually, the bonding situation between Nb(2) and the bridging imido ligands mediates between the amido and imido one. The value of 1.786(4) Å found in the similar dinuclear complex 7 (see below) can be used for comparison for pure imido C$_6$F$_5$N$^{2-}$ 6e$^-$ bonding mode and the value of ~ 2.0 Å is expected for amido situation. The Nb(2)–N(6) bond length of 1.89(1) Å and the Nb(2)–N(7) bond length of 1.84(2) Å lie between the imido and amido one, although the M–N–C angles of 139(1)$^\circ$ and 147(1)$^\circ$ are rather consistent with amido situation [5].

Unfortunately, in folded tetrahedral DAD$^{2-}$ complexes with two equal substituents the supine-prone nomenclature is not applicable. In order to simplify further speculation a new definition can be suggested for this case. For example, with respect to the group X$_1$ the complex [(DAD)M(X$_1$)(X$_2$)], X$_1$ = X$_2$, exhibit supine conformation and with respect to the X$_2$ prone. Thus, the group X$_1$ can be considered to be pro-supine and X$_2$ pro-prone.

![Diagram](image)

Applying this terminology to the molecular structure of 5 the imido group Nb(2)–N(7)–C(31) has a pro-supine conformation and Nb(2)–N(6)–C(25) has a pro-prone one.

Two described (DAD$^{2-}$)Nb cores are connected at a shared edge N(6)–N(7) in 5. The bridging M$_2$N$_2$ unit shows enormous asymmetry with two long donor–acceptor distances to the supine core with Nb(1) and two short imido/amido distances to the tetrahedral surrounded Nb(2). The diamagnetic nature of 5 forces both cores to be d$^0$ metal centres. Consequently, the [(DAD)Nb(2)(NC$_6$F$_5$)$_2$] unit should be formally negatively charged and two strong electron withdrawing C$_6$F$_5$ groups help to stabilise it. In contrast the electron donating 1Bu imido group stabilises the formally positively charged [(DAD)Nb(N$^t$Bu)] fragment. In an extreme mesomeric
description the molecule consists of two formally charged parts, [(DAD)Nb(N\text{Bu})]^+ and [(DAD)Nb(NC\text{F}_5)_2]_2^-, which form the dinuclear adduct 5.

The tetrahedral fragment [(DAD)Nb(NC\text{F}_5)_2]^- is isolobal to compounds of the type [(DAD)M(NR)_2], M = Cr, Mo, W [15]; and [Cp_2(R,R'-DAD)M], M = Ti, Zr, Hf) [16] (Fig. 8). For both types of complexes dynamic behaviour was observed in solution. The non-equivalence of imido or Cp groups, which derives from the folded conformation of the (DAD^2-)M moiety, disappears in the NMR spectra by warming. Theoretical studies show that this process is based on the MN_2C_2 ring inversion (‘flipping’ of the DAD^2- double bond), where planar metallacycle with DAD^2- ligand is the transition state [12]. Consequently two different sets of signals are expected for C_6F_5 rings in low temperature limiting ^{19}\text{F}-NMR spectra of 5.

Fig. 8. Isolobal analogy for 5-7.

Indeed, the room temperature ^{19}\text{F}-NMR spectrum of 5 consists of two sets of signals typical for C_6F_5 rings proposed from the molecular structure. Furthermore, 5 shows two different
sets of signals for DAD\(^{2-}\) units in symmetrical surroundings in the \(^1\)H- and \(^{13}\)C-NMR spectra at room temperature.

The latter signals exhibit some tendency to coalesce above 400 K. The \(^{19}\)F-NMR spectra also show some broadening at this temperature. This process is accompanied by the decomposition of 5 and the formation of 6, free DAD ligand and some other products, which makes any calculations of the thermodynamic parameters impossible. The decomposition of 5 remarkably stops when the ratio of 5:6 reaches about 2:1. The same ratio between these complexes was observed after sublimation.

The magnetic non-equivalence of the two bridging N–C\(_{6}F_{5}\) groups at 400 K shows that the inversion (‘flipping’) of the DAD\(^{2-}\) ligand in the tetrahedral core \([(\text{DAD})\text{Nb}(\text{NC}_{6}\text{F}_{5})_{2}]^{-}\) of 5 is associated with a high activation energy.

\[
\begin{align*}
\text{M} & = \text{Nb (6)} \\
\text{Ta (7)}
\end{align*}
\]

Surprisingly, complexes 6 and 7, in contrast to complex 5, exhibit only one set of signals for two DAD\(^{2-}\) ligands in \(^1\)H- and \(^{13}\)C-NMR spectra. Moreover, two different C\(_{6}F_{5}\) groups in proportion 2:1 are localised in the \(^{19}\)F-NMR spectra instead of three different groups with equal intensities expected from the comparison of the data for 5. The \(^1\)H-, \(^{13}\)C- and \(^{19}\)F-NMR spectra of 6 and 7 are temperature independent in the region 180–400 K. According to these data 6 and 7 might possess a different dinuclear structure than 5, e.g. with one or three bridging imido ligands. In order to gain insight into this possible bonding situation the molecular structure of 7 was resolved (Fig. 9) by single crystal X-ray analysis.
Fig. 9. The molecular structure of 7•C₆H₅CH₃ with thermal ellipsoids at 30% probability (hydrogen and fluorine atoms as well as a solvate molecule of toluene are omitted for clarity). Space group P 2₁/c, Z = 4. Selected bond length [Å] and angles [°]: Ta(1)–N(1) 1.968(4), Ta(1)–N(4) 1.985(4), Ta(1)–N(13) 1.905(4), Ta(1)–N(20) 1.876(4), Ta(1)–C(2) 2.456(5), Ta(1)–C(3) 2.457(5), N(1)–C(2) 1.402(7), N(4)–C(3) 1.395(7), C(2)–C(3) 1.378(8), Ta(2)–N(13) 2.226(4), Ta(2)–N(20) 2.357(4), Ta(2)–N(27) 1.787(4), Ta(2)–N(34) 2.009(4), Ta(2)–N(37) 1.997(4), Ta(2)–C(35) 2.498(5), Ta(2)–C(36) 2.514(5), N(34)–C(35) 1.370(7), N(37)–C(36) 1.386(7), C(35)–C(36) 1.380(7), Ta(1)–N(13)–N(14) 137.6(3), Ta(1)–N(20)–N(21) 144.7(3), Ta(1)–N(13)–Ta(2) 97.1(2), Ta(1)–N(20)–Ta(2) 93.6(2), N(1)–Ta(1)–N(4) 89.0(2), N(13)–Ta(1)–N(1) 118.0(2), N(20)–Ta(1)–N(4) 122.5(2), Ta(2)–N(27)–C(28) 174.7(4), N(27)–Ta(2)–N(13) 113.0(2), N(27)–Ta(2)–N(20) 104.2(2), N(27)–Ta(2)–N(34) 111.5(2), N(27)–Ta(2)–N(37) 106.6(2), N(34)–Ta(2)–N(37) 83.8(2).

Amazingly, the molecular structure of 7 is similar to that found for 5. The molecule again consists of two different units. The coordination sphere of Ta(1) is a distorted tetrahedron in the first core and the coordination polyhedron of Ta(2) is a tetragonal pyramid with the metal–to–base plane N(13)–N(20)–N(34)–N(37) distance of 0.6851(2) Å in the second core. Two polyhedra are connected at a shared edge N(13)–N(20). The unit with Ta(2) as the central atom exhibits a supine conformation with respect to the DAD²⁻ and C₆F₅N²⁻ groups. The imido Ta(2)–N(27) bond length is 1.787(4) Å and the imido Ta(2)–N(27)–C(28) angle is 174.7(4)° indicating the usual 6e⁻ bonding situation. Compared to this bond length the distances from Ta(2) to the
bridging nitrogen atoms $N(13)$ and $N(20)$ are considerably longer, 2.226(4) and 2.357(4) Å respectively. The same situation was observed in the molecular structure of 5. Furthermore, the bridging nitrogen atoms again exhibit an intermediate imido/amido bonding situation to the tantalum atom in the second core, the Ta–N distances being 1.905(4) and 1.876(4) Å and Ta–N–C angles 137.6(3)° and 144.7(3)°. Both DAD$^{2-}$ ligands exhibit standard structural parameters, which are characteristic for this type of ligands and discussed above.

According to the molecular structure of 7 two different sets of signals for two DAD$^{2-}$ ligands and three sets of signals for the $C_6F_5$ rings are expected. Although the NMR spectra in d$^8$-toluene do not show any temperature dependence in the range of 180–400 K, two different DAD$^{2-}$ ligands can be observed in $^1H$-NMR in CD$_2$Cl$_2$ at approx. 170 K. At this temperature the $C_6F_5$ groups also begin to coalesce and would possibly form three sets of signals at lower temperatures. Unfortunately, the observed dynamic picture is not complete and another process, for example the ‘freezing’ of rotation around $\sigma$–bonds, cannot be excluded.

In principle, an extremely rapid ‘flipping’ of the DAD$^{2-}$ double bond (I $\rightarrow$ II in Scheme 2) in the tetrahedral core of 6 and 7 would afford magnetic equivalence of the two imido $C_6F_5$ rings (rings A and B in Scheme 2). Actually, this process is less probable because it should have been observed for 5 as well, where similar imido groups are non-equivalent even at 400 K. Furthermore, the DAD$^{2-}$ ligands (D and E in Scheme 2) would stay non-equivalent after ‘flipping’. This disproves such a mechanism.

Rearrangement of electron density in the bridging $M_2N_2$ core can lead to the formation of two tetrahedral [(DAD)M(NC$_6$F$_5$)] units bridged by an imido ligand. It is obvious that such a rearrangement has a low energetic barrier. There are two possible isomers (III or IV), which can be thus formed. According to the crystal structures of 2-5, 7 and crystallographic investigations on other imido DAD$^{2-}$ complexes of niobium and tantalum [4, 17], these complexes prefer a supine conformation in the solid state. The same tendency can be expected in solution, because a ‘flipping’ dynamic process was not found to be characteristic for them and no formation of prone isomers was detected.
Thus, the formation of the *prone-supine* isomer IV seems to be less probable than the formation of the *supine-supine* isomer III. Additionally, the second rearrangement process will afford dinuclear molecule V, which has to exhibit the same NMR spectra as I. If this process is rapid on the NMR time scale then the DAD$^{2-}$ groups D and E will be equivalent. Furthermore, C$_6$F$_5$ rings B and C are also in exchange that has to afford their equivalence. In contrast to this, the bridging imido ring A exhibits a ‘pro-prone’ conformation in both molecules I and V and should produce a second set of signals in the $^{19}$F-NMR spectra, whereas rings C and D produce the first one. These speculations are in good agreement with the spectroscopic data observed for 6 and 7, although an explanation that 6 and 7 exist in solution in the static form III also seems to be acceptable.

There are two remarks to the question why this rearrangement does not take place in solution for 5. Firstly, electronegative C$_6$F$_5$ rings stabilise the negative charge and therefore molecule A should be considerably more stable than C (Scheme 3). Secondly, 5 may also exist in solution in form B, which would exhibit the same pattern of signals in NMR as form A. This assumption seems to be the most probable one. Indeed, the $^1$H-NMR spectra of 5 in form A should consist of two sets of the DAD$^2$ signals in asymmetrical surroundings, because there is
no mirror plane containing bridging nitrogen atoms and both metals. In contrast to this the room
temperature $^1$H- and $^{13}$C-NMR spectra of 5 consist of two different sets of signals for DAD$_2^-$
units in symmetrical surroundings. The latter is more consistent with form B (Scheme 3).

![Scheme 3](image1)

**Scheme 3.** Other possible isomers for 5 than crystallographically characterised A.

The chemical formation of the dinuclear species 5-7 can be rationalised in the way
presented in Scheme 4. The formed desired product of two metatheses reactions IV or the
product of a metathesis reaction III can react either with the starting material or with other
metathesis products to form dinuclear compounds and an amine. This condensation of molecules
seems to be irreversible not only under sublimation conditions but also in solution. For example,
complex [(DAD)$_2$Ta$_2$(NAr$_F$)$_3$] 7 does not react with C$_6$F$_5$NH$_2$ excess and formation of
mononuclear compounds was not observed.

![Scheme 4](image2)

**Scheme 4.** Formation of dinuclear compounds 5-7 in metathesis reaction.
It is interesting that 'Bu and Dip complexes 1-4 are monomeric and do not exhibit any tendency to condensation. The difference in their chemical activity compared to derivatives with C₆F₅ ring can be explained by a larger acidity and consequently proton mobility in the C₆F₅NH⁻ group compared to the DipNH⁻ or 'BuNH⁻, which induces further condensation of C₆F₅ derivatives.

The derivatives of asymmetrical 1,1-dimethylhydrazine have been discussed to be ideal single source precursors for CVD of metal nitride films, because the cleavage of the nitrogen–nitrogen bond leads to the formation of the stable Me₂N-radical in gas phase [18d]. There are only a few described hydrazido²⁻ compounds of niobium and tantalum [18].

Actually, Me₂NNH₂ is a reducing agent and hydrazido²⁻ ligand may reduce the metal centre. For example, in contrast to monooimido substances of the type [M(NR)Cl₂L₂] [19], M = Nb and Ta; R = alkyl, aryl and SiMe₃, L = THF, DME and Py; none of the corresponding monohydrazido²⁻ compounds are known for niobium and tantalum. The bis-isodiazene metalate complex was obtained by applying a similar procedure for the preparation of monooimido complexes to R₂NNH₂ [20].
The metal centre in complexes 1 and 2 is not as electron deficient as, for example, in TaCl5. Consequently, 1 and 2 are not prone to be easily reduced. Thus the metathesis with Me2NNH2 was thought to be a good preparative method for synthesis of the DAD2– derivative containing hydrazido2– moiety.

The reaction of 2 with Me2NNH2 proceeds very rapidly at room temperature and only dinuclear complex 8 was isolated independently on the amount of Me2NNH2 used. Complex 8 can be sublimed under mild conditions for purification but decomposes slowly in solution even at room temperature. Warming or excess of Me2NNH2 accelerates this decomposition.

A crystal suitable for X-ray analysis was obtained by cooling a concentrated hexane solution of 8 to –30°C. The molecular structure of 8 is presented in Fig. 10. This is the first structurally characterised example of a hydrazido2– complex of tantalum [14].

The dinuclear molecule consists of two [(DAD)Ta(NtBu)] units, which are bonded by a hydrazido2– (Me2NN2–) ligand. The nitrogen atoms N(1) and N(2) of the DAD2– ligand, the imido nitrogen N(3) and the two nitrogen atoms N(4) and N(5) of the η2–bonded hydrazido2– ligand form the polyhedron in the case of Ta(1). Four nitrogen atoms N(4), N(6), N(7) and N(8) form the tetrahedron of the second core. The cores show supine conformation with respect to the imido and DAD2– ligands. The imido structural parameters are typical for the 6e– bonding mode: short M–N distances Ta(1)–N(3) of 1.769(3) Å, Ta(2)–N(8) of 1.791(3), and nearly linear angles Ta(1)–N(3)–C(11) of 177.6(3)°, Ta(2)–N(8)–C(27) 173.3(3)°. The parameters of the DAD2–M
metallacycles in 8 are very similar to those found in other complexes discussed above, with the M–N bond lengths being 2.006(3), 2.025(3), 2.009(3) and 2.006(3) Å, the N–C bond lengths 1.396(5), 1.383(5), 1.393(6) and 1.390(6) Å and the C–C bond lengths 1.377(6) and 1.366(7) Å. The metal–to–ligand plane distances are found to be 1.0818(1) for Ta(1) and 1.1161(1) Å for Ta(2).

Fig. 10. The molecular structure of [(DAD)$_2$Ta$_2$(N$^t$Bu)$_2$(NNMe$_2$)] 8 with thermal ellipsoids at 30% probability (hydrogen and fluorine atoms as well as a solvate molecule of toluene are omitted for clarity). Space group P 2$_1$/n, Z = 4. Selected bond length [Å] and angles [°]: Ta(1)–N(1) 2.006(3), Ta(1)–N(2) 2.025(3), Ta(1)–N(3) 1.769(3), Ta(1)–N(4) 2.087(3), Ta(1)–N(5) 2.205(3), Ta(1)–C(1) 2.565(3), Ta(1)–C(2) 2.554(4), N(1)–C(1) 1.396(5), N(2)–C(2) 1.383(5), C(1)–C(2) 1.377(6), Ta(2)–N(4) 1.981(3), Ta(2)–N(6) 2.009(3), Ta(2)–N(7) 2.006(3), Ta(2)–N(8) 1.791(3), Ta(2)–C(17) 2.495(5), Ta(2)–C(18) 2.503(3), N(6)–C(17) 1.393(6), N(7)–C(18) 1.390(6), C(17)–C(18) 1.366(7), Ta(1)–N(3)–C(11) 177.6(3), N(2)–Ta(1)–N(1) 85.77(12), N(3)–Ta(1)–N(5) 103.1(1), Ta(1)–N(4)–Ta(2) 153.7(2), Ta(2)–N(8)–C(27) 173.3(3), N(8)–Ta(2)–N(4) 109.5(1), N(8)–Ta(2)–N(6) 115.1(1), N(8)–Ta(2)–N(7) 114.8(1).
An example with the bridging R$_2$NN$^{2-}$ ligand can be found in the half-sandwich chemistry of niobium [18a]. But the bonding situation in 8 differs from that in the complex [($\eta^5$-C$_5$H$_5$)Nb(NNMe$_2$)Cl$_2$]$_2$, where two ($\eta^5$-C$_5$H$_5$)NbCl$_2$(NNMe$_2$) cores are combined via a weak 2e$^-$ donor–acceptor interaction with a metal–nitrogen bond length of 2.28(1) Å. The analogous bond length Ta(2)–N(4) in 8 is 1.981(3) Å and has to be referred to the amido bonding parameter with strong π-interaction.

Furthermore, the bridging nitrogen atom is more strongly bonded with the second metal centre in [($\eta^5$-C$_5$H$_5$)Nb(NNMe$_2$)Cl$_2$]$_2$ with an M–N distance of 1.88(1) Å compared to 8, where this interaction is weakened (Ta(1)–N(4) 2.087(3) Å) but still indicates some π-character of the bonding. Additionally, the nitrogen–nitrogen bond N(4)–N(5) in 8 (1.458(4) Å) is significantly longer than in [($\eta^5$-C$_5$H$_5$)Nb(NNMe$_2$)Cl$_2$]$_2$ (1.39(2) Å) and is the longest one known up to date [14] for bridging or terminal Me$_2$NN$^{2-}$ ligand bonded to a transition metal. This reveals the decrease of the nitrogen–nitrogen–metal π-interaction, which is responsible for the shortening of the nitrogen–nitrogen bond in Me$_2$NN$^{2-}$ complexes with transition metals (1.21-1.41 Å) [14] compared to that in the free hydrazine Bz$_2$NNH$_2$ (approx. 1.45 Å) [21] and salt Me$_2$NH$^+$NH$_2$Cl$^-$ (1.455(2) and 1.443(2) Å) [22]. The second nitrogen atom of the Me$_2$NN$^{2-}$ ligand donates its free electron pair to one of the tantalum atoms (N(5)–Ta(1) 2.205(3) Å) and causes chemical non-equivalence of the two [(DAD)Ta(N'tBu)] fragments. Furthermore both DAD$^{2-}$ ligands are in asymmetrical surroundings: the first because of coordination of the NMe$_2$ group and the second because of a twisted form of the two metal cores.

The NMR spectra of 8 show temperature dependence, which is presented in Fig. 11 and Fig. 12 for $^1$H-NMR. An $^1$H-NMR spectrum at 180 K reflects the molecular structure determined by X-ray analysis.
Fig. 11. The $^1$H-DNMR spectra of 8 (500 MHz, $^d^8$-toluene, CH protons of DAD$^{2-}$ are shown).

Fig. 12. The $^1$H-DNMR spectra of 8 (500 MHz, $^d^8$-toluene, aliphatic range).

The DAD$^{2-}$ units in the asymmetrical surroundings give two sets of two poorly resolved doublets in CH-region at 180 K. In the aliphatic area two signals for the non-equivalent methyl groups of NNMe$_2$ and six different $^t$Bu signals are observed. The additional coordination of the second nitrogen atom of the hydrazido$^{2-}$ ligand to one of the two [(DAD)Ta(N$^t$Bu)] units causes
non-equivalence of the methyl groups in NMe₂. Thus, four 'Bu signals arise from the two asymmetrical and non-equivalent DAD²⁻ ligands and two from the non-equivalent imido groups.

According to the molecular structure of 8 the imido nitrogen of the Me₂NN²⁻ ligand has some π-character in the bonding with both tantalum centres. Two mesomeric forms (I) can describe this fact for 8. This chameleon behaviour of the ‘imido’ Me₂NN²⁻ nitrogen atom explains the low rotation barrier around the tantalum–nitrogen bond. The free rotation leads to the equivalence of the DAD²⁻ signals (CH and 'Bu protons) and methyl groups of the Me₂NN²⁻ moiety. According to that only 2 singlets are observed at room temperature in the CH-region, one singlet for the methyl groups of the hydrazido²⁻ ligand and four singlets with intensity 9:9:18:18 for 'Bu groups (two symmetrical non-equivalent [(DAD)Ta(N'Bu)] units).

Further warming of a sample causes a broadening of the signals, and the CH-protons as well as the 'Bu signals coalesce to give one set of signals for [(DAD)Ta(N'Bu)] moiety at 400 K. This can be explained by migration of the donor–acceptor bonded nitrogen atom of the hydrazido²⁻ ligand (II) between two tantalum cores.

Indeed, with an excess of Me₂NNH₂ the NMR experiment shows formation of another product, which seems to be a monomeric hydrazido¹⁻ complex [(DAD)Ta(N'Bu)(NHNMe₂)] according to the NMR data. Unfortunately, this complex is unstable at room temperature and decomposes forming free DAD ligand.
In principle, the experiments with Me$_2$NNH$_2$ show that its derivatives are thermally unstable. This prohibits the use of such complexes as precursors for CVD. On the other hand, Me$_2$NNH$_2$ can be taken as a second nitrogen source in deposition experiments and mixed with a potential precursor in the reactor. For example, complex [(DAD)Ta(N$_t$Bu)(NH$_t$Bu)] (2) does not show any decomposition in solution after warming at 130°C for two weeks. It seems to be reasonable to use 2 with Me$_2$NNH$_2$ in a dual source CVD process instead of isolating the unstable tantalum hydrazides.

**Reactions with ammonium salts**

The reaction of [(DAD)Ta(N$_t$Bu)(NH$_t$Bu)] (δ$_{CH}$ = 5.62 ppm in $^1$H-NMR) with 2 equivalents of DipNH$_3$Cl was carried out in a NMR tube. It proceeds very rapidly at room temperature and a new DAD$^{2-}$ compound with broad $CH$ signal at 6.03 ppm was observed in the proton spectrum. Furthermore, signals characteristic for DipNH$_2$ and $t$BuNH$_2$ (but not identical to the free amines!) were detected. This compound seems to be an amine mononuclear adduct of [(DAD)Ta(N$_t$Bu)(μ-Cl)]$_2$ [4] (δ$_{CH}$ = 6.07 ppm) with DipNH$_2$ or $t$BuNH$_2$.

After warming for 2h at 110°C the formation of a new product containing DAD$^{2-}$ ligand was detected. This product exhibits similar spectroscopic data to that observed in the NMR reaction of [(DAD)Ta(N$_t$Bu)(μ-Cl)]$_2$ with DipNH$_2$ or DipNH$_3$Cl, which is presumably the amine
adduct \([(\text{DAD})\text{Ta(NDip)Cl(DipNH}_2)]\) [17]. The latter mononuclear complex yields dimer \([(\text{DAD})\text{Ta(NDip)(µ-Cl)})_2]\) after sublimation.

In conclusion, the first step in the reaction of 2 with DipNH_3Cl might be the formation of the chlorido complex \([(\text{DAD})\text{Ta(N'tBu)(Cl)(RNH}_2)]\), \(R = \text{'Bu or Dip}\), where the ammonium salt DipNH_3Cl acts as a source of HCl. The second metathesis step is known from previous investigations on \([(\text{DAD})\text{Ta(N'tBu)(µ-Cl)})_2]\) [17], where the more electronegative aromatic DipN group was found to substitute the 'BuN group forming the complex with increased M–N bonding energy.

This example shows that the amido group in imido amido DAD^{2−} complexes can be cleanly cleaved using soft HCl source without any decomposition of the bonding between the metal centre and the DAD^{2−} ligand.

**Reactions with other organic acids**

The basicity of the amido group in \([(\text{DAD})\text{M(N'tBu)(NH'tBu)}]\), \(M = \text{Nb (1) and Ta (2)}\), was used in protolysis reactions with other organic compounds containing acidic protons. Commonly, the metathesis reactions of the amido ligand with organic acids produce very good yields and proceed cleaner than the same reactions of the chlorido complexes.
[(DAD)M(N^tBu)(μ-Cl)]_2 or [(DAD)M(N^tBu)(Cl)(py)] with conjugated salts as nucleophiles [4].

In all these protolysis reactions the metal ene-diamido moiety (DAD^2-)M is resistant to substitution. The reaction of 1 and 2 with one equivalent of ^tBuOH and acacH yields previously described tert-butoxy and acetylacetonato imido derivatives [4].

\[
\begin{align*}
\text{N} & \text{N} \\
\text{M} & \text{N} & \text{N} \\
\text{H} & \text{N} & \text{O} \\
\text{O} & \text{O} & \text{H} \\
\end{align*}
\]

\(\text{M} = \text{Nb (57%)}\)  
\(\text{Ta (93%)}\)

\[
\begin{align*}
\text{N} & \text{N} \\
\text{N} & \text{N} & \text{M} & \text{N} \\
\text{H} & \text{N} & \text{H} & \text{N} & \text{O} & \text{O} \\
\text{acacH} & \text{Li} & \text{Li} & \text{Li} & \text{Li} \\
\text{M} = \text{Nb (49%) (9)} \quad \text{Ta (70%) (10)}
\end{align*}
\]

**Reaction with lithium alkyls**

Complexes [(DAD)M(N^tBu)(NH^tBu)], \(M = \text{Nb (1) and Ta (2)}\), react with strong bases such as n-BuLi or MeLi to form the deprotonation products 9 and 10. Compounds 9 and 10 are extremely sensitive and their slightly yellow solutions become red after standing under Argon in Schlenk tubes for several days. Indeed, the pure pale yellow 9 and 10 can be obtained only by reaction with MeLi at \(-80^\circ\text{C}\) or after sublimation; otherwise the solution is always coloured slightly red.
The presence of lithium in 9 and 10 was confirmed by the \(^7\)Li-NMR spectroscopy, showing a signal at 3.1 ppm. The \(^1\)H-NMR spectra of 9 and 10 are temperature dependent. This dynamic behaviour is discussed below in DNMR studies in detail. A crystal of 10 suitable for X-ray analysis was obtained by cooling a concentrated hexane solution to –30°C in a Glove Box. The molecular structure of 10 is presented in Fig. 13a-c.

This structure is a rare example of a lithium bisimido complex of a transition metal without any donating solvent molecule coordinated to the lithium [14]. The structurally characterised dimer [{Nb(N\textit{t}Bu)\textsubscript{3}(NH\textit{t}Bu)\textsubscript{2}}Li\textsubscript{2}]\textsubscript{2} [23a] and two other known bisimido lithium complexes of group V elements [Nb(NMes)\textsubscript{3}(\textit{n}Bu){Li(THF)\textsubscript{2}}\textsubscript{2}] [23b] and [{(\textit{η}\textsubscript{5}-C\textsubscript{5}Me\textsubscript{5})Ta(NDip)\textsubscript{2}}{Li(OEt\textsubscript{2})\textsubscript{2}}] [23c] can be taken for structural comparison. The coordination sphere of the tantalum atoms is tetrahedral similar to the corresponding protonated form 2. The molecule consists of two [(DAD)Ta(N\textit{t}Bu)\textsubscript{2}Li] units, which are bonded by additional coordination of each lithium atom to an imido group from the another unit. The latter form asymmetrical bridging units, in which nitrogen imido atoms N(8) and N(4) are coordinated to only one lithium and N(7) and N(3) to both lithium atoms. The lithium atoms lie within their own [(DAD)Ta(N\textit{t}Bu)\textsubscript{2}Li] core somewhat out of the metal–bisimido plane (Fig. 13c).

Furthermore, Li(1) exhibits two short contacts with nitrogen atoms N(7) and N(4) of 1.97(2) and 2.03(2) Å, and one long contact of 2.35(2) Å with N(3). An additional ‘agostic’ interaction with carbon atom C(32) of 2.46(2) Å is also observed. A small elongation of the short contacts can be seen on Li(2), Li(2)–N(3) 2.00(1) Å and Li(2)–N(8) 2.07(1) Å, which is compensated by a shortening of the long contacts to N(7) 2.23(1) Å and to C(12) 2.40(2) Å. Comparable ‘agostic’ lithium–carbon contacts of 2.50(2) and 2.66(2) Å were also discussed for [{Nb(N\textit{t}Bu)\textsubscript{3}(NH\textit{t}Bu)\textsubscript{2}}Li\textsubscript{2}] [23a]. The short lithium–lithium distance of 2.20(2) Å in 10 is also found in other dimeric organic lithium amides [14] and in [W(N\textit{t}Bu)\textsubscript{4}Li\textsubscript{2}] [23d].
Fig. 13a. The molecular structure of **10**•C₆H₁₄ with thermal ellipsoids at 30% probability (hydrogen atoms and a solvate molecule of hexane are omitted for clarity). Space group P 2₁/c, Z = 4. Selected bond length [Å] and angles [°]: Ta(1)–N(1) 1.999(5), Ta(1)–N(2) 2.026(5), Ta(1)–N(3) 1.893(5), Ta(1)–N(4) 1.819(5), Ta(1)–C(2) 2.510(6), Ta(1)–C(1) 2.523(7), Ta(2)–N(5) 2.006(5), Ta(2)–N(6) 2.014(5), Ta(2)–N(7) 1.917(6), Ta(2)–N(8) 1.816(5), Ta(2)–C(19) 2.551(7), Ta(2)–C(20) 2.540(8), N(1)–C(1) 1.419(8), C(2)–C(2) 1.372(9), C(1)–C(2) 1.36(1), N(5)–C(19) 1.406(8), N(6)–C(20) 1.385(9), C(19)–C(20) 1.38(1), N(7)–Li(1) 1.97(2), N(3)–Li(1) 2.35(2), N(4)–Li(1) 2.03(2), C(32)–Li(1) 2.46(2), N(8)–Li(2) 2.07(1), C(32)–Li(1) 2.46(2), N(8)–Li(2) 2.07(1), N(3)–Li(2) 2.00(1), N(7)–Li(2) 2.23(1), C(12)–Li(2) 2.40(2), Ta(1)–N(3)–C(11) 137.0(4), Ta(1)–N(4)–C(15) 153.8(5), Ta(2)–N(7)–C(29) 135.5(4), Ta(2)–N(8)–C(33) 157.0(4), N(2)–Ta(1)–N(1) 87.7(2), N(2)–Ta(1)–N(3) 119.7(2), N(2)–Ta(1)–N(4) 119.1(2), N(3)–Ta(1)–N(4) 102.4(2), N(5)–Ta(2)–N(6) 87.0(2), N(8)–Ta(2)–N(5) 114.3(2), N(7)–Ta(2)–N(6) 118.6(2), N(8)–Ta(2)–N(7) 101.7(2).

Fig. 13b. The conformation of the (DAD²)Ta cores in **10** (the tBu groups and lithium atoms are omitted for clarity).
Two (DAD\textsuperscript{2−})Ta cores are twisted in the dimer (Fig. 13b) so that \(^1\)Bu groups of the one DAD\textsuperscript{2−} moiety are under the influence of the coordination of the double bond in the second [(DAD)Ta(\(^1\)Bu)\textsubscript{2}]\textsuperscript{−} unit. The nitrogen atoms N(8) and N(4), which are coordinated to only one lithium atom, exhibit ‘pro-supine’ conformation with respect to the DAD\textsuperscript{2−} ligand (Fig. 13c).

The increase of the Ta–N bond lengths in 10 (Ta(1)–N(3) 1.893(5) Å, Ta(1)–N(4) 1.819(5) Å, Ta(2)–N(8) 1.816(5) Å, Ta(2)–N(7) 1.917(6) Å) in comparison with the imido bond length in 2 (1.761(7) Å) indicates some weakening of the \(\pi\)–interaction between the metal centre and both imido nitrogen atoms. Additionally, the bond with nitrogen atoms N(3) and N(7), which are coordinated to two lithium atoms, are considerably longer (approx. 0.1 Å) than the analogous bond with N(4) and N(8), which are coordinated only to one lithium atom. This is accompanied by a decrease in the imido metal–nitrogen–carbon angles from 176.9(6)° in 2 to Ta(1)–N(4)–C(15) 153.8(5)° and Ta(2)–N(8)–C(33) 157.0(4)° for the imido moieties with monocoordinated nitrogen atoms and to Ta(1)–N(3)–C(11) 137.0(4)° and Ta(2)–N(7)–C(29) 135.5(4)° for the imido moieties with twice coordinated nitrogen atoms in 10. The latter angles are even smaller than this parameter of 142.9(6)° in the amido group in 2 showing a large extent of deviation from the linear \(sp\)–hybridisation of N(3) and N(7). In contrast to this tendency of the angles to bend, the metal–nitrogen distances are still considerably shorter than the amido one in 2 (1.992(7) Å) supposing that the interaction is still stronger than in an amido situation. In conclusion, each tetrahedral core contains two slightly different intermediate imido/amido ligands: two of them, namely Ta(1)–N(4)–C(15) and Ta(2)–N(8)–C(33), are coordinated to one lithium atom and are likely to have more imido character. The other two ligands, namely Ta(1)–N(3)–C(11) and Ta(2)–N(7)–C(29) 135.5(4)°, are coordinated to both lithium atoms,
demonstrating an elongation of the M–N bonds and a bending of M–N–C angles compared to the former ligands, which correlates with a more amido character of bonding.

The ionic description [23] for the bonding situation in [(DAD)M(NR)\(_2\) Li\(^+\)] core applied to the molecular structure of 10 explains the formation of the dimer. Indeed, the lithium cation bonded to the [(DAD)Ta(N\(^{\text{t}Bu}\)\(_2\))]\(^-\) core is an extremely strong Lewis acid, which coordinates to the nitrogen–metal bond of the second core and makes additional interaction with a carbon atom of the \(^{\text{t}Bu}\) imido group.

Nevertheless, the nitrogen lithium bond is partially covalent in 9 and 10 explaining that they can be sublimed under mild conditions. Surprisingly, complexes 9 and 10 do not show pronounced nucleophilic properties and do not react with Me\(_3\)SiCl. Furthermore, they are even Lewis acids building stable 1:2 adducts with THF, which were characterised by NMR spectroscopy. The latter complexes seem to have monomeric structures showing that a coordinative solvent can destroy the dimeric nature of 9 and 10.

The reaction of 9 and 10 with free DAD ligand leads to the formation of deep red mononuclear complexes 11 and 12 in good yield. Compounds 11 and 12 are poorly soluble in hexane and better in Et\(_2\)O and cannot be sublimed in vacuum.
The lithium signal appears at ~2.2 ppm in the $^7$Li-NMR spectra of 11 and 12, which is shifted to high field compared to that of dimeric complexes 9 and 10. The $^1$H-NMR spectra of 11 and 12 exhibit similar temperature dependence as dimeric complexes 9 and 10. This dynamic behaviour is discussed in detail below in the DNMR studies.

A crystal of 11 suitable for X-ray analysis was obtained by cooling a concentrated Et$_2$O solution to –30°C. The molecular structure of 11 is presented in Fig. 14. The NbN$_4$ coordination sphere is tetrahedral. The lithium atom also has tetrahedral surroundings and is coordinated by two imido nitrogen atoms and two nitrogen atoms from the non-reduced DAD ligand (for clarity the donor–acceptor bonded non-reduced DAD ligand is written with small characters in formulas, e.g. dad). The molecule possesses a symmetry plane containing atoms Nb(1), N(1), N(2) and Li(1), which makes corresponding $\delta_{\text{CH}}$ signals of DAD and DAD$^{2-}$ ligands equivalent. The folded (DAD$^{2-}$)Nb metallacycle indices magnetic non-equivalence of the two bridging imido groups: Nb(1)–N(1)–C(1) exhibits ‘pro-supine’ and Nb(1)–N(1)–C(1) ‘pro-prone’ conformation.

The imido nitrogen–lithium bond lengths are 2.027(6) Å and 2.147(6) Å, N(2)–Li(1) and N(1)–Li(1), respectively. The imido group with the shorter N–Li contact, exhibits a more bent character: Nb(1)–N(2)–C(4) 147.3(2)$^\circ$ and Nb(1)–N(1)–C(1) 157.0(2)$^\circ$, while the metal–nitrogen bonds Nb(1)–N(1) and Nb(1)–N(2) still have the same lengths in regard to 3$\sigma$, 1.845(3) Å and 1.854(3) Å, which are in accord with a character between an imido and amido situation.

![Fig. 14. The molecular structure of 11 with thermal ellipsoids at 30% probability (hydrogen atoms are omitted for clarity). Space group P n m a, Z = 4. Selected bond length [Å] and angles [°]: Nb(1)–N(1) 1.845(3), Nb(1)–N(2) 1.854(3), Nb(1)–N(3) 2.056(2), Nb(1)–C(7) 2.506(2),](image-url)
N(3)–C(7) 1.386(3), C(7_8)–C(7) 1.372(3), Li(1)–N(1) 2.147(6), Li(1)–N(2) 2.027(6), Li(1)–N(4) 2.136(5), N(4)–C(12) 1.260(3), C(12)–C(12_8) 1.473(4), Nb(1)–N(1)–C(1) 157.0(2), Nb(1)–N(2)–C(4) 147.3(2), N(1)–Nb(1)–N(3) 119.10(8), N(2)–Nb(1)–N(3_8) 115.50(8), N(3_8)–Nb(1)–N(3) 86.61(8), N(1)–Li(1)–N(4_8) 123.3(2), N(2)–Li(1)–N(4_8) 124.1(2), N(4)–Li(1)–N(4_8) 80.4(2).

**Table 2.** Comparison of bond lengths [Å] in different DAD complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Li – N</th>
<th>N – C</th>
<th>C – C</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Bu-DAD [24]</td>
<td>—</td>
<td>1.264 – 1.267</td>
<td>1.468 (2)</td>
</tr>
<tr>
<td>[(DAD(^-))Li(dad)] [25]</td>
<td>1.992(7)</td>
<td>1.318(6)</td>
<td>1.399(6)</td>
</tr>
<tr>
<td></td>
<td>1.997(7)</td>
<td>1.316(5)</td>
<td></td>
</tr>
<tr>
<td>[(DAD(^-))Li(dad)] [25]</td>
<td>2.134(7)</td>
<td>1.248(5)</td>
<td>1.488(6)</td>
</tr>
<tr>
<td></td>
<td>2.148(7)</td>
<td>1.235(6)</td>
<td></td>
</tr>
<tr>
<td>dad in 11</td>
<td>2.136(5)</td>
<td>1.260(3)</td>
<td>1.473(4)</td>
</tr>
<tr>
<td>DAD(^2-) in 11</td>
<td>—</td>
<td>1.386(3)</td>
<td>1.372(3)</td>
</tr>
</tbody>
</table>

Four nitrogen atoms (two from imido and two from DAD ligands) form a tetrahedron around the lithium atom. The above mentioned symmetry plane forces the lithium–nitrogen bonds with the non-reduced DAD ligand Li(1)–N(4) and Li(1)–N(4_8) to be identical 2.136(5) Å. Similar values of 2.148(7) Å and 2.134(7) Å have been observed for the non-reduced DAD ligand in [(DAD\(^-\))Li\(^+\)(dad)] [25]. Furthermore, the bond lengths for the DAD backbone do not show large deviation from the free DAD ligand [24] (Table 2), while the DAD\(^-\) moiety in [(DAD\(^-\))Li\(^+\)(dad)] and DAD\(^2-\) in 11 exhibit a shortening of the carbon–carbon and an elongation of the carbon–nitrogen bonds caused by population of the \(\pi^*\)–orbital with an electron. In conclusion, the molecular structure of 11 can be described to consist of a tetrahedral anion [(DAD\(^2-\))Nb(N\(^t\)Bu\(_2\))] to which a [Li(dad)]\(^+\) cation is coordinated.

A by-product of the above mentioned reactions of [(DAD)M(N\(^t\)Bu)(NH\(^t\)Bu)], M = Nb (1) and Ta (2), with MeLi and n-BuLi, which are not only strong bases but also strong nucleophiles, can be free DAD ligand. As it was shown, the latter forms stable adducts of the type [(DAD)M(N\(^t\)Bu\(_2\))Li(dad)], M = Nb (11) and Ta (12), with the desired products [(DAD)M(N\(^t\)Bu\(_2\))Li\(_2\)], M = Nb (9) and Ta (10). This explains why the reaction mixture of 1 and 2 with RLi is always coloured slightly red and sublimation is necessary for the purification of the products.
DNMR studies on complexes 9–12

Although complexes 9-10 and 11-12 exhibit 3 signals for $^{1}$Bu-groups in the $^{1}$H-NMR spectra at room temperature, their assignment and temperature dependence is somewhat different. Because the spectra for 11 and 12 are easier to understand they will be discussed first.

The temperature dependent NMR spectra of 11 and 12 are presented in Fig. 15 and Fig. 16 for 11. The four signals for $^{1}$Bu groups at 220 K have relative intensities of 18:9:18:9.

**Fig. 15.** The $^{1}$H-DNMR spectra of 11 (500 MHz, d$_{8}$-toluene, aliphatic range).
Fig. 16. The $^1$H-DNMR spectra of 11 (500 MHz, d$_8$-toluene, the $\delta_{CH}$ signal of non-reduced DAD ligand).

One of the signals (1) with an intensity of 18 as well as the CH-protons (not shown in the figures) of the DAD$_2^-$ moiety do not show any temperature dependence. They have to be assigned to the DAD$_2^-$ ligand in a symmetrical surrounding. This equivalence was also observed in the crystal structure of 11, where the mirror plane divides the molecule in such a way that two parts of both ligands (DAD$_2^-$ and non-reduced DAD) are geometrically equivalent. Two signals (2) with an intensity of 9 coalesce at approx. 295 K and give one singlet with an intensity of 18 at 350 K. They are assigned to two bridging imido groups. Their non-equivalence at low temperatures correlates with the molecular structure of 11 (Fig. 14). The nature of the non-equivalence arises from the folded conformation of the DAD$_2^-$M metallaclycle. At high temperatures both imido groups are magnetically equivalent. The same process was observed in complexes [(DAD)M(NR)$_2$], M = Cr, Mo, W; R = tBu, Mes [15]. Taking into account, that the unit [(DAD)M(N$^t$Bu)$_2$], M = Nb and Ta, in 11 and 12 is isoelectronic to [(DAD)M(NR)$_2$], M = Cr, Mo and W, the similarity of behaviour is quite understandable. The dynamic process in [(DAD)M(NR)$_2$] was referred to the inversion of the DAD$_2^-$ ligand (‘flipping’ process).
The last sharp signal (3) at 220 K with an intensity of 18 broadens with an increase in temperature (Fig. 15). The same tendency was observed for the CH protons (4) of the non-reduced DAD ligand coordinated to the lithium atom (Fig. 16). A cross-experiment with excess of DAD added to a sample of 12 (Fig. 17) reveals that non-reduced DAD ligand from 12 is in exchange with the molecules in solution at high temperatures.

**Fig. 17.** The $^1$H-NMR spectra of 12 and a mixture of 12 with DAD (~ 5 eq.) at 220 and 300 K (500 MHz, d$_8$-toluene).
This exchange based on the dissociation of 12 is prevented at low temperatures and signals for the dad ligand in 12 and free DAD in solution can be localised independently in the NMR spectra at 220 K.

For 9 and 10 at low temperatures four proton signals of equal intensities were observed in the aliphatic area of the $^1$H-NMR spectra (Fig. 18). The $CH$ signal of the DAD$^{2-}$ group has the typical form of AA’ spin systems and indicates the presence of two magnetically equivalent DAD$^{2-}$ ligands in asymmetrical surroundings. It is consistent with two magnetically equivalent [(DAD)M(N’Bu)$_2$Li] cores in the dimer. Thus two $^1$Bu signals come from the asymmetrical DAD$^{2-}$ moiety. The twisted conformation of the two [(DAD)M(N’Bu)$_2$]$^{-}$ units (see the molecular structure of 10, Fig. 13a-c) puts the $^1$Bu groups of the DAD$^{2-}$ ligand into an asymmetric environment (Fig. 13b). The different steric surroundings of the $^1$Bu groups of the DAD$^{2-}$ ligands causes their magnetic non-equivalence with respect to both cores. The other two signals arise from the non-equivalent $^1$Bu-imido groups because of the above mentioned folded conformation of the (DAD$^{2-}$)M unit.
When warming up, both pairs of the tBu signals coalesce and two singlets are observed above room temperature, while methine CH–DAD$^{2-}$ protons appear as a singlet. The coalescence of the imido signals can be explained by ‘flipping’ of the DAD$^{2-}$ bond in the [(DAD)M(N'tBu)$_2$]$^-$ unit, which is also observed in 11 and 12. The question arises by which mechanism may tBu groups of a DAD$^{2-}$ ligand become equivalent.

Three possible mechanisms are presented in Fig. 19 and Fig. 20. The simplest one is a dissociation of the dimer in solution (Fig. 19, A). The mononuclear species should exhibit similar NMR spectra as 11 and 12 with signals for the DAD$^{2-}$ ligand in symmetrical surroundings. This is in good agreement with the physical properties of 9 and 10, which can be sublimed under mild conditions in vacuum. Furthermore, complexes 11 and 12 dissociate in solution with elaboration of the non-reduced DAD ligand, which is an additional indication for the dissociation mechanism.

Furthermore, pseudo-rotation B could lead to the same observations (Fig. 19). If one core rotates rapidly with respect to the other one the tBu groups of the DAD$^{2-}$ ligands will not ‘feel’ the imido groups and therefore coordination of the DAD$^{2-}$ double bond in the second core. This mechanism is less probable because a very bulky moiety has to be moved.
Fig. 19. Possible dynamic mechanisms in 9 and 10.

Fig. 20. Concerted mechanism of dynamic rearrangement in 9 and 10. The construction of I is taken from Fig. 13b. Lithium atoms and t-Bu groups are omitted for clarity.

The last mechanism is presented in Fig. 20. This demonstrates that ‘flipping’ of the double bond can afford magnetic equivalence of the DAD$^{2-}$t-Bu groups. Their non-equivalence is
based on the influence of the non-equivalent imido ligands from the other core. The ‘flipping’ in the DAD\(^2\)\(^-\) ligand destroys this non-equivalence as it was demonstrated for 11 and 12. There are four possible isomers (I–IV), which can be imagined in solution after such ‘flipping’. Two of them are identical by pairs. Furthermore, one can expect that isomers I and II will possess the same spectroscopic properties, because two [(DAD)M(N\(^t\)Bu)\(_2\)Li] units in dimer [(DAD)M(N\(^t\)Bu)\(_2\)Li]\(_2\) are magnetically equivalent within I even at 180 K. Additionally, I and II are mirror isomers.

In order to define which of these mechanisms could be assigned to this system the thermodynamic activation parameters were calculated. To estimate the parameters for the barriers in 9-12 Band-Shape Analysis [13] and the Win-Dyna 32 program [26] were applied. The values of the rate constants \(k\) were obtained from the \(^1\)H-NMR spectra at different temperatures (\(T\)). This dependence, \(k\) versus \(T\), was fitted to the standard Eyring equation [13] to determine the thermodynamic parameters of activation entropy \(\Delta S^\neq\) and enthalpy \(\Delta H^\neq\):

\[
k = \frac{\sigma k_B T}{h} e^{-\frac{\Delta H^\neq - T\Delta S^\neq}{RT}}
\]

where \(k_B\) is Boltzmann’s constant, \(T\) is absolute temperature, \(h\) is Planck’s constant and \(R\) is the universal gas constant. The transmission coefficient \(\sigma\) was taken equal to one for this type of barrier. The logarithmic form [27] allows calculating \(\Delta H^\neq\) and \(\Delta S^\neq\) values from the experimental data set of the rate constants (\(k\)) depending on the temperature (\(T\)) by linear fit.

\[
\log(k / T) = 10.32 - \frac{\Delta H^\neq}{19.13} \left(\frac{1}{T}\right) + \frac{\Delta S^\neq}{19.13}
\]

For linear fitting the PFIT45W program was applied [28]. A temperature uncertainty of 0.5 K and a relative uncertainty of 20% in the rate constants were taken to estimate the error of the fitted parameters. For simulations the \(^t\)Bu imido signals were taken in the case of 11 and 12. For 9 and 10 the \(^t\)Bu signals of imido groups and DAD\(^2\)\(^-\) ligand were independently subjected to the simulation procedure. Surprisingly, the simulation of the NMR data for 10 was also successful using a combined imido–DAD\(^2\)\(^-\) set of signals, while this attempt for 9 failed. In the latter case the equivalence in the DAD\(^2\)\(^-\) unit seems to be reached earlier with temperature.
increase than the ‘flipping’ of the double bond. Thus only one set of activation parameters was obtained for 10 and two independent sets for 9. The calculated values of activation entropy $\Delta S^\ddagger$ and enthalpy $\Delta H^\ddagger$ are listed in Table 1 and the experimental data are shown in Fig. 21.

The activation parameters for complexes 11 and 12 are in good agreement with the ‘flipping’ (inversion) mechanism in the DAD$^2$ − moiety. For this mechanism a positive enthalpy $\Delta H^\ddagger$ and a value close to zero for $\Delta S^\ddagger$ are expected [12, 15].

The shape of all $\text{tBu}$ signals (DAD$^2$ − and imido) in the $^1$H-NMR spectra of 10 can be simulated with one rate constant at each temperature. This means that only one energetic barrier is present, which correlates with the ‘concerted’ mechanism initiated by the ‘flipping’ of the DAD$^2$ − double bond. In the case of 9 the activation enthalpy and entropy values for imido and DAD$^2$ − $\text{tBu}$ groups are somewhat different, but lie within the error range. Actually this difference is so small that a ‘concerted’ mechanism can be still considered.

Fig. 21. The Eyring equation plot for complexes 9-12.
Table 3. Activation entropy ($\Delta S^*$) and enthalpy ($\Delta H^*$) values calculated from the DNMR experiments for 9-12.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta G_{298}^*$, kJ·mol$^{-1}$ [29]</th>
<th>$\Delta H^*$, kJ·mol$^{-1}$</th>
<th>$\Delta S^*$, J·mol$^{-1}$·K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 (imido)</td>
<td>61 ± 6</td>
<td>65 ± 3</td>
<td>12 ± 11</td>
</tr>
<tr>
<td>9 (DAD$^2$)</td>
<td>59 ± 7</td>
<td>61 ± 4</td>
<td>7 ± 12</td>
</tr>
<tr>
<td>10 (DAD$^2$ + imido)</td>
<td>56 ± 4</td>
<td>54 ± 2</td>
<td>-4 ± 6</td>
</tr>
<tr>
<td>11</td>
<td>58 ± 4</td>
<td>55 ± 2</td>
<td>-12 ± 7</td>
</tr>
<tr>
<td>12</td>
<td>51 ± 4</td>
<td>49 ± 2</td>
<td>-8 ± 7</td>
</tr>
</tbody>
</table>

Furthermore, all calculated thermodynamic parameters for 9-12 are very close to each other so that the barriers might have a similar origin. The $\Delta S^*$ values for the barrier in 9-12 are close to zero, which is in accordance with a non-dissociative mechanism of dynamic rearrangement.

Conclusions

The synthesis of novel highly volatile imido amido diazadiene DAD$^2$– complexes [(DAD)M(N$^t$Bu)(NH$^t$Bu), M = Nb (1) and Ta (2)], was optimised for large-scale preparation in order to test them as precursors in CVD (Chemical Vapour Deposition) of metal(III) nitride films. Metathesis reactions of 1 and 2 proceed cleanly with organic molecules, which possess acidic protons, such as $^t$BuOH and acacH, to produce previously described DAD$^2$– imido complexes [17]. The reaction with primary amines produces different products depending on the nature of the substituents. In reaction with bulky DipNH$_2$ the monomeric products [(DAD)M(NDip)(NHDip)], M = Nb (3) and Ta (4), were isolated, while only dinuclear species [(DAD)$_2$M$_2$(NC$_6$F$_5$)$_3$], M = Nb (6) and Ta (7), and [(DAD)$_2$Nb(N$^t$Bu)(NC$_6$F$_5$)$_2$] (5) were obtained by reaction with C$_6$F$_5$NH$_2$. This difference in the chemical activity can be explained by the larger acidity of the C$_6$F$_5$NH$^-$ group in comparison with DipNH$^-$; This is assisted by steric hindrance of the Dip residue, which decreases the activity of the hydrogen atom of the amido group and consequently prevents further condensation. The reaction of 2 with Me$_2$NNH$_2$ leads to the formation of the first structurally characterised hydrazido$^2$– complex of tantalum [(DAD)$_2$Ta$_2$(N$^t$Bu)$_2$(NNMe$_2$)] (8), which is unstable and slowly decomposes in solution even at room temperature.

The amido protons in 1 and 2 can be exchanged by lithium using strong bases MeLi or $^n$BuLi in hexane. The extremely sensitive lithium complexes [(DAD)M(N$^t$Bu)$_2$Li], M = Nb (9)
and Ta (10), have a dimeric structure and exhibit strong Lewis acidity reacting with free DAD and forming monomeric complexes [(DAD)M(N'Bu)₂Li(dad)], M = Nb (11) and Ta (12). The [(DAD)M(N'Bu)₂]⁻ core in 9-12 is isoelectronic to [(DAD)M(N'Bu)₂], M = Cr, Mo, W; and exhibits a similar dynamic behaviour in solution, which can be referred to the ‘flipping’ of the DAD²⁻ double bond.

The molecular structures of 2–5, 7 and 8 reveal a trend of the DAD²⁻ imido complexes to form the supine conformation.

**Experimental Part**

**General:** All reactions and manipulations were carried out under argon using standard Schlenk tube techniques. Solvents and liquid starting materials were refluxed in the presence of an appropriate drying agent and distilled: C₆D₆ and hexane (Na/K alloy); THF and Et₂O (Na/benzophenone); toluene (Na); amines and 'BuOH (CaH₂); acacH (P₂O₅). Literature methods were employed for the synthesis of starting materials and 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene (DAD) [30a], Li₂DAD [4], [M(N'Bu)(NH'Bu)Cl₂(NH₂'Bu)]₂ [30b], [M(N'Bu)(NH'Bu)Cl₂py₂] [2] (M = Nb, Ta). Melting points were measured with a Büchi MP B-540 (uncorrected). C, H and N analyses were carried out with a Heraeus CHN-Rapid analyser. Mass spectra were taken on Varian MAT CH-7a (EI, 70 eV). ¹H- and ¹³C{¹H}-NMR spectra were recorded with Bruker AMX300, AMX400 and DRX500; chemical shifts were referenced (in ppm) to the ¹H (δ 7.15) and ¹³C (δ 128.0) residual signals of the C₆D₆, ¹H (δ 2.03) and ¹³C (δ 20.3) residual signals of the methyl group of d₈-toluene. Infrared spectra were recorded with Bruker IFS 88 FT; samples (if not specified) as Nujol mulls or solutions between KBr plates.

**Preparation of [(DAD)Nb(N'Bu)(NH'Bu)] 1.**

**Method A.** 5.00 g of DAD (10.7 mmol) were added to a solution of 1.80 g (5.3 mmol) [Nb(N'Bu)(NH'Bu)Cl₂(NH₂'Bu)]₂ in 80 mL THF and the resulting mixture was stirred for approx. 30 min at room temperature. Then 0.26 g (10.6 mmol) of Mg-powder were added and stirred for 10h. After complete dissolution of Mg the solvent was removed and the yellow oil was extracted with 2 x·25 mL hexane. Evaporating hexane with further sublimation (80°C, 10⁻² mbar) produced a slightly yellow solid. Yield: 3.95 g (92%).

**P.S.** This method can be used for large scale syntheses direct from NbCl₅ without purification of the intermediate product [NbCl₂(N'Bu)(NH'Bu)(NH₂'Bu)]₂. Typically ~12 eq of
1BuNH2 (225 mL, 2.15 mol) were added dropwise to a suspension of 50.0 g NbCl5 (0.19 mol) in 500 mL toluene under ice cooling. After stirring for 8h the yellow solution was filtered off and the solvent removed in vacuum. The crude oily intermediate was dissolved in 300 mL THF and 1 eq of DAD (31.2 g, 0.19 mol) followed by 4.5 g of Mg powder (0.19 mol) were added. The reaction mixture was stirred for 12h after which the solvent was removed in vacuum. The hexane extraction with 2 x 150 mL yielded a yellow oil, which was purified by sublimation as described above. Yield 30.8 g (41%).

Method B. 0.36 g of DAD (2.2 mmol) were added to a solution of 1.00 g (2.2 mmol) [Nb(NtBu)(NHtBu)Cl2py2] in 80 mL THF and the resulting mixture was stirred for approx. 30 min at room temperature. Then 0.06 g (2.5 mmol) of Mg-powder were added and stirred for 10h. After complete dissolution of Mg the solvent was removed and the green oil was extracted with 2 x 5 mL of hexane. Evaporating hexane with further sublimation (80°C, 10⁻² mbar) yielded a slightly yellow solid. Yield: 0.15 g (17%).

Method C. A solution of Li₂DAD (0.78 g, 4.3 mmol) in 10 mL THF was added dropwise at −80°C to a solution of 2.00 g [Nb(NtBu)(NHtBu)Cl2py2] (4.3 mmol) in 40 mL THF. The reaction mixture was warmed to room temperature and stirred for 8h. After this time the solvent was removed in vacuum and the product extracted with 2 x 10 mL of hexane. Sublimation at 80°C/10⁻² mbar produced a slightly yellow solid. Yield: 0.25 g (14%). Tm.p. 70.6°C. Anal. Calcd for C₁₈H₃₉N₄Nb (M = 404.44 g mol⁻¹): C 53.46, H 9.72, N 13.85. Found: C 52.87, H 9.59, N 13.56. MS-EI: 404 (M⁺, 22%), 389 (M⁺ – Me, 10%), 57 (100%). ¹H-NMR (C₆D₆, 300 MHz, 300 K): 5.86 (s, 2H, CH-DAD), 4.10 (s, 1H, NH), 1.54 (s, 9H, NtBu), 1.33 (s, 18H, tBu-DAD), 1.26 (s, 9H, NH₂Bu). ¹³C{¹H}-NMR (C₆D₆, 75 MHz, 300 K): 104.2 (CH-DAD), 64.0 (NCMe), 55.7 (CMe₃-DAD), 53.4 (NHCMMe), 35.1 (NCMe₂), 34.1 (NHCMMe), 31.9 (CMe₃-DAD). IR (KBr, cm⁻¹): 3021(w), 1456(w), 1389(w), 1361(m), 1260(s), 1242(w), 1221(s), 1148(w), 1136(w), 1107(w), 1064(w), 1024(w), 980(w), 950(w), 870(w), 814(w), 771(w), 754(w), 592(w), 572(w), 515(w).

Preparation of [(DAD)Ta(NtBu)(NHtBu)] 2.

Method A. 1.26 g of DAD (7.5 mmol) were added to a yellow solution of 3.50 g (3.7 mmol) [Ta(NtBu)(NHtBu)Cl₂(NH₂tBu)]₂ in 40 mL THF and the resulting mixture was stirred for approx. 30 min at room temperature. Then 0.19 g (7.8 mmol) of Mg-powder were added and stirred for 10h. After complete dissolution of Mg THF was removed and the yellow oil was extracted by 2 x 25 mL hexane. Evaporating hexane with further sublimation (80°C, 10⁻² mbar) produced a slightly yellow solid. Yield: 1.54 g (42%).
P.S. This method can be used for large scale syntheses direct from TaCl₅ without purification of the intermediate product [TaCl₂(N₅Bu)(NH₅Bu)(NH₅Bu)]₂. Typically 10 eq of ⁴BuNH₂ (145.8 mL, 1.40 mol) were added dropwise to a suspension of 50.0 g TaCl₅ (139.6 mmol) in 500 mL toluene under ice cooling. After stirring for 8h the yellow solution was filtered off and the solvent removed in vacuum. The crude oily intermediate was dissolved in 250 mL THF and 1 eq of DAD (23.5 g, 139.6 mmol) followed by 3.39 g of Mg powder (139.6 mmol) were added. The reaction mixture was stirred for 12h after which the solvent was removed in vacuum. The hexane extraction with 2 x 150 mL produced a yellow oil, which was purified by sublimation as described above. Yield 35.7 g (52%).

Method B. 1.52 g of DAD (9.0 mmol) were added to a solution of 5.00 g (9.0 mmol) [Ta(N₅Bu)(NH₅Bu)Cl₂py₂] in 100 mL THF and the resulting mixture was stirred for approx. 30 min at room temperature. Then 0.22 g (9.0 mmol) of Mg-powder were added and stirred for 10h. After complete dissolution of Mg the solvent was removed and the brown oil was extracted with 2 x·50 mL of pentane. Evaporating pentane with further sublimation (80°C, 10⁻² mbar) produced a slightly yellow solid. Yield: 3.00 g (68%). Tₘ.p. 69.9°C. Anal. Calcd for C₁₈H₃₉N₄Ta (M = 492.49 g mol⁻¹): C 43.90, H 7.98, N 11.38. Found: C 42.56, H 7.89, N 10.88. MS-EI: 492 (M⁺, 33%), 477 (M⁺ – Me, 100%), 436 (M⁺ – Me₂C=CH₂, 10%), 421 (M⁺ – Me – Me₂C=CH₂, 10%), 380 (M⁺ – 2·Me₂C=CH₂, 1%), 365 (M⁺ – Me – 2·Me₂C=CH₂, 2%), 309 (M⁺ – Me – 3·Me₂C=CH₂, 1%). ¹H-NMR (C₆D₆, 300 MHz, 300 K): 5.62 (s, 2H, CH-DAD), 3.41 (s, 1H, NH), 1.56 (s, 9H, N₅Bu), 1.32 (s, 18H, N₅Bu-DAD), 1.27 (s, 9H, NH₅Bu). ¹³C{¹H}-NMR (C₆D₆, 75 MHz, 300 K): 102.6 (CH-DAD), 64.9 (NCMe₁), 55.7 (CMe₁-DAD), 53.5 (NHCMe₁), 35.3 (NHCMe₁), 35.2 (NCMe₂), 32.0 (CMe₂-DAD). IR (KBr, cm⁻¹): 3246(w), 3030(w), 1504(w), 1456(s), 1388(w), 1361(s), 1352(m), 1280(s), 1221(s), 1140(m), 1107(w), 1072(w), 1037(w), 1024(w), 985(m), 960(w), 920(w), 870(m), 816(w), 781(w), 771(m), 756(w), 590(w), 567(m), 527(m), 445(w).

Preparation of [(DAD)Nb(NDip)(NHDip)] 3. A solution of 0.88 g DipNH₂ (5.0 mmol, 2 eq) in 10 mL hexane was added to a solution of 1.00 g (2.5 mmol) [(DAD)Nb(N₅Bu)(NH₅Bu)] (1) in 10 mL hexane at 0°C. The mixture was stirred for 24h at room temperature. Then the solvent was reduced to 5 mL and left stand at room temperature for crystallisation. After crystals had formed the flask was cooled to 0°C for complete isolation of the product. Yield: 0.69 g (46 %). Tₘ.p. 138.8°C. Anal. Calcd for C₃₄H₅₅N₄Nb (M = 612.75 g mol⁻¹): C 66.65, H 9.05, N 9.14. Found: C 66.28, H 8.73, N 9.14. MS-EI: 612 (M⁺, 9%), 162 (100%). ¹H-NMR (C₆D₆, 200 MHz, 300 K): 7.15–6.92 (m, 6H, Dip), 5.74 (s, 2H, CH-DAD), 5.19 (bs, 1H, NH), 4.00 and 3.42 (sept,
2H, $^3$J$_{HH}$ = 6.8 Hz, CH-DipN and CH-DipNH), 1.28 (s, 18H, tBu-DAD), 1.25 and 1.21 (d, 12H, $^3$J$_{HH}$ = 6.8 Hz, CH$_3$-DipN and CH$_3$-DipNH). $^{13}$C{$^1$H}-NMR (C$_6$D$_6$, 75 MHz, 300 K): 153.2, 146.7, 142.2, 139.8, 123.0, 122.9, 122.8 and 122.7 (arom. DipNH and DipN), 104.4 (CH-DAD), 58.4 (CMe$_3$-DAD), 31.1 (CMe$_3$-DAD), 29.2 and 28.2 (CH-DipNH and CH-DipN), 24.3 and 23.5 (CH$_3$-DipNH and CH$_3$-DipN). IR (KBr, cm$^{-1}$): 3262(m), 3050(w), 3027(w), 1586(m ), 1493(w), 1456(s), 1425(s), 1379(w), 1341(s), 1291(s), 1250(s), 1219(s), 1150(m), 1045(m ), 1022(w), 982(s), 951(m ), 934(m ), 889(w), 878(s), 860(s), 820(m), 806(w), 795(m), 779(s), 748(s), 729(w), 696(m), 627(w), 602(m), 583(m), 569(m), 548(w), 523(m), 459(m), 428(w).

Preparation of [(DAD)Ta(NDip)(NHDip)] 4. A solution of 0.72 g DipNH$_2$ (4.0 mmol, 2 eq) in 10 mL hexane was added to a solution of 1.00 g (2.0 mmol) [(DAD)Ta(NtBu)(NtBu)] (1) in 10 mL hexane at 0°C. The mixture was stirred for 24h at room temperature. Then the solvent was reduced to 5 mL and left at room temperature for crystallisation. After crystals had formed the flask was cooled to –30°C for complete isolation of the product. Yield: 0.64 g (45 %). T$_{m.p.}$ 149.8°C. Anal. Calcd for C$_{34}$H$_{55}$N$_4$Ta (M = 700.79 g mol$^{-1}$): C 58.27, H 7.91, N 7.99. Found: C 57.43, H 7.93, N 7.90. MS-EI: 700 (M$^+$, 100%), 524 (M$^+$ – DipNH, 56%). $^1$H-NMR (C$_6$D$_6$, 300 MHz, 300 K): 7.19–6.92 (m, 6H, Dip), 5.67 (s, 2H, CH-DAD), 4.69 (bs, 1H, NH), 3.97 and 3.47 (sept, 2H, $^3$J$_{HH}$ = 6.7 Hz, CH-DipN and CH-DipNH), 1.27 (s, 18H, tBu-DAD), 1.24 and 1.22 (d, 12H, $^3$J$_{HH}$ = 6.7 Hz, CH$_3$-DipN overlapped with CH$_3$-DipNH). $^{13}$C{$^1$H}-NMR (C$_6$D$_6$, 75 MHz, 300 K): 145.8, 142.8, 141.0, 123.7, 122.9, 122.5 and 122.0 (arom. DipNH and DipN), 102.9 (CH-DAD), 57.9 (CMe$_3$-DAD), 31.1 (CMe$_3$-DAD), 29.2 and 27.9 (CH-DipNH and CH-DipN), 24.3 and 23.5 (CH$_3$-DipNH and CH$_3$-DipN). IR (KBr, cm$^{-1}$): 3270(m), 3048(w), 3032(w), 1620(w), 1588(w), 1431(m), 1364(s), 1323(w), 1296(w), 1251(w), 1221(s), 1159(w), 1142(m), 1115(w), 1099(w), 1074(w), 1057(w), 1045(w), 1024(w), 988(m), 963(w), 934(w), 889(w), 876(m), 864(w), 818(w), 802(w), 797(w), 777(w), 770(w), 750(m), 723(w), 698(w), 583(w), 567(w), 521(w), 446(w).

Preparation of [(DAD)$_2$Nb$_2$(NArF)$_2$(NtBu)] 5 and [(DAD)$_2$Nb$_2$(NArF)$_3$] 6.

Method A. 0.91 g ArF-NH$_2$ (4.9 mmol, 2 eq) were added to a solution of 1.00 g (2.5 mmol) [(DAD)Nb(NtBu)(NtBu)] (1) in 30 mL hexane at room temperature. The mixture was stirred for 24h. Removing the solvent and sublimation (160°C, 10$^{-4}$ mbar) produced 0.75 g of a mixture of 5 and 6 in proportion 2:1 (61% yield). Analytically pure 6 was obtained from the
mixture as a yellow-orange solid after washing with two 25 mL portions of cold hexane. 5 was isolated as orange crystals by crystallisation of the obtained hexane solution at −30°C.

**Method B.** THF was added to a mixture of [(DAD)Nb(N'Bu)(µ-Cl)]₂ (1.00 g, 1.3 mmol) and ArF₂NHLi (0.51 g, 2.7 mmol) and the solution obtained was stirred for 24h. The hexane extraction followed by sublimation (160°C, 10⁻⁴ mbar) produced 0.50 g of 5 and 6 in proportion 2:1 (37% yield).

**5:** T_m.p. 171.6°C. Anal. Calcd for C₃₆H₄₉N₇F₁₀Nb₂ (M = 955.63 g mol⁻¹): C 45.25, H 5.17, N 10.26. Found: C 44.11, H 5.01, N 9.86. MS-EI: 955 (M⁺, 100%), 940 (M⁺ – Me, 8%). ¹H-NMR (C₆D₆, 200 MHz, 300 K): 5.99 and 5.21 (s, 2H, CH-DAD), 1.45 (s, 9H, N₄Bu), 1.21 and 0.96 (s, 18H, tBu-DAD). ¹³C{¹H}-NMR (C₆D₆, 125 MHz, 300 K): 110.3 and 102.8 (C₇H-DAD), 67.1 (NCMe₃), 59.0 and 58.0 (CMe₃-DAD), 33.1 (NCMe₃), 30.9 and 30.2 (CMe₃-DAD). ¹⁹F-NMR: -147.6 and -149.9 (pseudo-d, 2F, o-ArF), -166.6 and -167.2 (pseudo-t, 2F, m-ArF), -168.7 and -169.1 (pseudo-t, 1F, p-ArF). IR (KBr, cm⁻¹): 3019(w), 1622(w), 1505(s), 1451(m), 1389(w), 1364(m), 1333(w), 1319(m), 1252(m), 1238(w), 1219(s), 1176(m), 1155(w), 1132(w), 1107(w), 1040(w), 1030(s), 984(s), 889(m), 831(w), 822(m), 785(w), 775(w), 712(w), 648(w), 585(w), 573(w), 530(m), 469(w), 446(w).

**6:** T_m.p. 178.1°C. Anal. Calcd for C₃₈H₄₀N₇F₁₅Nb₂ (M = 1065.58 g mol⁻¹): C 42.83, H 3.78, N 9.20. Found: C 41.10, H 3.84, N 8.67. MS-EI: 1064 (M⁺ – H, 60%), 57 (100%). ¹H-NMR (C₆D₆, 200 MHz, 300 K): 5.52 (s, 2H, CH-DAD), 1.05 (s, 18H, tBu-DAD). ¹³C{¹H}-NMR (C₆D₆, 125 MHz, 300 K): 105.7 (C₇H-DAD), 59.6 (CMe₃-DAD), 30.2 (CMe₃-DAD). ¹⁹F-NMR: -149.9 (pseudo-d, 2F, o-ArF), -165.9 – -166.9 (m, 9F, o-ArF₁,₂ overlapped with p-ArF₁,₂). IR (KBr, cm⁻¹): 3018(w), 1622(m), 1505(s), 1471(m), 1391(w), 1366(s), 1335(s), 1311(m), 1249(w), 1219(s), 1175(w), 1134(w), 1108(w), 1053(s), 1030(s), 988(s), 947(w), 889(m), 861(w), 825(s), 784(m), 776(m), 722(w), 652(w), 619(w), 585(w), 571(w), 537(m), 513(w), 474(w), 449(w).

**Preparation of [(DAD)₂Ta₂(NArF)₃]**. 1.49 g ArF₂NH₂ (8.1 mmol, 2 eq) were added to a solution of 2.00 g (4.1 mmol) [(DAD)Ta(N'Bu)(NH'Bu)] (2) in 50 mL hexane at room temperature. The mixture was stirred for 24h. Removing the solvent and sublimation (160°C, 10⁻⁴ mbar) produced pure product. Yield: 2.20 g (87%). T_m.p. 167.4°C. Anal. Calcd for C₃₈H₄₀N₇F₁₅Ta₂ (M = 1241.66 g mol⁻¹): C 36.76, H 3.25, N 7.90. Found: C 35.48, H 3.43, N 7.57. MS-EI: 1241 (M⁺, 4%), 183 (100%). ¹H-NMR (C₆D₆, 300 MHz, 300 K): 5.45 (s, 2H, CH-DAD), 1.05 (s, 18H, tBu-DAD). ¹³C{¹H}-NMR (C₆D₆, 75 MHz, 300 K): 105.7 (CH-DAD), 59.6 (CMe₂-DAD), 30.2 (CMe₂-DAD). ¹⁹F-NMR: -149.9 (pseudo-d, 2F, o-ArF), -150.3 (pseudo-d, 4F, o-ArF), -165.9 – -166.9 (m, 9F, m-ArF₁,₂). IR (KBr, cm⁻¹): 3019(w), 1622(m), 1505(s), 1471(m), 1391(w), 1366(s), 1335(s), 1311(m), 1249(w), 1219(s), 1175(w), 1134(w), 1108(w), 1053(s), 1030(s), 988(s), 947(w), 889(m), 861(w), 825(s), 784(m), 776(m), 722(w), 652(w), 619(w), 585(w), 571(w), 537(m), 513(w), 474(w), 449(w).
4F, o-ArF\(^2\)) -165.9 – -166.5 (m, 7F, m-ArF\(^{1.2}\) overlapped with p-ArF\(^1\)), -167.7 (pseudo-t, 2F, p-ArF\(^2\)). IR (KBr, cm\(^{-1}\)): 3038(w), 1626(w), 1593(w), 1507(s), 1391(w), 1368(m), 1333(m), 1312(w), 1267(w), 1248(w), 1219(s), 1179(w), 1146(m), 1109(w), 1074(w), 1053(s), 1034(s), 1020(s), 1005(s), 986(s), 885(s), 828(s), 806(w), 783(s), 741(m), 723(w), 689(m), 671(w), 658(w), 608(s), 584(w), 569(w), 557(w), 540(w), 511(w), 498(w), 475(w), 459(w).

**Preparation of [(DAD)\(_2\)Ta\(_2\)(N\(_\text{ntBu}\))\(_2\)(NNMe\(_2\))]** 8. 77 µL Me\(_2\)NNH\(_2\) (1.0 mmol, 1 eq) were added to a solution of 0.50 g (1.0 mmol) [(DAD)Ta(N\(_\text{ntBu}\))(N\(_\text{ntBu}\))] (2) in 25 mL hexane at room temperature. The solution was stirred for 2h. Removing the volatiles produced pure product, which can be sublimed at 100°C/10\(^{-4}\) mbar. Yield: 0.37 g (81%). T\(_\text{m.p.}\) 125.4°C. Anal. Calcd for C\(_{30}\)H\(_{64}\)N\(_8\)Ta\(_2\) (M = 898.79 g mol\(^{-1}\)): C 40.09, H 7.18, N 12.47. Found: C 38.18, H 7.16, N 10.65. MS-EI: 898 (M\(^+\), 20%), 842(M\(^+\) – Me\(_2\)C=CH\(_2\), 6%), 730 (M\(^+\) – DAD – Me, 18%), 715 (M\(^+\) – DAD – Me, 100%). \(^1\)H-NMR (C\(_6\)D\(_6\), 300 MHz, 300 K): 5.91 and 5.68 (s, 2H, CH-DAD), 2.79 (s, 6H, NNMe\(_2\)), 1.58 and 1.38 (s, 9H, N\(_\text{ntBu}\)), 1.36 and 1.34 (s, 18H, N\(_\text{ntBu}\)-DAD).

**Preparation of [(DAD)Nb(N\(_\text{ntBu}\))\(_2\)Li\(_2\)]** 9. 3.1 mL of 1.6M solution MeLi in Et\(_2\)O (5.0 mmol) were added slowly to a solution of 2.00 g [(DAD)Nb(N\(_\text{ntBu}\))(N\(_\text{ntBu}\))] (2) (5.0 mmol) in 40 mL Et\(_2\)O at –80°C. After warming to room temperature the reaction mixture was stirred for 2h. Then the solvent was removed in vacuum and the yellow solid residue was sublimed (170°C, 10\(^{-4}\) mbar). This yielded 1.00g (49%) of analytically pure product. T\(_\text{m.p.}\) 201.8°C; 235°C(dec.). Anal. Calcd for monomer C\(_{18}\)H\(_{38}\)LiN\(_4\)Nb (M = 410.38 g mol\(^{-1}\)): C 52.68, H 9.83, N 13.65. Found: C 47.37, H 8.53, N 11.77. MS-EI: 765 (M\(_2^+\) –Me\(_2\)C=CH\(_2\), 1%), 708 (M\(_2^+\) – 2Me\(_2\)C=CH\(_2\), 2%), 410 (M\(^+\), 35%), 395 (M\(^+\) – Me, 42%), 354 (M\(^+\) – Me\(_2\)C=CH\(_2\), 38%), 57 (100%). \(^1\)H-NMR (C\(_6\)D\(_6\), 300 MHz, 300 K): 5.73 (s, 2H, CH-DAD), 1.58 (bs, 9H, N\(_\text{ntBu}\)), 1.44 (s, 18H, \(^1\)Bu-DAD), 1.30 (bs, 9H, N\(_\text{ntBu}\)). \(^1\)H-NMR (d\(_8\)toluene, 500 MHz, 250 K): 5.61 (AA’ spin
system, 2H, $^3J_{AA'} = 3.1$ Hz, CH-DAD), 1.55 (s, 9H, N$'Bu$), 1.43 and 1.35 (s, 9H, $'$Bu-DAD), 1.24 (s, 9H, N$'Bu$). $^{13}$C$\{^1$H$\}$-NMR (C$_6$D$_6$, 75 MHz, 300 K): 105.4 (CH-DAD), 62.8 (NCMe$_3$), 55.8 (CMe$_3$-DAD), 36.2 (NCMe$_3$), 32.3 (CMe$_3$-DAD). $^7$Li-NMR (d$^8$-toluene, 194 MHz, 300 K): 3.1. IR (KBr, cm$^{-1}$): 3017(w), 1616(w), 1393(w), 1362(m), 1348(m), 1248(w), 1213(s), 1201(s), 1144(m), 1078(w), 1065(s), 1024(w), 1015(w), 943(w), 858(m), 828(m), 801(m), 772(m), 721(w), 621(w), 579(w).

**Preparation of [(DAD)Ta(N$'t$Bu)$_2$Li]$_2$** 10. 3.8 mL of 1.6M solution MeLi in Et$_2$O (6.1 mmol) were added slowly to a solution of 3.00 g [(DAD)Ta(N$'t$Bu)(N$'t$Bu)] (2) (6.1 mmol) in 40 mL Et$_2$O at 0°C. After warming to room temperature the reaction mixture was stirred for 2h. Then the solvent was removed in vacuum and the yellow solid residue was sublimed (170°C, 10$^{-4}$ mbar). This yielded 1.94g (64%) of analytically pure product. T$_{m.p.}$ 252°C(dec.). Anal. Calcd for monomer C$_{18}$H$_{38}$LiN$_4$Ta ($\text{M} = 498.42$ g mol$^{-1}$): C 43.38, H 7.68, N 11.24. Found: C 38.10, H 6.62, N 9.53. MS-EI: 941 (M$^+$, 65%), 498 (M$^+$, 100%).

$^1$H-NMR (C$_6$D$_6$, 500 MHz, 300 K): 5.71 (s, 2H, CH-DAD), 1.46 (bs, 18H, N$'t$Bu), 1.42 (s, 18H, $'$Bu-DAD). $^1$H-NMR (d$^8$-toluene, 500 MHz, 300 K): 5.61 (s, 2H, CH-DAD), 1.35 (s, 36H, N$'t$Bu overlapped with $'$Bu-DAD). $^1$H-NMR (d$^8$-toluene, 500 MHz, 230 K): 5.61 and 5.56 (d, $^3$J$_{HH} = 3.2$ Hz, CH-DAD), 1.25 (s, 9H, N$'Bu$). $^{13}$C$\{^1$H$\}$-NMR (d$^8$-toluene, 125 MHz, 300 K): 102.6 (CH-DAD), 64.9 (NCMe$_3$), 55.8 (CMe$_3$-DAD), 37.1 (NCMe$_3$), 32.2 (CMe$_3$-DAD). $^7$Li-NMR (C$_6$D$_6$, 194 MHz, 300 K): 3.2. $^7$Li-NMR (d$^8$-toluene, 194 MHz, 300 K): 3.1. IR (KBr, cm$^{-1}$): 3034(w), 1510(w), 1389(w), 1360(s), 1352(s), 1281(w), 1250(m), 1215(s), 1184(s), 1144(m), 1111(w), 1099(w), 1065(w), 1026(s), 1013(s), 957(w), 874(m), 816(w), 802(w), 789(w), 771(m), 723(w), 652(m), 581(w), 559(w), 502(w), 447(w).

**Preparation of [(DAD)Nb(N$'t$Bu)$_2$Li(dad)]** 11. 140 mg (0.17 mmol) of [(DAD)Nb(N$'t$Bu)$_2$Li]$_2$ (9) and 100 mg of DAD (0.59 mmol) were mixed inside a Glove Box. 20 mL of hexane were added and the obtained red suspension was stirred for 2h at room temperature. Then the solvent was decanted and the product was washed with 10 mL hexane. A second crop was obtained from the hexane solution by crystallisation at −30°C. Yield 140 mg (62%). T$_{m.p.}$ 192.0°C. Anal. Calcd for C$_{28}$H$_{58}$LiN$_6$Nb ($\text{M} = 578.66$ g mol$^{-1}$): C 58.12, H 10.10, N 14.52. Found: C 46.56, H 7.55, N 10.98. MS-EI: not successful. $^1$H-NMR (C$_6$D$_6$, 300 MHz, 300 K): 7.41 (bs, 2H, CH-dad), 5.84 (s, 2H, CH-DAD), 1.58 (s, 18H, $'$Bu-DAD), 1.33 (bs, 36H, N$'Bu$ overlapped with $'$Bu-dad). $^1$H-NMR (d$^8$-toluene, 400 MHz, 220 K): 6.75 (s, 2H, CH-dad), 5.78
(s, 2H, CH-DAD), 1.59 (s, 18H, \textsuperscript{1}Bu-DAD), 1.58 (s, 9H, N'\textsuperscript{Bu}), 1.24 (s, 18H, tBu-dad), 1.19 (s, 9H, N'\textsuperscript{Bu}). \textsuperscript{13}C\{\textsuperscript{1}H\}-NMR (C\textsubscript{6}D\textsubscript{6}, 75 MHz, 300 K): 155.0 (CH-dad), 105.0 (CH-DAD), 58.9 (CMe\textsubscript{3}-dad), 55.0 (CMe\textsubscript{3}-DAD), 37.0 (NCMe\textsubscript{3}), 31.9 (CMe\textsubscript{3}-DAD), 30.6 (CMe\textsubscript{3}-dad). \textsuperscript{13}C\{\textsuperscript{1}H\}-NMR (d\textsuperscript{8}-toluene, 100 MHz, 220 K): 154.4 (CH-dad), 104.5 (CH-DAD), 62.3 and 62.1 (NCMe\textsubscript{3}), 58.4 (CMe\textsubscript{3}-dad), 54.8 (CMe\textsubscript{3}-DAD), 37.1 and 36.3 (NCMe\textsubscript{3}), 32.6 (CMe\textsubscript{3}-DAD), 30.2 (CMe\textsubscript{3}-dad).

7Li-NMR (C\textsubscript{6}D\textsubscript{6}, 194 MHz, 300 K): 2.2. 7Li-NMR (d\textsuperscript{8}-toluene, 194 MHz, 300 K): 2.2. IR (KBr, cm\textsuperscript{-1}): 3017(w), 1659(w), 1632(w), 1605(w), 1507(w), 1456(s), 1393(m), 1381(s), 1360(s), 1344(m), 1252(w), 1238(w), 1219(s), 1142(m), 1111(m), 1086(s), 1036(w), 1024(w), 1018(w), 978(w), 957(w), 928(w), 885(w), 858(m), 808(w), 795(w), 762(m), 723(w), 534(w), 513(w), 498(m), 476(w), 449(w).

Preparation of [(DAD)Ta(N\textsuperscript{t}Bu\textsubscript{2})2Li(dad)] 12. 0.50 g (0.50 mmol) of [(DAD)Ta(N\textsuperscript{t}Bu\textsubscript{2})2Li\textsubscript{2}] (10) and 0.17 g of DAD (1.00 mmol) were mixed inside a Glove Box. 20 mL of hexane were added and the obtained red suspension was stirred for 2h at room temperature. Then the solvent was decanted and the product washed with 10 mL hexane. A second crop was obtained from the hexane solution by crystallisation at –30°C. Yield 0.58 g (87%). T\textsubscript{m.p.} 199.8°C. Anal. Calcd for C\textsubscript{28}H\textsubscript{58}LiN\textsubscript{6}Ta (M = 666.70 g mol\textsuperscript{-1}): C 50.44, H 8.77, N 12.61. Found: C 46.09, H 8.95, N 11.30. MS-EI: not successful.

1H-NMR (C\textsubscript{6}D\textsubscript{6}, 400 MHz, 300 K): 7.28 (bs, 2H, CH\textsubscript{3}-dad), 5.80 (s, 2H, CH\textsubscript{3}-DAD), 1.57 (s, 18H, tBu-DAD), 1.38 (s, 18H, N\textsuperscript{t}Bu), 1.30 (bs, 18H, tBu-dad). 1H-NMR (d\textsuperscript{8}-toluene, 400 MHz, 240 K): 6.94 (bs, 2H, CH\textsubscript{3}-dad), 5.71 (s, 2H, CH-DAD), 1.57 (s, 18H, \textsuperscript{1}Bu-DAD), 1.38 (s, 18H, N'\textsuperscript{Bu}), 1.30 (bs, 18H, \textsuperscript{1}Bu-dad). 13C\{\textsuperscript{1}H\}-NMR (C\textsubscript{6}D\textsubscript{6}, 125 MHz, 300 K): 102.3 (CH-dad), 62.2 (NCMe\textsubscript{3}), 55.3 (CMe\textsubscript{3}-DAD), 37.9 (NCMe\textsubscript{3}), 32.8 (CMe\textsubscript{3}-DAD), 30.3 (CMe\textsubscript{3}-dad). 13C\{\textsuperscript{1}H\}-NMR (d\textsuperscript{8}-toluene, 125 MHz, 240 K): 154.7 (CH-dad), 101.9 (CH-DAD), 58.5 (CMe\textsubscript{3}-dad), 55.1 (CMe\textsubscript{3}-DAD), 38.1 and 37.3 (NCMe\textsubscript{3}), 32.6 (CMe\textsubscript{3}-DAD), 30.4 (CMe\textsubscript{3}-dad). 7Li-NMR (C\textsubscript{6}D\textsubscript{6}, 155 MHz, 300 K): 2.1. 7Li-NMR (d\textsuperscript{8}-toluene, 194 MHz, 300 K): 2.1. IR (KBr, cm\textsuperscript{-1}): 3032(w), 1659(w), 1632(w), 1604(w), 1516(w), 1458(s), 1381(s), 1360(m), 1343(m), 1281(w), 1254(w), 1238(w), 1219(s), 1208(s), 1142(m), 1111(m), 1086(s), 1036(w), 1024(w), 1018(w), 978(w), 957(w), 928(w), 885(w), 858(m), 808(w), 795(w), 762(m), 723(w), 584(m), 561(w), 534(w), 513(w), 498(m), 476(w), 449(w).

Reaction of 1 and 2 with \textsuperscript{1}BuOH and acacH. Typically 1.0 g of the starting material was dissolved in 10 mL hexane. A hexane solution (10 mL) containing exactly 1 equivalent of the reagent was added slowly at –80°C. After stirring at room temperature for 4h the volatiles
were removed in vacuum leaving analytically pure compound. For the analytical and spectroscopic data see ref. 17.

**Reaction of 2 with DipNH$_2$.** To a solution of 2 (15 mg, 31 µmol) in 1 mL C$_6$D$_6$, DipNH$_2$ (12 µL, 64 µmol) was added at –80°C. The mixture was warmed to 350 K and the $^1$H-NMR spectra were recorded at various times. $^1$H-NMR (d$_8$-toluene, 500 MHz, 300 K) for IM$_1$: aromatic Dip signals and all aliphatic signals cannot be clearly defined, 5.68 (s, 2H, CH-DAD), 4.02 (bs, 1H, NH), 3.57 (bs, $^3$J$_{HH}$ = 6.9 Hz, C$_H$-NDip); IM$_2$: $^1$H-NMR (d$_8$-toluene, 500 MHz, 300 K): 7.07 (d, 2H, $^3$J$_{HH}$ = 7.6 Hz, m-NDip), 6.83 (t, 1H, $^3$J$_{HH}$ = 7.6 Hz, p-NDip), 5.68 (s, 2H, CH-DAD), 5.50 (bs, 1H, NH), 4.11 (sept, $^3$J$_{HH}$ = 6.9 Hz, CH-NDip), 1.31 (d, 12H, $^3$J$_{HH}$ = 6.9 Hz, C$_H$-NDip) 1.20 (s, 18H, 'Bu-DAD).

**Reaction of 4 with $^1$BuNH$_2$.** To a solution of 4 (20 mg, 29 µmol) in 1 mL C$_6$D$_6$, $^1$BuNH$_2$ (30 µL, 287 µmol) was added at room temperature. The $^1$H-NMR spectra were recorded at various times.

**Reaction of 2 with Me$_2$NNH$_2$ excess.** To a solution of 2 (15 mg, 31 µmol) in 1 mL C$_6$D$_6$, Me$_2$NNH$_2$ (24 µL, 315 µmol) was added at room temperature. The $^1$H-NMR spectra were recorded at various times. $^1$H-NMR (500 MHz, C6D6) of the proposed mononuclear complex [(DAD)Ta(N'tBu)(NHNMe$_2$)]: 5.81 (s, 2H, CH-DAD), 4.15 (bs, 1H, NH), 2.31 (s, 6H, Me$_2$N), 1.42 (s, 2H, N'tBu), 1.36 (s, 18H, 'Bu-DAD). The formation of the same product was observed in the NMR reaction of 8 with Me$_2$NNH$_2$ excess at room temperature.

**Reaction of 2 with DipNH$_3$Cl.** DipNH$_3$Cl [31] (8.6 mg, 40 µmol) and 2 (9.9 mg, 20 µmol) were placed in a NMR tube and suspended in 1 mL C$_6$D$_6$. The mixture was heated for 2h at 110°C and the $^1$H-NMR spectra were recorded at various times. $^1$H-NMR (500 MHz, C$_6$D$_6$) of the proposed mononuclear complex [(DAD)Ta(NDip)(Cl)(H$_2$NR)]: $^1$H-NMR (C$_6$D$_6$, 500 MHz, 300 K): 7.20 (d, 2H, $^3$J$_{HH}$ = 7.6 Hz, m-NDip), 6.95 (t, 1H, $^3$J$_{HH}$ = 7.6 Hz, p-NDip), 6.07 (s, 2H, CH-DAD), 4.47 (sept, $^3$J$_{HH}$ = 6.9 Hz, CH-NDip), 1.41 (d, 12H, $^3$J$_{HH}$ = 6.9 Hz, CH$_3$-NDip), 1.30 (s, 18H, 'Bu-DAD).

$^1$H-, $^{13}$C- and $^7$Li- NMR spectra of [(DAD)M(N'tBu)$_2$Li(THF)$_2$]. M = Nb. $^1$H-NMR (C$_6$D$_6$, 500 MHz, 300 K): 5.77 (s, 2H, CH-DAD), 3.72 (m, 8H, THF), 1.51 (s, 18H, 'Bu-DAD), 1.44 (m, 8H, THF), 1.34 (bs, 18H, N'tBu). $^{13}$C {$^1$H}-NMR (C$_6$D$_6$, 125 MHz, 300 K): 104.9 (CH-
DAD), 68.7 (THF), 62.3 (NCMe₃), 54.8 (CMe₃-DAD), 36.4 (NCMe₃), 32.8 (CMe₃-DAD), 25.5 (THF). ⁷Li-NMR (C₆D₆, 194 MHz, 300 K): 2.2. M = Ta. ¹H-NMR (C₆D₆, 500 MHz, 300 K): 5.72 (s, 2H, CH-DAD), 3.73 (m, 8H, THF), 1.49 (s, 18H, tBu-DAD), 1.46 (m, 8H, THF), 1.32 (s, 18H, NtBu). ¹³C{¹H}-NMR (C₆D₆, 125 MHz, 300 K): 102.2 (CH-DAD), 68.7 (THF), 62.1 (NCMe₃), 55.1 (CMe₃-DAD), 37.4 (NCMe₃), 32.8 (CMe₃-DAD), 25.5 (THF). ⁷Li-NMR (C₆D₆, 194 MHz, 300 K): 2.1.

References

[4] see Chapter V.
[9] see Chapter I.
Chapter VII


[15] see Chapter IV.


[17] see Chapter VI.


\[ k = \frac{\sigma k_B T}{h} e^{-\frac{\Delta H^* - T\Delta S^*}{RT}} \]

\[
\ln(k) = \ln\left(\frac{\sigma k_B}{h}\right) + \ln(T) - \frac{\Delta H^* - T\Delta S^*}{RT}
\]

\[
\ln(k) - \ln(T) = \ln\left(\frac{\sigma k_B}{h}\right) - \frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R}
\]

\[
\log(k / T) = 10.32 - \frac{\Delta H^*}{19.13} T + \frac{\Delta S^*}{19.13}; \sigma = 1
\]


[29] \( \Delta G_{298}^* = \Delta H^* - 298 \cdot \Delta S^* \)


[31] DipNH3Cl was prepared from DipNH2 and a solution of HCl in Et2O.
Chapter VIII

The Chemical Vapour Deposition (CVD) of TaN Films
Using Imido DAD Complexes as Single Source Precursors

Introduction

The metal nitrides of the formula $M_{1.0}N_{1.0}$, where M is a group IV or V element, possess a wide range of useful properties. Their hardness and good electrical conductivity allow using them as barrier materials in microelectronics. A barrier of this electroceramic material between a copper strip conductor and a silicon wafer (Fig. 1) prevents the diffusion of copper atoms into the silicon layer at high fabrication temperatures. The formation of copper silicides or copper-doped silicon can be inhibited by defending the copper–silicon interface against degradation [1].

Fig. 1. Scheme of a metal nitride barrier between copper and silicon.

From all possible metal nitrides, titanium nitride (TiN) has been extensively investigated as a barrier material between copper and silicon [1, 2]. It was shown that TiN films are deposited with a characteristic columnar grain boundary structure forming potential diffusion canals for copper atoms. This problem becomes more prominent for thin barrier layers (< 10 nm thickness). New barrier materials are required to solve the copper migration problem.
According to the most recent investigations thin TaN films were found to be a superior barrier material owing to their disordered grain boundary structure, which makes copper diffusion ineffective [1].

Chemical Vapour Deposition (CVD) might be the most preferable film-forming process and can realistically deliver the required conformal coverage. In contrast to the Physical Vapour Deposition (PVD), in which highly reactive atoms or small molecules immediately adhere to growing film surfaces, molecules are able to absorb/desorb on the film surface in CVD [1]. As a result, shape factor features are poorly realised by PVD techniques, especially on the sides and corners.

The upper temperature limit of 400°C in the semiconductor processing industry and very negative reduction potential of Ta(V) to Ta(III) define the problems of precursors in use. Ta₃N₅ is an isolator with large resistivity (> 10⁶ µΩ·cm) and its presence in the barrier film will destroy the electrical conductivity. For example, TaN films can be deposited using CVD of TaCl₅ with nitrogen/hydrogen mixtures at high temperatures (over 900°C) but the required temperatures are far beyond industrial use [1, 3]. On the other hand the films obtained from the [Ta(NMe₂)₅]/NH₃ system (200–400°C) [3] were found to be Ta₃N₅ in contrast to the [Ti(NR₂)₄]/NH₃ (R = Me, Et) system, which delivers TiN films at 200–450°C [1].

\[
\begin{align*}
\text{TaCl}_5 & \xrightarrow{\text{H}_2/\text{N}_2} \text{TaN} \\
> 900^\circ\text{C} \\
\text{Ta(NMe}_2)_5 & \xrightarrow{\text{NH}_3} \text{Ta}_3\text{N}_5 \\
200 - 400^\circ\text{C}
\end{align*}
\]

Other tested nitrogen containing amides/imides such as [Ta(NEt₂)₃], [Ta(N⁺Bu)(NEt₂)₃] and dimer [Ta(N⁺Bu)(NH⁺Bu)Cl₂(NH₂⁺Bu)]₂ produced either Ta₃N₅ or carbon rich films with large resistivity [1, 4, 5]. Applicable films were only obtained by use of the plasma assisted CVD with TaBr₅ and from the substance isolated after reaction of TaCl₅ with Me₂NNH₂ excess, which was claimed to be a hydrazido complex [Ta(NNMe₂)(NNHMe₂)Cl₂(NH₂NNMe₂)]ₙ [4, 5].
An advantage of 1,1-dimethylhydrazido$^{2-}$ derivatives is a weak nitrogen–nitrogen bond, which might break under deposition conditions to form stable Me$_2$N–radical and metal–nitride species. In this case the incorporation of carbon into films should be considerably lower compared to imido/amido precursors with metal–carbon bonds.

It was anticipated that redox active ligands could solve the problems associated with the oxidation state of tantalum in the obtained films. In our investigation we chose 1,4-diazadienes (R,R’–DAD$^{2-}$) as a redox active ligand. The desired process of degradation of the highly covalent Ta(V) precursors is shown in the following Scheme:

With respect to the design of volatile precursors, several $^{1}$Bu imido DAD$^{2-}$ (R = $^{1}$Bu, R’ = H) complexes of tantalum, synthesised and discussed in previous Chapters, were tested in
CVD of TaN films. The CVD experiments were carried out and analysed in the group of Dr. W. Stolz with active participation of M. Pokoj and Dr. K. Volz (Department of Physics, University of Marburg).

Results and discussion

The infrastructure of the CVD system used requires a large amount (> 20 g) of precursors, which had to be tested. The second requirement is a high volatility and relative thermal stability so that they can be transported with a carrier gas without decomposition via a two meter pathway (Fig. 2) to the reactor zone.

From the wide spectrum of the described R,R’–DAD ligands we chose 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene (tBu,H–DAD or simply DAD). This derivative has several advantages, namely, it is very simple to synthesise on large scale and it possesses a high vapour pressure. Therefore, it can be easily sublimed or even distilled under reduced pressure. It is interesting that its metalorganic derivatives also show high volatility and most of them can be purified by sublimation, especially, in combination with the tBuN^2– ligand [6].

Three complexes were selected for the test in CVD of TaN films: [(DAD)Ta(N^tBu)(NH^tBu)] (1) [6d], [(DAD)Ta(N^tBu)(η^3-BH_4)] (2) [6c] and [(DAD)Ta(N^tBu)(η^3-C_3H_5)] (3) [6c]. Complex 1 was prepared by an optimised large scale two step synthesis from TaCl_5, 2 and 3 were obtained in good yields from the reaction of the dimeric complex [(DAD)Ta(N^tBu)(μ-Cl)]_2 with NaBH_4 and C_3H_5MgBr, respectively.

![Complexes 1, 2, and 3](image-url)

Thermal stability

Complexes 1-3 possess sufficient volatility and can be easily sublimed below their melting point at 10^-2 mbar. Furthermore, 1 and 3 do not show any decomposition in C_6D_6
solution after 2 weeks at 130°C (NMR experiment). Furthermore, after CVD experiments with 1 as the precursor, the bubbler’s residue was extracted with hexane and analysed by NMR spectroscopy. The extract was found to contain only pure 1 without any traces of decomposition.

Unfortunately, boronate complex 2 is unstable and decomposes in solution even at room temperature [6c]. Nevertheless, it can be sublimed below its melting point almost without loss.

**Measurements of the vapour pressure**

In order to have some quantitative information about the volatility of our complexes simple experiments to estimate their vapour pressure were employed. The substance was placed into a Schlenk flask directly attached to a manometer [7] via joint. The evacuated system was brought to different temperatures, at which the pressure was measured. The results are presented in Fig. 1.

![Fig. 1. Vapour pressure measurements for DAD and 1 calibrated with DMSO.](image)

Pure DMSO was taken for the calibration and its measured vapour pressure curve is very similar to that calculated with *ACD Labs* Program [8]. The analogous measurements for the
DAD ligand confirm its unusual high volatility, which is comparable to DMSO, despite its large molecular weight of 168.28 g mol\(^{-1}\). The DAD ligand melts at approx. 50°C [9] and some vapour pressure ‘leap’ has been observed in this region. In contrast to this the vapour pressure of 1 does not show large changes in values in the region of the melting point of approx. 70°C (Chapter VI). Although the pressure values for 1 are considerably smaller than those for the DAD ligand, a value realistic for CVD experiments of approx. 5 mbar can be reached in an acceptable range close to 100°C.

**Film depositions with 1-3**

The CVD reactor with the source supply of the system is presented in Fig. 2a-b. As mentioned above, complexes containing tantalum have to be transported via 2 m stainless steel tubes to the CVD reactor. The stainless steel source bubbler was placed in a thermostat. The transport lines can be warmed up to desired temperatures in order to control the partial pressure of the investigated substance in a carrier gas and as a consequence the films growth rate.

![Fig. 2a. The reactor for CVD of TaN films.](image)
According to the Energy Dispersive X-ray Analysis (EDX) metal containing films were obtained using 1-3 as single-source precursors. The film growth rate estimated using Scanning Electron Microscope (SEM) lies in the range of 0.5-1.0 nm/min and this result is presented in Fig. 3 for 1 at a deposition temperature of 400°C.
Fig. 3. The film thickness determined by Scanning Electron Microscope (SEM) on time (obtained from 1 at a deposition temperature of 400°C).

The region of optimised deposition temperatures lies between 350°C and 500°C for 1-3 and for the commercially available products Ta(NMe₂)₅ and Ta(NBu)(NEt₂)₃, which were taken for comparison. This temperature range fits well for the semiconductor industry. The films’ composition (C, N, O and Ta) was estimated from the EDX measurements (Fig. 4). Although this method is not the best one for the quantitative determination of light elements, it allows rapid estimation of the approximate composition of the obtained films.

There are several important conclusions from the EDX measurements, which should be pointed out:

- all films contain approximately 50% tantalum and this indicates that the metal is reduced in comparison with the oxidation state (V) in the precursors
- the oxygen found in all films appears after exposing the processed targets to air, which probably reacts with unsaturated valences of the metal
- in all cases carbon was incorporated besides nitrogen indicating not only formation of tantalum nitride but also tantalum carbides
Fig. 4. The composition of the films obtained from different amido precursors.

The formation of tantalum oxide is not very dramatic and can be avoided by an annealing process with Me₂NNH₂. Tantalum carbides formed during film deposition are isolators and destroy the desired electrical conductivity. The carbon incorporation does not seem to be an exclusive problem of the DAD²⁻ ligand (Fig. 4) but belongs to the whole class of the amido/imido compounds containing carbon-nitrogen bonds. Nevertheless the DAD²⁻ ligand can be an additional source of carbon atoms in deposited films. As it was shown, the EI-MS spectra of the complexes with groups V and VI elements containing DAD²⁻ reveal the β-abstraction of hydrogen accompanied by isobutene elimination from the DAD²⁻ ligand to be the main decomposition pathway [6]. A particle formed after two isobutene eliminations has two possibilities for further decomposition in the CVD reactor. The desired reductive elimination path (B) could reduce the metal centre and no carbon incorporation from the DAD²⁻ ligand into the films should be expected. It cannot be excluded that the carbon atoms of the double bond will be incorporated into films (A), if reductive elimination does not take place.
It is remarkable that the concentration of the nitrogen atoms in the films obtained from hydroborate complex 2 is considerably smaller in comparison with the other precursors, while the other atomic concentrations do not change within statistical ranges. A possible explanation is the formation of solid phases containing boron, which cannot be detected with EDX.

It was anticipated that allyl complex 3 containing a stable allyl radical C\textsubscript{3}H\textsubscript{5} as a leaving group might display lower carbon content after decomposition. However the CVD experiments indicates an opposite trend, namely, more carbon was detected in the films obtained using 3 as precursor. This supposes that it is difficult to break a metal–carbon bond once formed and films obtained from precursors containing metal–carbon bonds will be always carbon enriched.

**Conclusion**

Ceramic films with ~ 50 atom % of tantalum were obtained from 1-3 using the CVD technique. The optimum decomposition temperatures and growth rates fit well with industrial processing requirements. The average oxidation state of the metal in the films is significantly lower than V, a precondition for electrical conductivity, which will be the matter of the further investigations. The films contain surface oxygen originating from air, which seems to react with the unsaturated valences of the metal-containing surface. Unfortunately, incorporation of carbon atoms into films was detected by EDX analysis. Actually, this tendency is common for all amido or imido amido tantalum compounds containing nitrogen–carbon bonds. In this aspect the DAD\textsuperscript{2–} based systems are not superior to the commercially available amido and imido amido precursors. However, with respect to cost of synthesis and long term stability [(DAD)Ta(N\textsuperscript{t}Bu)(NH\textsuperscript{t}Bu)] (1) has some advantages compared to the known systems.
References


[6] see (a) Chapter IV; (b) Chapter V; (c) Chapter VI; (d) Chapter VII.


Chapter IX

Mononuclear Imido Amido Complexes via Exhaustive Ammonolysis of Niobium and Tantalum Pentachloride with \textit{tert}-Butyl Amine

Abstract

Reaction of MCl$_5$ (M = Nb, Ta) with excess of \textit{t}BuNH$_2$ in the presence of pyridine leads to formation of mononuclear complexes [M(N$^{t}$Bu)(NH$^{t}$Bu)Cl$_2$Py$_2$], M = Nb (1), Ta (2). These new key compounds are characterized by $^1$H-, $^{13}$C-NMR spectroscopy, mass spectrometry and elemental analyses. A single crystal structure analysis of [Ta(N$^{t}$Bu)(NH$^{t}$Bu)Cl$_2$Py$_2$] (2) reveals, that surprisingly chloro and not pyridine ligands are \textit{trans} to the strongest $\pi$ donor ligands [N$^{t}$Bu]$^2$- and [NH$^{t}$Bu]$^-$. 

Introduction

The chemistry of niobium and tantalum imido complexes has experienced a great development in the last two decades; one aspect of interest is the isolobal relation of imido and cyclopentadienyl ligands [1]. Aminolysis of niobium and tantalum pentachloride with primary amines typically leads to either ammonium imido metallates [2] or neutral dinuclear amine adducts [M(NR)(NHR)(NH$_2$R)Cl$_2$]$_2$ [3]. Strategies to get mononuclear neutral imido complexes in large scale preparations, that are interesting for industrial applications of these metals involve the use of N-silylated amines [4] or ZnCl$_2$ as Lewis acid in order to remove chloride from chloro metallates [2].

We reported the synthesis of two neutral key complexes [M(N$^{t}$Bu)Cl$_3$Py$_2$], M = Nb and Ta [5] (Scheme 1). The NMR spectra of these octahedrally coordinated complexes reveal two chemically non-equivalent pyridine ligands. That led us to the conclusion, that one weakly
bonded pyridine is bonded trans to the imido ligand, the other one cis. This conclusion was confirmed later by the crystal structure determination of [Nb(N^tBu)Cl_3Py_2] (A1) [6a] and [Ta(N^tBu)Cl_3Py_2] (A2) [6b]. Here we report the simple large scale preparation of mononuclear complexes [M(N^tBu)(NH^tBu)Cl_2Py_2], M = Nb (1), Ta (2) and the surprising result of the crystal structure determination of 2.

**Results and discussion**

**Preparation and characterisation**

The 20 gram scale reaction of MCl_5 with large excess of ^1^BuNH_2 (> 5 eq.) in CH_2Cl_2 in the presence of pyridine affords imido amido complexes 1 and 2 in good yield of about 80%. 1 and 2 are soluble in CH_2Cl_2/hexane (1:1) mixture and can be easily separated from ammonium and pyridinium salts. ^1^H-NMR spectra reveal that two pyridine ligands are present per imido and amido functionality. In contrast to [M(N^tBu)Cl_3Py_2] (A1, A2), both pyridine rings are chemically equivalent. The cis pyridine complex 1 and trans complexes II or III are the only isomers of an octahedral MABC_2D_2 complex type in accord with this observation (Scheme 2).

![Scheme 1. Preparation of 1 and 2.](image)
Scheme 2. Possible isomers in octahedral complex [M(NR)(NHR)Cl$_2$Py$_2$].

Taking into consideration, that the two strongest $\pi$-donors at a $d^0$ metal centre disfavour the *trans* configuration in order to avoid $\pi$-bonding competition with one and the same empty metal $d$ orbital, we anticipated, that isomer III is the most likely one: with anionic chloro ligands and not neutral pyridines *trans* to the ligands with the highest thermodynamic *trans* effect, [NtBu]$^2^-$ und [NHtBu]$^-$ (Scheme 2).

In other imido amido or imido alkoxy derivatives of tantalum, a configuration with anionic and not neutral ligands in *trans* position to the two strongest $\pi$ donors was found or proposed [4, 7]. In order to prove this and our proposal we have carried out an X-ray crystallographic study of 2.

**X-ray study of 2**

All attempts to grow a crystal of 2 suitable for the single X-ray diffraction experiment from CH$_2$Cl$_2$ failed, but the target compound was found to crystallize as a solvate with two non-coordinated THF molecules per formula unit by layering a THF solution with hexane at room temperature. The molecular structure of 2 is presented in Figure 1, selected bond distances and angles in Table 1. The coordination sphere at the tantalum atom is a slightly distorted
octahedron; pyridine ligands are occupying \textit{trans} and chlorine atoms as well as imido and amido ligands \textit{cis} positions.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Molecular structure of 2. THF solvate molecules are omitted for clarity.}
\end{figure}

Table 1. Selected bond distances (Å) and angles (°) for 2.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta(1) – Cl(1)</td>
<td>2.573(9)</td>
</tr>
<tr>
<td>Ta(1) – Cl(2)</td>
<td>2.52(1)</td>
</tr>
<tr>
<td>Ta(1) – N(1)</td>
<td>2.26(2)</td>
</tr>
<tr>
<td>Ta(1) – N(2)</td>
<td>2.25(2)</td>
</tr>
<tr>
<td>Ta(1) – N(3)</td>
<td>2.00(1)</td>
</tr>
<tr>
<td>Ta(1) – N(4)</td>
<td>1.73(1)</td>
</tr>
<tr>
<td>H(3A) – Cl(2)</td>
<td>2.36(7)</td>
</tr>
<tr>
<td>N(1) – Ta(1) – N(2)</td>
<td>166.9(9)</td>
</tr>
<tr>
<td>N(3) – Ta(1) – N(4)</td>
<td>99.4(5)</td>
</tr>
<tr>
<td>C(11) – N(3) – Ta(1)</td>
<td>140.9(8)</td>
</tr>
<tr>
<td>C(15) – N(4) – Ta(1)</td>
<td>169(1)</td>
</tr>
</tbody>
</table>

Table 2 displays a comparison of selected bond parameters of similar complexes. Interestingly the difference in Ta–Cl bond lengths \textit{trans} to imido and \textit{trans} to amido ligands is more prominent in [Ta(N'^{1}Pr)(NH'^{1}Pr)(NH'^{2}Pr)_2Cl_2] (0.128(5) Å) [7] than in 2 (0.05(2) Å). The amido group in 2 seems to exhibit a similar \textit{trans} effect compared to the imido ligand: Ta(1)–Cl(1) \textit{trans} to Ta(1)–N(3)\text{amido} (2.57(1) Å) is slightly longer than Ta(1)–Cl(2) \textit{trans} to Ta(1)–N(4)\text{amido}. We assume, that the strong correlation of parameters during the refinement of the \textit{pseudo} symmetrical chlorine positions leads to this unusual result (see experimental part). The
opposite expected trend in bond lengths has been observed in \([\text{Ta}(\text{N}^3\text{Pr})(\text{NH}^1\text{Pr})(\text{NH}_2^1\text{Pr})_2\text{Cl}_2]\) (Table 2).

**Table 2.** Comparison of some bond distances (Å) and angles (°) in selected imido complexes of tantalum.

<table>
<thead>
<tr>
<th>Bond Distance or Angle</th>
<th>2 [5, 6b]</th>
<th>([\text{Ta}(\text{N}^3\text{Pr})(\text{NH}^1\text{Pr})(\text{NH}_2^1\text{Pr})_2\text{Cl}_2]) [7]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M – Cl ((\text{trans} \text{ imido}))</td>
<td>2.51(1)</td>
<td>2.632(3)</td>
</tr>
<tr>
<td>M – Cl ((\text{trans} \text{ amido}))</td>
<td>2.573(9)</td>
<td>2.504(2)</td>
</tr>
<tr>
<td>M – \text{N}^\text{imido}</td>
<td>1.73(1)</td>
<td>1.745(5)</td>
</tr>
<tr>
<td>M – \text{N}^\text{amido}</td>
<td>2.00(1)</td>
<td>1.964(8)</td>
</tr>
<tr>
<td>M – \text{N}_1^\text{Py}</td>
<td>2.264(2)</td>
<td>2.273(5)</td>
</tr>
<tr>
<td>M – \text{N}_2^\text{Py}</td>
<td>2.246(2)</td>
<td>2.452(5)</td>
</tr>
<tr>
<td>M – \text{N}^\text{imido} – C</td>
<td>169(1)</td>
<td>175.0(5)</td>
</tr>
<tr>
<td>M – \text{N}^\text{amido} – C</td>
<td>140.9(8)</td>
<td>–</td>
</tr>
<tr>
<td>\text{H}^\text{amido} – Cl</td>
<td>2.36(7)</td>
<td>–</td>
</tr>
</tbody>
</table>

The N bonded hydrogen atom has been located and refined isotropically. Interestingly, there is an intramolecular Cl···H\(^\text{amido}\) contact. The sum of the van der Waals radii of chlorine and hydrogen atoms (2.75 Å) [8] is considerably longer than the H(3a)–Cl(2) distance of 2.36(7) Å.

Currently we are investigating the reactivity pattern of these imido amido complexes with respect to nucleophilic substitutions and metathesis reactions.

**Experimental Part**

**General:** All reactions and manipulations were carried out under argon using standard Schlenk tube techniques. Solvents were refluxed in the presence of an appropriate drying agent and distilled: hexane (Na/K alloy), THF (Na/benzophenone), \(\text{CH}_2\text{Cl}_2\), CDCl\(_3\), \(^1\text{BuNH}_2\) and pyridine (CaH\(_2\)). Melting points were measured with a Büchi MP B-540 (uncorrected). C, H and N analyses were carried out with a Heraeus CHN-Rapid analyser. Mass spectra were taken on Varian MAT CH-7a (El, 70 eV). \(^1\text{H}\)- and \(^{13}\text{C}\{\(^1\text{H}\}\})\)-NMR spectra were recorded with Bruker AMX300; chemical shifts were referenced to the \(^1\text{H}\) (δ 7.24) and \(^{13}\text{C}\) (δ 77.0) residual signals of the CDCl\(_3\).
Preparation of \([\text{Nb(N}^\text{t} \text{Bu})(\text{NH}^\text{t} \text{Bu})\text{Cl}_2\text{Py}_2]\) (1). A solution of \(^1\text{BuNH}_2\) (10 eq., 77.3 mL, 739.8 mmol) in 100 mL CH\(_2\text{Cl}_2\) was added dropwise to a suspension of 20.0 g NbCl\(_5\) (74.0 mmol) in 250 mL CH\(_2\text{Cl}_2\) at 0°C (ice bath). After addition the reaction mixture was warmed up to room temperature and stirred for 4 h. The obtained suspension was cooled again to 0°C and a solution of 4 eq. Py (24.0 mL, 296.7 mmol) in 50 mL CH\(_2\text{Cl}_2\) was added. After 4 h stirring at room temperature 100 mL of hexane were added and soluble parts were separated by filtration via Celite. The residue was washed two times with 100 mL CH\(_2\text{Cl}_2/\text{hexane}\) 1:1 mixture until its colour changed to colourless. The volatiles from combined extracts were removed in vacuum, the oily residue was washed with hexane to obtain a light-yellow microcrystalline product, which was dried at 10\(^{-3}\) mbar. Yield 26.8 g (78 %), M.p. >120°C (dec.). Anal. Calcd. for C\(_{18}\text{H}_{29}\text{N}_4\text{Cl}_2\text{Nb} (M = 465.27 \text{ g·mol}^{-1}): C 46.47, H 6.28, N 12.04. Found: C 47.95, H 6.03, N 12.38. MS-EI: 413 (M\(^+\)– HCl – Me, 6%), 291 (M\(^+\)– 2 Py – Me, 69%), 256 (M\(^+\)– 2 Py – Cl – Me, 28%), 235 (M\(^+\)– 2 Py – (CH\(_3\))\(_2\text{CCH}_2\) – Me, 91%), 39 (100%). \(^1\text{H}-\text{NMR} (\text{CDCl}_3, 300 \text{ MHz, 300 K}): \delta = 1.31 (s, 9H, NHC(CH\(_3\))\(_3\)), 1.34 (s, 9H, NC(CH\(_3\))\(_3\)), 7.40 (pseudo-t, 4H, m-H\text{py}), 7.83 (t, J = 7.4 Hz, 2H, p-H\text{py}), 9.25 (pseudo-d, J = 5.0 Hz, 4H, o-H\text{py}), 10.90 (bs, 1H, NH\text{C}(CH\(_3\))\(_3\)). \(^{13}\text{C}\{^1\text{H}\}-\text{NMR} (\text{CDCl}_3, 75 \text{ MHz, 300 K}): 30.8 (NC(CH\(_3\))\(_3\)), 33.0 (NHC(CH\(_3\))\(_3\)), 58.7 (NH\text{C}(CH\(_3\))\(_3\)), 67.9 (s, NC(CH\(_3\))\(_3\)), 124.0 (m-Py), 139.0 (p-Py), 153.4 (o-Py). IR (PE, Nujol, cm\(^{-1}\)): 434 m, 375 m, 303 s, 259 s, 216 s, 162 m, 120 m. IR (KBr, Nujol, cm\(^{-1}\)): 1607 s, 1485 m, 1447 s, 1358 s, 1343 m, 1240 vs, 1219 vs, 1177 w, 1159 m, 1127 m, 1072 vs, 1046 s, 1026 w, 1013 s, 968 s, 882 w, 802 w, 766 m, 723 w, 696 vs, 660 w, 640 s, 612 s, 584 m, 567 s, 538 m, 434 m.

Preparation of \([\text{Ta(N}^\text{t} \text{Bu})(\text{NH}^\text{t} \text{Bu})\text{Cl}_2\text{Py}_2]\) (2). The preparation followed exactly the same steps as for 1 starting from 20.0 g TaCl\(_5\). Yield 25.9 g (84 %). M.p. >120°C (dec.). Anal. Calcd. for C\(_{18}\text{H}_{29}\text{N}_4\text{Cl}_2\text{Ta} (M = 553.31 \text{ g·mol}^{-1}): C 39.07, H 5.28, N 10.13. Found: C 40.15, H 5.17, N 10.02. MS-EI: 379 (M\(^+\)– 2 Py – Me, 20%), 323 (M\(^+\)– 2 Py – (CH\(_3\))\(_2\text{CCH}_2\) – Me, 42%), 266 (TaCl\(_2\text{NH}_{\text{Me}}\), 5%), 41 (100%). \(^1\text{H}-\text{NMR} (\text{CDCl}_3, 300 \text{ MHz, 300 K}): 1.28 (s, 9H, NHC(CH\(_3\))\(_3\)), 1.31 (s, 9H, NC(CH\(_3\))\(_3\)), 7.44 (pseudo-t, 4H, m-H\text{py}), 7.83 (tt, J = 7.7 Hz, J = 1.5 Hz, 2H, p-H\text{py}), 8.60 (bs, 1H, NH\text{C}(CH\(_3\))\(_3\)), 9.40 (dd, J = 6.9 Hz, J = 1.5 Hz, 4H, o-H\text{py}). \(^{13}\text{C}\{^1\text{H}\}-\text{NMR} (\text{CDCl}_3, 75 \text{ MHz, 300 K}): 32.3 (NC(CH\(_3\))\(_3\)), 33.9 (NHC(CH\(_3\))\(_3\)), 56.4 (NH\text{C}(CH\(_3\))\(_3\)), 64.8 (s, NC(CH\(_3\))\(_3\)), 124.1 (m-Py), 139.2 (p-Py), 153.5 (o-Py). IR (PE, Nujol, cm\(^{-1}\)): 436 m, 374 m, 273 s, 222 s, 167 s, 120 m. IR (KBr, Nujol, cm\(^{-1}\)): 1609 s, 1487 m, 1449 s, 1364 s, 1356 s, 1263 s, 1213 s, 1181 w, 1159 m, 1072 vs, 1047 s, 1026 w, 1015 s, 976 s, 880 w, 802 w, 785 m, 766 vs, 721 w, 696 vs, 640 s, 610 m, 585 m, 561 m, 532 w.
Data collection and structure refinement for 2 x 2 THF. 2 x 2 THF crystallizes in the monoclinic space group Cc with \( a = 11.7220(15) \), \( b = 16.1797(14) \), \( c = 15.9663(19) \) Å, \( \beta = 91.122(10) \)°, \( D_{\text{calc}} = 1.524 \) g·cm\(^{-3}\) for \( Z = 4 \). A colourless plate with the dimensions 0.21 x 0.12 x 0.09 mm\(^3\) has been mounted on a STOE IPDS2 diffractometer at 193 K using the „oil drop method“. 9047 reflections have been measured using graphite monochromated MoK\( \alpha \) radiation (\( \Theta_{\text{max}} = 25^\circ \)). 4769 were unique (\( R_{\text{int}} = 0.036 \)), 4424 „observed“ (\( I > 2\sigma(I) \)). The data have been corrected for absorption effects using the indexed faces of the crystal (\( \mu = 38.19 \) cm\(^{-1}\)). The structure has been solved with direct methods and refined using the full matrix least squares procedure [9], all non hydrogen atoms anisotropic, carbon bonded hydrogens „riding“ on calculated positions with fixed isotropic temperature factors. The N bonded hydrogen has been located and refined isotropically. The crystal happened to be a „racemic twin“ („Flack parameter“ \( = 0.55(3) \)). Due to heavy pseudo symmetry and large correlations between parameters, restraints for distances and displacement factors have been included during the refinement for the rings, the \(^1\)Bu groups and the solvent molecules. A refinement in the space group C 2/c was not successful: in this space group there is only one independent Cl position and one disordered position for N(3)/N(4). This disorder is not present in the space group Cc. Inspection of Fourier maps confirms the asymmetry of the Ta environment with respect to the amido/imido ligands. Final residuals: wR2 (all unique reflections): 0.1142, R1 (observed reflections): 0.0441, Goof: 1.09 for 328 refined parameters.

References


Summary

The present work describes new perspectives in chemistry of 1,4-diaza-1,3-diene (R,R’–DAD) ligands. From the wide spectrum of described R,R’–DAD ligands 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene (‘Bu,H–DAD or simply DAD) was chosen. This derivative has several advantages, namely, it is very simple to synthesise on large scale and it possesses a high vapour pressure needed for the design of covalent complexes of high volatility carrying this ligand. DAD is a redox active ligand, which can be easily introduced into complexes in its fully reduced ene-diamido form DAD$^{2-}$.

A fruitful liaison of the DAD ligand and π–basic imido ligands uncovered a new class of volatile DAD$^{2-}$ imido complexes of niobium and tantalum, which were tested in Chemical Vapour Deposition (CVD) process as possible precursors of metal nitride M$_{1.0}$N$_{1.0}$ films – barrier materials between copper strip conductors and silicon wafers in microelectronics (Chapter VIII).
Several different synthetic methods to the key compounds \[ (\text{DAD})M(\text{N}^\text{tBu})(\mu\text{-Cl})_2 \] (A) and \[ (\text{DAD})M(\text{N}^\text{tBu})(\text{NH}^\text{tBu}) \] (B), \( M = \text{Nb} \) and \( \text{Ta} \), were developed. Reaction conditions were optimised for large scale syntheses using \( \text{MCl}_5 \) as starting materials (Scheme 1).

**Scheme 1.** Synthesis of the key compounds \[ (\text{DAD})M(\text{N}^\text{tBu})(\mu\text{-Cl})_2 \] (A) and \[ (\text{DAD})M(\text{N}^\text{tBu})(\text{NH}^\text{tBu}) \] (B), \( M = \text{Nb} \) and \( \text{Ta} \).

The chemical reactivity of the dimeric chloro complexes A and its monomeric pyridine analogues \[ (\text{DAD})M(\text{N}^\text{tBu})(\text{Cl})(\text{py}) \], \( M = \text{Nb} \) and \( \text{Ta} \), in nucleophilic substitution, reduction and metathesis reactions with amines was investigated (Scheme 2, Chapter V and VI).
Scheme 2. Reactivity of [(DAD)M(N\text{t}Bu)(\mu-Cl)]_2 (A) and its monomeric pyridine analogues [(DAD)M(N\text{t}Bu)(Cl)(py)], M = Nb and Ta.
Amido imido complexes [(DAD)M(N^tBu)(NH^tBu)] (B), M = Nb and Ta, were found to be active in metathesis reactions with amines, acidic organic molecules and lithium alkyls (Chapter VII, Scheme 3).

**Scheme 3.** Metathesis reactions of [(DAD)M(N^tBu)(NH^tBu)] (B), M = Nb and Ta (Chapter VII).

The amido group of [(DAD)M(N^tBu)(NH^tBu)] (B), M = Nb and Ta, selectively reacts with organic molecules having acidic protons, such as tBuOH and acacH, to evolve tBuNH₂. The reaction with primary amines yields different products depending on the nature of the substituents. Thus in reaction of B with bulky DipNH₂ the monomeric products [(DAD)M(NDip)(NHDip)] were isolated, while only dimeric species [(DAD)₂M₂(NC₆F₅)₃] and [(DAD)₂Nb(N^tBu)(NC₆F₅)₂] were obtained by reaction with the more acidic C₆F₅NH₂. The reaction of [(DAD)Ta(N^tBu)(NH^tBu)] with Me₂NNH₂ leads to the formation of the first structurally characterised hydrazido²⁻ complex of tantalum [(DAD)₂Ta₂(N^tBu)₂(NNMe₂)].
amido protons in B can be exchanged by lithium using strong bases such as MeLi or "BuLi. The extremely sensitive lithium complexes [(DAD)M(N'Bu)₂Li]₂ have a dimeric structure and exhibit Lewis acidity reacting with free DAD ligand and forming monomeric complexes [(DAD)M(N'Bu)₂Li(dad)].

The complete set of complexes for the elements VI group with the common formula [(DAD)M(NR)₂], M = Cr, Mo, W; R = 'Bu, Mes; was synthesised (Chapter IV). The target compounds of molybdenum and tungsten were obtained by reaction of [M(NR)₂Cl₂L₂], L = DME and pyridine, with DAD in the presence of magnesium. Under the same conditions the chromium compound [Cr(NtBu)₂Cl₂] formed a dinuclear d¹–d¹ complex [Cr₂(N'Bu)₂(µ–N'Bu)]₂(µ–DAD)] (C) with an uncommon coordinated bridging DAD²⁻ ligand. Complex [(DAD)Cr(N'Bu)₂] was isolated in the reaction of [Cr(NtBu)₂Cl₂] with Li₂DAD.

Interestingly, no reduction was observed in the reaction of compounds of the type [W(NR)Cl₄(L)] with Li₂DAD, complexes [(DAD)W(NR)Cl₂], R = Ph and Cy, were obtained in good yields (Chapter II). The DAD²⁻ ligand seems to be more electron efficient and decreases the Lewis acidity of the metal centre compared to the well-investigated ortho-phenylenediamido ligand system [o-(Me₃SiN)₂C₆H₄]²⁻.
Compound \([\text{Mo}(\text{N}^\text{Bu})(\text{O})\text{Cl}_2(\text{dme})]\) was converted into the DAD\(^{2-}\) complex [(DAD)\text{Mo}(\text{N}^\text{Bu})(\mu-\text{O})]_2 by treatment with Li\(_2\text{DAD}\) (Chapter III).

According to X-ray analysis, tetrahedral and tetragonal pyramidal coordination polyhedra were observed for the newly synthesised imido DAD\(^{2-}\) complexes of group V and VI elements. The DAD\(^{2-}\) M metallacycle has folded conformation: the metal centre is not located in the plane formed by \(\text{N}_2\text{C}_2\) atoms of the DAD\(^{2-}\) moiety. Typical metal–to–plane distances are \(\sim 1\) Å. In comparison with the free DAD ligand and its donor–acceptor complexes with \(d^0\) metals a decrease of C–C bond distance and an increase of C–N bond distances is observed. This tendency is not unusual for \(R,R’\)–DAD\(^{2-}\) \(d^0\) complexes with early transition metals and allows considering \(R,R’\)–DAD\(^{2-}\) as an ene-diamido ligand.
All complexes characterised in this work by X-ray analysis exhibit supine conformation with respect to the imido group with one exception: a disorder of the double bond carbon atoms in \([\text{DAD}]\text{Nb}(\text{N}^t\text{Bu})(\text{Cl})(\text{py})\] with the site occupation factor of 18% leads to prone conformation.

The tetrahedral complexes with \(X \neq NR'\) and tetragonal pyramidal complexes, in which dissociation of \(X\) or \(X'\) ligand is impossible, do not show temperature dependence of their NMR spectra in solution. This is consistent with either the rapid supine–prone rearrangement, which cannot be localised on the NMR time scale or with the presence of only one isomer supine or prone.

The dynamic behaviour observed for pyridine containing complexes \([\text{DAD}]M(\text{N}^t\text{Bu})(X)(\text{py})\] and dimeric complexes \([\text{DAD}]M(\text{N}^t\text{Bu})(\mu-\text{Cl})\] \(_2\) (A), \(M = \text{Nb}\) and \(\text{Ta}\), \(X = \text{Cl}\) and \(\text{Bz}\), proceeds via an intramolecular dissociation/association mechanism, for which thermodynamic parameters of the dissociation barrier were calculated on the basis of NMR spectroscopy (Chapter V).

In the tetrahedral complexes of the type \([\text{DAD}]M(\text{NR})_2\], \(M = \text{Cr}\), \(\text{Mo}\), \(\text{W}\); \(R = \text{tBu}\), \(\text{Mes}\), as well as in the isoelectronic unit \([\text{DAD}]M(\text{N}^t\text{Bu})_2\] , \(M = \text{Nb}\) and \(\text{Ta}\), of complexes \([\text{DAD}]M(\text{N}^t\text{Bu})_2\text{Li}\] \(_2\) and \([\text{DAD}]M(\text{N}^t\text{Bu})_2\text{Li(dad)}\], ring inversion was observed in solution.
Based on NMR experiments (2D-EXSY and 1D Band Shape Analysis) calculations of the thermodynamic parameter for the DAD$^{2-}$ ring inversion (‘flipping’ of the DAD$^{2-}$ double bond) reveal activation entropy values $\Delta S^*$ close to zero for all complexes. The activation enthalpy has the most prominent contribution in the formation of the ‘flat’ transition state. This transition state seems to be significantly stabilised in the case of chromium compared to molybdenum and tungsten as indicated by a huge difference > 50 kJ mol$^{-1}$ in activation enthalpies and > 200 K in coalescence temperatures.

Ceramic films with ~ 50 atom % of tantalum were obtained in cooperation with the workgroup of PD Dr. W. Stolz (WZMW, University of Marburg) from [(DAD)Ta(N$^t$Bu)(NH$^t$Bu)], [(DAD)Ta(N$^t$Bu)(η$^3$-BH$_4$)] and [(DAD)Ta(N$^t$Bu)(η$^3$-C$_3$H$_5$)] using the CVD technique (Chapter VIII). The optimum of decomposition temperatures of about 400°C and growth rates of approximately 0.6 nm/min fit the industrial requirements well. The average oxidation state of the metal in the films is significantly lower than V, which is a precondition for electrical conductivity.

![Schematic diagram](image.png)

Fig. 1. The film thickness determined by Scanning Electron Microscope (SEM) on time (obtained from [(DAD)Ta(N$^t$Bu)(NH$^t$Bu)] at a deposition temperature of 400°C).

The films contain surface oxygen originated from air, which seems to react with the unsaturated metal-containing surface. Unfortunately, incorporation of carbon atoms into films was detected by EDX analysis. Actually, this tendency is common for all known amido or imido amido tantalum compounds containing nitrogen–carbon bonds. In this aspect the DAD$^{2-}$ based systems are not superior to the commercial available amido and imido amido precursors. However, with respect to cost of synthesis and long term stability, [(DAD)Ta(N$^t$Bu)(NH$^t$Bu)] has some advantages compared to the known systems.
Crystallographic Appendix

Chapter I.

Crystal structure of [Nb(N-2,4,6-C₆H₂Cl₃)Cl₃(dad)] 5, Dr. Klaus Harms

Identification code: merk02a
Habitus, colour: prism, orange red
Crystal size: 0.33 x 0.15 x 0.12 mm³
Crystal system: Monoclinic
Space group: P 2₁/c Z = 4
Unit cell dimensions:
- a = 11.4784(7) Å, α = 90°
- b = 13.0270(9) Å, β = 108.214(5)°
- c = 18.3165(11) Å, γ = 90°
Volume: 2601.6(3) Å³
Cell determination: 30144 reflections
Empirical formula: C₁₇H₂₄Cl₈N₃Nb
Formula weight: 646.90
Density (calculated): 1.652 Mg/m³
Absorption coefficient: 1.295 mm⁻¹
F(000): 1296
Diffractometer type: IPDS2
Wavelength: 0.71073 Å
Temperature: 193(2) K
Theta range for data collection: 1.87 to 25.00°
Index ranges: -13≤h≤13, -15≤k≤15, -21≤l≤21
Data collection software: STOE Win-Xpose (X-Area)
Cell refinement software: STOE Win-Cell (X-Area)
Data reduction software: STOE Win-Integrate (X-Area)
Reflections collected: 21462
Independent reflections: 4586 [R(int) = 0.0335]
Completeness to theta = 25.00°: 100.0 %
Observed reflections: 4052[I>2sigma(I)]
Reflections used for refinement: 4586
Extinction coefficient: X = 0.0029(3)
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.8601 and 0.6745
Largest diff. peak and hole: 0.427 and -0.710 e.Å⁻³
Solution: Direct methods
Refinement: Full-matrix least-squares on F²
Treatment of hydrogen atoms: Mixture of constr. and free ref.
Programs used:
- SHELXS-97 (Sheldrick, 1997)
- SHELXL-97 (Sheldrick, 1997)
- DIAMOND 2.1, STOE IPDS software
- 4586 / 0 / 304

Goodness-of-fit on F²: 1.035
R index (all data): wR² = 0.0648
R index conventional [I>2sigma(I)]: R1 = 0.0236
Chapter II.

Crystal structure of [(DAD)W(NPh)Cl₂] 1, Dr. Klaus Harms

Identification code: merk05
Habitus, colour: prism, yellow
Crystal size: 0.27 x 0.16 x 0.11 mm³
Crystal system: Monoclinic
Space group: P 2₁/n  Z = 4
Unit cell dimensions:
- a = 10.5842(11) Å  α = 90°.
- b = 15.9211(11) Å  β = 103.474(8)°.
- c = 11.9470(11) Å  γ = 90°.
Volume: 1957.8(3) Å³
Cell determination: 25975 reflections
Empirical formula: C₁₆H₂₅Cl₂N₃W
Formula weight: 514.14
Density (calculated): 1.744 Mg/m³
Absorption coefficient: 6.173 mm⁻¹
F(000): 1000
Diffractometer type: IPDS2
Wavelength: 0.71073 Å
Temperature: 193(2) K
Theta range for data collection: 2.17 to 25.00°.
Index ranges: -12 <= h <= 12, -18 <= k <= 18, -12 <= l <= 14
Data collection software: STOE Win-Xpose (X-Area)
Cell refinement software: STOE Win-Cell (X-Area)
Data reduction software: STOE Win-Integrate (X-Area)
Reflections collected: 15737
Independent reflections: 3433 [R(int) = 0.0351]
Completeness to theta = 25.00°: 99.5 %
Observed reflections: 3035 [I > 2σ(I)]
Reflections used for refinement: 3433
Extinction coefficient: X = 0.00034(7)
Absorption correction: Integration (indexed faces + XSHAPE)
Max. and min. transmission: 0.4724 and 0.2836
Largest diff. peak and hole: 0.688 and -0.690 eÅ⁻³
Solution: Direct methods
Refinement: Full-matrix least-squares on F²
Treatment of hydrogen atoms: H1, H2 located and refined, others calculated
Programs used:
- SHELXS-97 (Sheldrick, 1997)
- SHELXL-97 (Sheldrick, 1997)
- DIAMOND 2.1, STOE IPDS software, X-SHAPE

Data / restraints / parameters:
3433 / 0 / 214

Goodness-of-fit on F²: 0.963
R index (all data): wR² = 0.0372
R index conventional [I > 2σ(I)]: R₁ = 0.0160
Chapter III.

Crystal structure of [(DAD)Mo(N\textsuperscript{t}Bu)(\mu-O)]\textsubscript{2}, Dr. Klaus Harms

![Crystal structure diagram]

Identification code  merk11
Habitus, colour  plate, red
Crystal size  0.33 x 0.15 x 0.01 mm\textsuperscript{3}
Crystal system  Orthorhombic
Space group  Pnma  \( Z = 4 \)
Unit cell dimensions  
\[ \begin{align*}
    a &= 19.913(3) \text{ Å}  \\
    b &= 18.437(2) \text{ Å}  \\
    c &= 9.5467(17) \text{ Å}
\end{align*} \]
\( \alpha = 90^\circ \)
\( \beta = 90^\circ \)
\( \gamma = 90^\circ \)
Volume  3504.9(9) Å\textsuperscript{3}
Cell determination  5818 peaks with Theta 2 to 25°.
Empirical formula  C\textsubscript{28}H\textsubscript{58}Mo\textsubscript{2}N\textsubscript{6}O\textsubscript{2}
Formula weight  702.68
Density (calculated)  1.332 Mg/m\textsuperscript{3}
Absorption coefficient  0.746 mm\textsuperscript{-1}
\( F(000) \)  1472
Diffractometer type  IPDS2
Wavelength  0.71073 Å
Temperature  193(2) K
Theta range for data collection  2.05 to 25.00°.
Index ranges  -23\( \leq h \leq 21 \), -21\( \leq k \leq 21 \), -11\( \leq l \leq 11 \)
Data collection software  STOE WinXpose (X-Area)
Cell refinement software  STOE WinCell (X-Area)
Data reduction software  STOE WinIntegrate (X-Area)
Reflections collected  13576
Independent reflections  2877 [\( R(int) = 0.1226 \)]
Completeness to theta = 25.00°  90.0 %
Observed reflections  1346[\( I > 2\sigma(I) \)]
Reflections used for refinement  2877
Absorption correction None
Largest diff. peak and hole  0.572 and -0.700 e.Å\textsuperscript{-3}
Solution  Direct methods
Refinement  Full-matrix least-squares on F\textsuperscript{2}
Treatment of hydrogen atoms  Calculated positions, fixed isotropic U's
Programs used  SHLEXS-97 (Sheldrick, 1997)
               SHELXL-97 (Sheldrick, 1997)
               SHELXTL, STOE IPDS2 software
Data / restraints / parameters  2877 / 0 / 205
Goodness-of-fit on F\textsuperscript{2}  0.753
R index (all data)  \( wR2 = 0.1128 \)
R index conventional [\( I > 2\sigma(I) \)]  R1 = 0.0485
Chapter IV.

Crystal structure of [(DAD)Cr(N\textsuperscript{t}Bu)\textsubscript{2}] 1, Dr. Klaus Harms

![Crystal structure diagram]

Identification code: aam265
Habitus, colour: prism, red
Crystal size: 0.36 x 0.21 x 0.18 mm\textsuperscript{3}
Crystal system: Monoclinic
Space group: P 2\textsubscript{1}/c \( Z = 4 \)
Unit cell dimensions:
\[ a = 14.6472(14) \text{ Å} \]
\[ b = 15.8431(12) \text{ Å} \]
\[ c = 9.8926(11) \text{ Å} \]

Volume: 2232.0(4) \text{ Å}\textsuperscript{3}
Cell determination: 7546 peaks with Theta 1.9 to 25.8°.
Empirical formula: C\textsubscript{18}H\textsubscript{38}CrN\textsubscript{4}
Formula weight: 362.52
Density (calculated): 1.079 Mg/m\textsuperscript{3}
Absorption coefficient: 0.518 mm\textsuperscript{-1}
F(000): 792
Diffractometer type: IPDS1
Wavelength: 0.71073 Å
Temperature: 193(2) K
Theta range for data collection: 1.92 to 25.00°.
Index ranges: \(-17<=h<=17, -18<=k<=18, -11<=l<=11\)
Data collection software: STOE Expose
Cell refinement software: STOE Cell
Data reduction software: STOE Integrate
Observations collected: 15903
Independent reflections: 3875 \([R(int) = 0.0608]\)
Completeness to theta = 25.00°: 98.5 %
Observed reflections: 2390\([I>2\sigma(I)]\)
Reflections used for refinement: 3875
Absorption correction: Analytical
Max. and min. transmission: 0.9324 and 0.8734
Largest diff. peak and hole: 0.366 and -0.256 e.Å\textsuperscript{-3}
Solution: Direct methods
Refinement: Full-matrix least-squares on F\textsuperscript{2}
Treatment of hydrogen atoms: Calculated, H2,H3 located and refined
Programs used:
- SIR92 (Giacovazzo et al., 1993)
- SHELXL-97 (Sheldrick, 1997)
- Diamond 2.1, STOE IPDS1 software

Data / restraints / parameters:
- 3875 / 0 / 228
- Goodness-of-fit on F\textsuperscript{2}: 0.841
- \( wR2 = 0.1014 \)
- R1 = 0.0417
Crystal structure of $[\text{Cr}_2(\text{N}^3\text{Bu})_2(\mu-\text{N}^3\text{Bu})_2(\mu-\text{DAD})]_2$, Dr. Klaus Harms

Identification code          aam52  
Habitus, colour              plate, dark red  
Crystal size                 0.54 x 0.30 x 0.06 mm$^3$  
Crystal system               Orthorhombic  
Space group                  P n m a   
Unit cell dimensions         $a = 11.1799(7)$ Å, $\alpha = 90^\circ$.  
                             $b = 16.8159(12)$ Å, $\beta = 90^\circ$.  
                             $c = 19.9181(13)$ Å, $\gamma = 90^\circ$.  
Volume                       3744.6(4) Å$^3$  
Cell determination          8000 peaks with Theta 1.5 to 26°.  
Empirical formula           $\text{C}_{32} \text{H}_{70} \text{Cr}_2 \text{N}_6$  
Formula weight              642.94  
Density (calculated)         1.140 Mg/m$^3$  
Absorption coefficient      0.608 mm$^{-1}$  
F(000)                      1408  
Diffractometer type         IPDS1  
Wavelength                   0.71073 Å  
Temperature                 193(2) K  
Theta range for data collection 1.58 to 25.98°.  
Index ranges                $-13 \leq h \leq 13$, $-20 \leq k \leq 20$, $-22 \leq l \leq 24$  
Data collection software    STOE Expose  
Cell refinement software    STOE Cell  
Data reduction software     STOE Integrate  
Reflections collected       21282  
Independent reflections     3770 [R(int) = 0.0476]  
Completeness to theta = 25.98° 99.2%  
Observed reflections        2144[I>2sigma(I)]  
Reflections used for refinement 3770  
Absorption correction      Gaussian  
Max. and min. transmission  0.9447 and 0.812  
Largest diff. peak and hole 0.417 and -0.245 e.Å$^{-3}$  
Solution                    Direct methods  
Refinement                  Full-matrix least-squares on F$^2$  
Treatment of hydrogen atoms Calculated, H100 located  
Programs used               SHELXS-97 (Sheldrick, 1997)  
                             SHELXL-97 (Sheldrick, 1997)  
                             Diamond 2.1, STOE IPDS1 software  
Data / restraints / parameters  
Goodness-of-fit on F$^2$     0.870  
R index (all data)           wR2 = 0.1069  
R index conventional [I>2sigma(I)] R1 = 0.0375
Crystal structure of [(DAD)Mo(N^Bu)_2] 3, Dr. Klaus Harms

Identification code  merk12
Habitus, colour  prism, orange
Crystal size  0.60 x 0.20 x 0.12 mm³
Crystal system  Monoclinic
Space group  P 2_1/c  Z = 4
Unit cell dimensions
a = 10.4527(6) Å  α = 90°.
b = 10.5740(4) Å  β = 93.267(7)°.
c = 20.8859(12) Å  γ = 90°.
Volume  2304.7(2) Å³
Cell determination  8000 peaks with Theta 2 to 26°.
Empirical formula  C_{18}H_{38}MoN_{4}
Formula weight  406.46
Density (calculated)  1.171 Mg/m³
Absorption coefficient  0.574 mm⁻¹
F(000)  864
Diffractometer type  IPDS1
Wavelength  0.71073 Å
Temperature  193(2) K
Theta range for data collection  1.95 to 25.90°.
Index ranges  -12<=h<=12, -12<=k<=12, -25<=l<=25
Data collection software  STOE Expose
Cell refinement software  STOE Cell
Data reduction software  STOE Integrate
Reflections collected  15890
Independent reflections  4458 [R(int) = 0.0612]
Completeness to theta = 25.90°  99.7 %
Observed reflections  3063[I>2sigma(I)]
Reflections used for refinement  4458
Absorption correction  Semi-empirical from equivalents
Max. and min. transmission  1.0109 and 0.85
Largest diff. peak and hole  0.348 and -0.444 e.Å⁻³
Solution  Direct methods
Refinement  Full-matrix least-squares on F²
Treatment of hydrogen atoms  Me-H calculated, others refined
Programs used  SHELXS-97 (Sheldrick, 1997)
                 SHELXL-97 (Sheldrick, 1997)
                 SHELXTL, STOE IPDS1 software
Data / restraints / parameters  4458 / 0 / 263
Goodness-of-fit on F²  0.863
R index (all data)  wR² = 0.0661
R index conventional [I>2sigma(I)]  R1 = 0.0299
Chapter V.

Crystal structure of \([(DAD)Nb(N^tBu)(Cl)(py)]_1\), Dr. Klaus Harms

Identification code: merk01
Habitus, colour: needle, colourless
Crystal size: 0.70 x 0.05 x 0.04 mm³
Crystal system: Monoclinic
Space group: \(P 2_1/c\)  
Z = 4
Unit cell dimensions: 
\(a = 13.9285(10)\ \text{Å}\) \(\alpha = 90^\circ\).
\(b = 9.8087(8)\ \text{Å}\) \(\beta = 106.990(5)^\circ\).
\(c = 17.6976(11)\ \text{Å}\) \(\gamma = 90^\circ\).
Volume: 2312.3(3) Å³
Cell determination: 22406 reflections
Empirical formula: \(\text{C}_{19}\text{H}_{34}\text{ClN}_4\text{Nb}\)
Formula weight: 446.86
Density (calculated): 1.284 Mg/m³
Absorption coefficient: 0.645 mm⁻¹
\(F(000)\): 936
Diffractometer type: Stoe IPDS-II
Wavelength: 0.71073 Å
Temperature: 193(2) K
Index ranges: -17 <= h <= 17, -12 <= k <= 12, -21 <= l <= 19
Data collection software: Stoe Win-Expose (X-Area)
Cell refinement software: Stoe Win-Cell (X-Area)
Data reduction software: Stoe Win-Integrate (X-Area)
Reflections collected: 40729
Independent reflections: 4648 [\(R(int) = 0.0725\)]
Completeness to theta = 26.26°: 99.4 %
Observed reflections: 3285 [\(|I| > 2\sigma(I)\)]
Reflections used for refinement: 4648
Extinction coefficient: X = 0.0012(2)
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.9747 and 0.6611
Largest diff. peak and hole: 0.287 and -0.385 e.Å⁻³
Solution: Direct methods
Refinement: Full-matrix least-squares on \(F^2\)
Treatment of hydrogen atoms: Calculated, H2, H3 located
Programs used:
- SHELXS-97 (Sheldrick, 1997)
- SHELXL-97 (Sheldrick, 1997)
- SHELXTL, STOE IPDS software

Data / restraints / parameters:
- \(4648 / 0 / 253\)
- Goodness-of-fit on \(F^2\): 0.882
- \(R\) index (all data): \(wR^2 = 0.0649\)
- \(R\) index conventional [\(|I| > 2\sigma(I)\)]: \(R1 = 0.0296\)
Crystal structure of [(DAD)Ta(N^tBu)(Cl)(py)] 2, Dr. Klaus Harms

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<td>WinGX, IPDS2 software</td>
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</tbody>
</table>

Data / restraints / parameters

Data / restraints / parameters

Goodness-of-fit on F² | 1.131 |
| R index (all data)    | wR2 = 0.0458 |
| R index conventional  | R1 = 0.0188 |
Crystal structure of [(DAD)Ta(N^tBu)(\mu-Cl)]_2 4, Dr. Klaus Harms

Identification code        aam35
Habitus, colour           nugget, colourless
Crystal size              0.45 x 0.27 x 0.18 mm^3
Crystal system            Orthorhombic
Space group               P b c a  Z = 8
Unit cell dimensions      
\[a = 16.8262(9) \text{ Å} \quad \alpha = 90^\circ.\]
\[b = 12.1040(6) \text{ Å} \quad \beta = 90^\circ.\]
\[c = 18.6145(9) \text{ Å} \quad \gamma = 90^\circ.\]
Volume                    3791.1(3) Å^3
Cell determination        79060 peaks with Theta 1.6 to 26°.
Empirical formula         C_{14}H_{29}ClN_3Ta
Formula weight            455.80
Density (calculated)      1.597 Mg/m^3
Absorption coefficient    5.933 mm\(^{-1}\)
F(000)                    1792
Diffractometer type       IPDS2
Wavelength                0.71073 Å
Temperature               193(2) K
Theta range for data collection 2.19 to 25.00°.
Index ranges             -20<=h<=20, -14<=k<=14, -22<=l<=22
Data collection software  STOE WinXpose (X-Area)
Cell refinement software  STOE WinCell (X-Area)
Data reduction software   STOE WinIntegrate (X-Area)
Reflections collected     43627
Independent reflections   3329 [R(int) = 0.0805]
Completeness to theta = 25.00° 99.7 %
Observed reflections      2810[I>2sigma(I)]
Reflections used for refinement 3329
Extinction coefficient    X = 0.00033(3)
Absorption correction     Gaussian
Max. and min. transmission 0.4585 and 0.2715
Largest diff. peak and hole 0.707 and -0.553 e.Å\(^{-3}\)
Solution                  Patterson (SHELXS-97), Structure expansion (DIRDIF)
Refinement                Full-matrix least-squares on F^2
Treatment of hydrogen atoms Me calculated, H2, H3 located, refined
Programs used             SHELXS-97 (Sheldrick, 1997), DIRDIF-99
                          SHELXL-97 (Sheldrick, 1997)
                          WinGX, Diamond, STOE IPDS2 software
Data / restraints / parameters 3329 / 0 / 185
Goodness-of-fit on F^2 1.113
R index (all data)        wR2 = 0.0585
R index conventional [I>2sigma(I)] R1 = 0.0273
Crystal structure of [(DAD)Ta(N有很大Bu)(Bz)(py)] 6, Dr. Klaus Harms

Identification code  merk06
Habitus, colour  prism, orange
Crystal size  0.5 x 0.4 x 0.3 mm³
Crystal system  Triclinic
Space group  P -1
Unit cell dimensions  
  a = 10.2096(6) Å  α = 113.812(4)°.
  b = 16.4282(10) Å  β = 98.066(5)°.
  c = 18.1685(11) Å  γ = 90.560(5)°.
Volume  2752.9(3) Å³
Cell determination  102013 peaks with Theta 1.4 to 26.2°.
Empirical formula  C_{26}H_{41}N_{4}Ta
Formula weight  590.58
Density (calculated)  1.425 Mg/m³
Absorption coefficient  4.011 mm⁻¹
F(000)  1192
Diffractometer type  IPDS2
Wavelength  0.71073 Å
Temperature  193(2) K
Theta range for data collection  1.42 to 25.00°.
Index ranges  -12 <= h <= 12, -19 <= k <= 19, -21 <= l <= 21
Data collection software  STOE WinXpose (X-Area)
Cell refinement software  STOE WinCell (X-Area)
Data reduction software  STOE WinIntegrate (X-Area)
Reflections collected  52916
Independent reflections  9684 [R(int) = 0.0505]
Completeness to theta = 25.00°  99.9 %
Observed reflections  8470[I > 2sigma(I)]
Reflections used for refinement  9684
Extinction coefficient  X = 0.00020(5)
Absorption correction  Semi-empirical from equivalents
Max. and min. transmission  0.31352 and 0.16662
Largest diff. peak and hole  1.438 and -1.066 e.Å⁻³
Solution  Direct methods
Refinement  Full-matrix least-squares on F²
Treatment of hydrogen atoms  Located, isotr. refinement, Me calculated
Programs used  SHELXS-97 (Sheldrick, 1997)
  SHELXL-97 (Sheldrick, 1997)
  SHELXTL, STOE IPDS2 software
Data / restraints / parameters  9684 / 0 / 690
Goodness-of-fit on F²  1.166
R index (all data)  wR² = 0.0660
R index conventional  [I > 2sigma(I)]  R1 = 0.0267
Crystal structure of [(DAD)Ta(NDip)(μ-Cl)]₂ 10, Dr. Klaus Harms

Identification code: aam240b
Habitus, colour: prism, yellow
Crystal size: 0.23 x 0.22 x 0.12 mm³
Crystal system: Monoclinic
Space group: P 2₁/n
Unit cell dimensions:
- a = 12.0782(11) Å
- b = 8.9703(10) Å
- c = 24.607(2) Å
- α = 90°
- β = 92.506(11)°
- γ = 90°
Volume: 2663.5(4) Å³
Cell determination: 7997 peaks with Theta 2 to 26°.
Empirical formula: C₅₁H₈₃Cl₂N₆Ta₂
Formula weight: 1213.03
Density (calculated): 1.513 Mg/m³
Absorption coefficient: 4.243 mm⁻¹
F(000): 1222
Diffractometer type: IPDS1
Wavelength: 0.71073 Å
Temperature: 193(2) K
Theta range for data collection: 2.42 to 25.99°.
Index ranges: -14<=h<=14, -10<=k<=11, -28<=l<=28
Data collection software: STOE Expose
Cell refinement software: STOE Cell
Data reduction software: STOE Integrate
Reflections collected: 25325
Independent reflections: 4986 [R(int) = 0.0358]
Completeness to theta = 25.00°: 96.6 %
Observed reflections: 4208[I>2sigma(I)]
Reflections used for refinement: 4986
Absorption correction: Analytical
Max. and min. transmission: 0.5887 and 0.4446
Largest diff. peak and hole: 0.937 and -0.852 e.Å⁻³
Solution: Diret methods
Refinement: Full-matrix least-squares on F²
Treatment of hydrogen atoms: Calculated, riding, H2,H3 located, refined
Programs used:
- SHELXS-97 (Sheldrick, 1997)
- SHELXL-97 (Sheldrick, 1997)
- Diamond 2.1, STOE IPDS1 software

Data / restraints / parameters: 4986 / 43 / 273
Goodness-of-fit on F²: 0.992
R index (all data): wR² = 0.0647
R index conventional [I>2sigma(I)]: R1 = 0.0254
Chapter VI.

Crystal structure of $[\eta^5\text{-Ind})(\text{DAD})\text{Ta(N}^\text{Bu})_4]$, Dr. Klaus Harms

Identification code
Habitus, colour
Crystal size
Crystal system
Space group
Unit cell dimensions
Volume
Cell determination
Empirical formula
Formula weight
Density (calculated)
Absorption coefficient
F(000)
Diffractometer type
Wavelength
Temperature
Theta range for data collection
Index ranges
Data collection software
Cell refinement software
Data reduction software
Reflections collected
Independent reflections
Completeness to theta = 26.26°
Observed reflections
Reflections used for refinement
Extinction coefficient
Absorption correction
Max. and min. transmission
Largest diff. peak and hole
Solution
Refinement
Treatment of hydrogen atoms
Programs used
Data / restraints / parameters
Goodness-of-fit on $F^2$
R index (all data)
R index conventional [I>2sigma(I)]

merk07
plate, yellow
0.30 x 0.30 x 0.06 mm$^3$
Orthorhombic
P n n a
$\alpha = 12.8814(6)$ Å
$\beta = 14.6959(6)$ Å
$\gamma = 12.6103(6)$ Å
4
2387.18(19) Å$^3$
72515 peaks with Theta 1.4 to 26.2°.
C$_{23}$H$_{36}$N$_3$Ta
535.50
1.490 Mg/m$^3$
4.616 mm$^{-1}$
1072
IPDS2
0.71073 Å
193(2) K
-15<=$h$<=$15$, -17<=$k$<=$18$, -15<=$l$<=$15$
STOE WinXpose (X-Area)
STOE WinCell (X-Area)
STOE WinIntegrate (X-Area)
63324
2496 [R(int) = 0.0281]
99.6 %
2352[I>2sigma(I)]
2496
X = 0.00209(13)
Integration
0.737 and 0.2376
0.449 and -0.612 e.Å$^{-3}$
Direct methods
Full-matrix least-squares on $F^2$
Me calculated, others located and refined
SHELXS-97 (Sheldrick, 1997)
SHELXL-97 (Sheldrick, 1997)
SHELXTL, STOE IPDS2 software
2496 / 0 / 155
1.066
wR2 = 0.0450
R1 = 0.0177
Crystal structure of [(DAD)Nb(N\text{t}Bu)(\eta^3-C_3H_5)] \(5\), Dr. Klaus Harms

Identification code \(172_2\)
Habitus, colour prism, colourless
Crystal size \(0.40 \times 0.27 \times 0.19 \text{ mm}^3\)
Crystal system Orthorhombic
Space group \(P\ b\ c\ a\) \(Z = 8\)
Unit cell dimensions \(a = 10.2247(4) \text{ Å}\) \(\alpha = 90^\circ\).
\(b = 15.0137(8) \text{ Å}\) \(\beta = 90^\circ\).
\(c = 27.1538(10) \text{ Å}\) \(\gamma = 90^\circ\).
Volume \(4168.4(3) \text{ Å}^3\)
Cell determination 36826 peaks with Theta 1.4 to 26.2°.
Empirical formula \(C_{17}H_{34}N_3\ Nb\)
Formula weight 373.38
Density (calculated) 1.190 Mg/m\(^3\)
Absorption coefficient 0.577 mm\(^{-1}\)
\(F(000)\) 1584
Diffractometer type IPDS2
Wavelength 0.71073 Å
Temperature 193(2) K
Theta range for data collection 2.49 to 25.00°.
Index ranges \(-12 \leq h \leq 12\), \(-17 \leq k \leq 17\), \(-32 \leq l \leq 32\)
Data collection software STOE WinXpose (X-Area)
Cell refinement software STOE WinCell (X-Area)
Data reduction software STOE WinIntegrate (X-Area)
Reflections collected 50812
Independent reflections 3666 [\(R(int) = 0.0880]\]
Completeness to theta = 25.00° 99.9 %
Observed reflections 2902[\(I>2\sigma(I)\)]
Reflections used for refinement 3666
Extinction coefficient \(X = 0.0013(3)\)
Absorption correction Gaussian
Max. and min. transmission 0.9197 and 0.8283
Largest diff. peak and hole 0.457 and -0.615 e.Å\(^{-3}\)
Solution Direct methods
Refinement Full-matrix least-squares on \(F^2\)
Treatment of hydrogen atoms Calculated positions, fixed isotr. U's
Programs used SHELXS-97 (Sheldrick, 1997)
SHELXL-97 (Sheldrick, 1997)
SHELXTL, STOE IPDS2 software

Data / restraints / parameters 3666 / 245 / 273
Goodness-of-fit on \(F^2\) 1.076
R index (all data) \(wR^2 = 0.1176\)
R index conventional [\(I>2\sigma(I)\)] \(R1 = 0.0427\)
Crystal structure of [(DAD)Nb(N'Bu)(acac)] 7, Dr. Klaus Harms

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<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<td>Identification code</td>
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<tr>
<td>Habitus, colour</td>
<td>prism, orange</td>
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<td>Crystal size</td>
<td>0.51 x 0.42 x 0.42 mm³</td>
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<tr>
<td>Crystal system</td>
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<td>Space group</td>
<td>P 21/n</td>
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<tr>
<td>Unit cell dimensions</td>
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</tr>
<tr>
<td>a</td>
<td>10.0936(5) Å</td>
</tr>
<tr>
<td>α</td>
<td>90°</td>
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<tr>
<td>b</td>
<td>9.3147(4) Å</td>
</tr>
<tr>
<td>β</td>
<td>98.449(6)°</td>
</tr>
<tr>
<td>c</td>
<td>24.9541(11) Å</td>
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<tr>
<td>γ</td>
<td>90°</td>
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<tr>
<td>Volume</td>
<td>2320.69(18) Å³</td>
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<tr>
<td>Cell determination</td>
<td>8000 peaks with Theta 2.2 to 26°.</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₁₉H₃₆N₃NbO₂</td>
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<td>Formula weight</td>
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<tr>
<td>Density (calculated)</td>
<td>1.235 Mg/m³</td>
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<td>Absorption coefficient</td>
<td>0.533 mm⁻¹</td>
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<td>F(000)</td>
<td>912</td>
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<td>Diffractometer type</td>
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<td>Wavelength</td>
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</tr>
<tr>
<td>Temperature</td>
<td>193(2) K</td>
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<tr>
<td>Theta range for data collection</td>
<td>3.02 to 25.92°</td>
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<tr>
<td>Index ranges</td>
<td>-12&lt;=h&lt;=12, -11&lt;=k&lt;=11, -30&lt;=l&lt;=30</td>
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<tr>
<td>Data collection software</td>
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<td>Cell refinement software</td>
<td>STOE Cell</td>
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<td>Data reduction software</td>
<td>STOE Integrate</td>
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<td>Reflections collected</td>
<td>17624</td>
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<tr>
<td>Completeness to theta = 25.92°</td>
<td>98.9 %</td>
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<tr>
<td>Observed reflections</td>
<td>3950[1&gt;2sigma(I)]</td>
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<td>Reflections used for refinement</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.7985 and 0.7556</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.371 and -0.421 e.Å⁻³</td>
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<tr>
<td>Solution</td>
<td>Direct methods</td>
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<tr>
<td>Refinement</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Treatment of hydrogen atoms</td>
<td>Located, isotropic refinement</td>
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<tr>
<td>Programs used</td>
<td>SHELXS-97 (Sheldrick, 1997)</td>
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<td>SHELXL-97 (Sheldrick, 1997)</td>
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<tr>
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<td>DIAMOND 2.1 (Brandenburg, 2001), STOE IPDS1 software</td>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F²</td>
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<td>R index (all data)</td>
<td>wR² = 0.0669</td>
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<tr>
<td>R index conventional [1&gt;2sigma(I)]</td>
<td>R1 = 0.0244</td>
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</table>
Crystal structure of [(DAD)Nb(μ-N^Bu)]_2 13, Dr. Klaus Harms

Identification code  215
Habitus, colour  prism, orange red
Crystal size  0.24 x 0.12 x 0.06 mm³
Crystal system  Monoclinic
Space group  P 2₁/n  Z = 2
Unit cell dimensions
\[ a = 10.5864(8) \, \text{Å} \], \[ α = 90° \].
\[ b = 9.6794(9) \, \text{Å} \], \[ β = 99.127(9)° \].
\[ c = 16.5589(12) \, \text{Å} \], \[ γ = 90° \].
Volume  1675.3(2) Å³
Cell determination  7383 peaks with Theta 2.2 to 26°.
Empirical formula  C_{28}H_{58}N_{6}Nb_{2}
Formula weight  664.62
Density (calculated)  1.318 Mg/m³
Absorption coefficient  0.709 mm⁻¹
F(000)  700
Diffractometer type  IPDS1
Wavelength  0.71073 Å
Temperature  193(2) K
Theta range for data collection 2.45 to 25.98°.
Index ranges  -12<=h<=13, -11<=k<=11, -20<=l<=20
Data collection software  STOE Expose
Cell refinement software  STOE Cell
Data reduction software  STOE Integrate
Reflections collected  12939
Independent reflections  3241 [R(int) = 0.0625]
Completeness to theta = 25.00°  99.5 %
Observed reflections  2170[|I>2sigma(I)|]
Reflections used for refinement  3241
Extinction coefficient  X = 0.0018(4)
Absorption correction  Semi-empirical from equivalents
Max. and min. transmission  0.9183 and 0.8961
Largest diff. peak and hole  0.534 and -0.718 e.Å⁻³
Solution  Direct methods
Refinement  Full-matrix least-squares on F²
Treatment of hydrogen atoms  Located, isotropic refinement
Programs used  SHELXS-97 (Sheldrick, 1997)
SHELXL-97 (Sheldrick, 1997)
SHELXTL, STOE IPDS1 software
Data / restraints / parameters  3241 / 0 / 280
Goodness-of-fit on F²  0.832
R index (all data)  wR² = 0.0566
R index conventional [I>2sigma(I)]  R1 = 0.0283
## Crystal structure of [(DAD)Ta(µ-N\(^3\)Bu)]\(_2\) 14, Dr. Klaus Harms

![Crystal structure diagram]

### Identification code
214b

### Habitus, colour
prism, red

### Crystal size
0.52 x 0.09 x 0.08 mm\(^3\)

### Crystal system
Monoclinic

### Space group
P 2\(/\)n \(Z = 2\)

### Unit cell dimensions
- \(a = 10.5643(13) \ \text{Å}\), \(\alpha = 90^\circ\)
- \(b = 9.6955(8) \ \text{Å}\), \(\beta = 98.996(15)^\circ\)
- \(c = 16.534(2) \ \text{Å}\), \(\gamma = 90^\circ\)

### Volume
1672.6(3) \(\text{Å}^3\)

### Cell determination
8000 peaks with Theta 2.2 to 26.2°.

### Empirical formula
\(\text{C}_{28} \text{H}_{58} \text{N}_6 \text{Ta}_2\)

### Formula weight
840.70

### Density (calculated)
1.669 Mg/m\(^3\)

### Absorption coefficient
6.562 mm\(^{-1}\)

### F(000)
828

### Diffractometer type
IPDS1

### Wavelength
0.71073 Å

### Temperature
193(2) K

### Theta range for data collection
2.44 to 25.98°.

### Index ranges
-12<=h<=12, -11<=k<=11, -20<=l<=20

### Data collection software
STOE Expose

### Cell refinement software
STOE Cell

### Data reduction software
STOE Integrate

### Reflections collected
20274

### Independent reflections
3088 \([R(int) = 0.0327]\)

### Completeness to theta = 25.00°
94.7 %

### Observed reflections
2701[\(I>\sigma(I)\)]

### Refinements used for refinement
3088

### Extinction coefficient
\(X = 0.00055(13)\)

### Absorption correction
Gaussian

### Max. and min. transmission
0.5417 and 0.1003

### Largest diff. peak and hole
1.271 and -0.886 e.Å\(^{-3}\)

### Solution
isostructual to Nb-compund

### Refinement
Full-matrix least-squares on F\(^2\)

### Treatment of hydrogen atoms
Me calculated, H1, H2 located, isotropical refinemnet

### Programs used
- SHELXS-97 (Sheldrick, 1997)
- SHELXL-97 (Sheldrick, 1997)
- SHELXTL, STOE IPDS1 software

### Data / restraints / parameters
3088 / 1 / 180

### Goodness-of-fit on F\(^2\)
0.976

### R index (all data)
wR2 = 0.0461

### R index conventional [I>2sigma(I)]
R1 = 0.0190
Chapter VII.

Crystal structure of [(DAD)Ta(N\text{Bu})(NH\text{Bu})]_2, Dr. Klaus Harms

Identification code merk03
Habitus, colour prism, yellow
Crystal size 0.36 x 0.30 x 0.24 mm$^3$
Crystal system Orthorhombic
Space group $P 2_1 2_1 2_1$
Unit cell dimensions
\begin{align*}
    a &= 9.7622(9) \text{ Å} \\
    b &= 11.3808(8) \text{ Å} \\
    c &= 21.1720(16) \text{ Å}
\end{align*}
\begin{align*}
    \alpha &= 90^\circ. \\
    \beta &= 90^\circ. \\
    \gamma &= 90^\circ.
\end{align*}
Volume 2352.2(3) Å$^3$
Cell determination 8000 reflections
Empirical formula $C_{18}H_{39}N_4Ta$
Formula weight 492.48
Density (calculated) 1.391 Mg/m$^3$
Absorption coefficient 4.678 mm$^{-1}$
$F(000)$ 992
Diffractometer type IPDS
Wavelength 0.71073 Å
Temperature 193(2) K
Theta range for data collection 2.03 to 25.00°.
Index ranges $-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-25 \leq l \leq 22$
Data collection software STOE Expose
Cell refinement software STOE Cell
Data reduction software STOE Integrate
Reflections collected 12604
Independent reflections 4133 [R(int) = 0.0561]
Completeness to theta = 25.00° 99.5 %
Observed reflections 2989[1>2sigma(I)]
Reflections used for refinement 4133
Absorption correction Analytical
Max. and min. transmission 0.6290 and 0.3179
Flack parameter (absolute struct.) 0.169(17), inversion twin
Largest diff. peak and hole 0.766 and -0.964 e.Å$^{-3}$
Solution Direct methods, diff. four. synth.
Refinement Full-matrix least-squares on $F^2$
Treatment of hydrogen atoms CH3, CH calc., NH isotr. ref., U(C)=1.5(1.2)*Ueq(C)
Programs used SHELXS-97 (Sheldrick, 1997)
SHELXL-97 (Sheldrick, 1997)
DIAMOND 2.1, STOE IPDS software

Data / restraints / parameters 4133 / 0 / 229
Goodness-of-fit on $F^2$ 0.875
R index (all data) $wR^2 = 0.0653$
R index conventional [1>2sigma(I)] $R1 = 0.0328$
Identification code  merk_28
Habitus, colour  prism, yellow
Crystal size  0.40 x 0.27 x 0.20 mm³
Crystal system  Triclinic
Space group  P -1  Z = 2
Unit cell dimensions  
  a = 11.4782(7) Å  α = 74.751(5)°.  
  b = 11.5640(7) Å  β = 70.059(5)°.  
  c = 14.3591(9) Å  γ = 86.997(5)°.  
Volume  1727.12(18) Å³
Cell determination  30149 peaks with Theta 1.5 to 26.2°.
Empirical formula  C₃₄ H₅₅ N₄ Nb
Formula weight  612.73
Density (calculated)  1.178 Mg/m³
Absorption coefficient  0.374 mm⁻¹
F(000)  656
Diffractometer type  IPDS2
Wavelength  0.71073 Å
Temperature  193(2) K
Theta range for data collection  1.56 to 26.20°.
Index ranges  -14<=h<=14, -14<=k<=14, -17<=l<=17
Data collection software  STOE WinXpose (X-Area)
Cell refinement software  STOE WinCell (X-Area)
Data reduction software  STOE WinIntegrate (X-Area)
Reflections collected  25401
Independent reflections  6906 [R(int) = 0.0357]
Completeness to theta = 26.20°  99.5 %
Observed reflections  6228[I>2sigma(I)]
Reflections used for refinement  6906
Extinction coefficient  X = 0.0027(5)
Absorption correction  Integration
Max. and min. transmission  0.9495 and 0.8749
Largest diff. peak and hole  0.363 and -0.435 e.Å⁻³
Solution  Direct methods
Refinement  Full-matrix least-squares on F²
Treatment of hydrogen atoms  Located, isotropic refinement (minor disorder calc.)
Programs used  SHELXS-97 (Sheldrick, 1997)
WinGX, STOE IPDS2 software
Data / restraints / parameters  6906 / 30 / 571
Goodness-of-fit on F²  1.045
R index (all data)  wR2 = 0.0632
R index conventional [I>2sigma(I)]  R1 = 0.0248
Crystal structure of [(DAD)Ta(NDip)(NHDip)] 4, Dr. Klaus Harms

Identification code merk09
Habitus, colour prism, colourless
Crystal size 0.58 x 0.36 x 0.15 mm³
Crystal system Triclinic
Space group P -1 Z = 2
Unit cell dimensions a = 11.5350(9) Å α = 68.320(6)°.
b = 11.6594(10) Å β = 73.147(6)°.
c = 14.6342(12) Å γ = 85.996(7)°.
Volume 1748.9(2) Å³
Cell determination 38274 peaks with Theta 1.5 to 26.2°.
Empirical formula C_{34}H_{55}N_{4}Ta
Formula weight 700.77
Density (calculated) 1.331 Mg/m³
Absorption coefficient 3.168 mm⁻¹
F(000) 720
Diffractometer type IPDS2
Wavelength 0.71073 Å
Temperature 193(2) K
Theta range for data collection 1.56 to 26.15°.
Index ranges -14<=h<=14, -14<=k<=14, -18<=l<=18
Data collection software STOE WinXpose (X-Area)
Cell refinement software STOE WinCell (X-Area)
Data reduction software STOE WinIntegrate (X-Area)
Reflections collected 23630
Independent reflections 6946 [R(int) = 0.0402]
Completeness to theta = 26.15° 99.2 %
Observed reflections 6393[|I|>2sigma(I)]
Reflections used for refinement 6946
Extinction coefficient X = 0.00096(14)
Absorption correction Integration
Max. and min. transmission 0.6718 and 0.3105
Largest diff. peak and hole 0.495 and -0.581 e.Å⁻³
Solution Direct methods
Refinement Full-matrix least-squares on F²
Treatment of hydrogen atoms Located, isotropic refinement, disordered calc.
Programs used SIR-92 (Giacovazzo et. al., 1992)
SHELXL-97 (Sheldrick, 1997)
SHELXTL, STOE IPDS2 software
Data / restraints / parameters 6946 / 0 / 566
Goodness-of-fit on F² 0.975
R index (all data) wR² = 0.0320
R index conventional [|I|>2sigma(I)] R1 = 0.0138
Crystal structure of \([\text{(DAD)}_2\text{Nb}_2(\text{NAr})_2(\text{N}^\text{Bu})]\) 5, Dr. Klaus Harms

Identification code  mer232
Habitus, colour  prism, orange
Crystal size  0.21 x 0.15 x 0.04 mm\(^3\)
Crystal system  Monoclinic
Space group  \(P \ 2_1\)
Unit cell dimensions  
\[a = 10.3449(8) \ \text{Å}, \quad \alpha = 90^\circ.\]
\[b = 18.5148(16) \ \text{Å}, \quad \beta = 113.334(5)^\circ.\]
\[c = 12.0193(9) \ \text{Å}, \quad \gamma = 90^\circ.\]
Volume  2113.8(3) Å\(^3\)
Cell determination  37288 peaks with Theta 1.8 to 26°.
Empirical formula  \(\text{C}_{36}\text{H}_{49}\text{F}_{10}\text{N}_{7}\text{Nb}_2\)
Formula weight  955.64
Density (calculated)  1.501 Mg/m\(^3\)
Absorption coefficient  0.620 mm\(^-1\)
\(F(000)\)  972
Diffractometer type  IPDS2
Wavelength  0.71073 Å
Temperature  293(2) K
Theta range for data collection  2.15 to 25.00°.
Index ranges  \(-12\leq h\leq 12, -22\leq k\leq 22, -14\leq l\leq 14\)
Data collection software  STOE WinXpose (X-Area)
Cell refinement software  STOE WinCell (X-Area)
Data reduction software  STOE WinIntegrate (X-Area)
Reflections collected  17537
Independent reflections  3744 [\(R(int) = 0.1159\)]
Completeness to theta = 25.00°  50.2 %
Observed reflections  2945[\(I>2\sigma(I)\)]
Reflections used for refinement  3744
Extinction coefficient  \(X = 0.0020(5)\)
Absorption correction  Integration
Max. and min. transmission  0.9706 and 0.8651
Flack parameter (absolute struct.)  -0.01(6)
Largest diff. peak and hole  0.265 and -0.287 e.A\(^{-3}\)
Solution  Direct methods
Refinement  Full-matrix least-squares on \(F^2\)
Treatment of hydrogen atoms  Calculated, riding model
Progrms used

Data / restraints / parameters

Goodness-of-fit on \(F^2\)  0.992
\(R\) index (all data)  \(wR2 = 0.1006\)
\(R\) index conventional [\(I>2\sigma(I)\)]  \(R1 = 0.0445\)
Crystal structure of [(DAD)$_2$Ta$_2$(NAr)$_3$]$_7$, Dr. Klaus Harms

Identification code am32
Habitus, colour prism, colourless
Crystal size 0.30 x 0.21 x 0.15 mm$^3$
Crystal system Monoclinic
Space group P 2$_1$/c, Z = 4
Unit cell dimensions

\[
\begin{align*}
\alpha &= 10.2955(10) \text{ Å} & \beta &= 90.848(11)°. \\
b &= 18.3988(14) \text{ Å} & \gamma &= 90°. \\
c &= 26.625(3) \text{ Å} & \\
\end{align*}
\]

Volume 5042.9(8) Å$^3$
Cell determination 8000 peaks with Theta 1.5 to 26°.
Empirical formula C$_{45}$H$_{48}$F$_{15}$N$_7$Ta$_2$
Formula weight 1333.80
Density (calculated) 1.757 Mg/m$^3$
Absorption coefficient 4.431 mm$^{-1}$
F(000) 2592
Diffractometer type IPDS1
Wavelength 0.71073 Å
Temperature 193(2) K
Theta range for data collection 1.89 to 26.00°.
Index ranges -12<=h<=12, -22<=k<=22, -32<=l<=32
Data collection software STOE Expose
Cell refinement software STOE Cell
Data reduction software STOE Integrate
Reflections collected 39210
Independent reflections 9375 [R(int) = 0.0580]
Completeness to theta = 25.00° 95.5 %
Observed reflections 6975 [I>2sigma(I)]
Reflections used for refinement 9375
Absorption correction Gaussian
Max. and min. transmission 0.5255 and 0.3676
Largest diff. peak and hole 1.172 and -0.787 e.Å$^{-3}$
Solution Direct methods
Refinement Full-matrix least-squares on F$^2$
Treatment of hydrogen atoms Calculated, fixed isotropic U’s
Programs used SIR92 (Giacovazzo et al, 1993)
SHELXL-97 (Sheldrick, 1997)
Diamond 2.1, STOE IPDS1 software

Data / restraints / parameters 9375 / 1 / 622
Goodness-of-fit on F$^2$ 0.884
R index (all data) wR2 = 0.0650
R index conventional [I>2sigma(I)] R1 = 0.0291
Crystal structure of [(DAD)$_2$Ta$_2$(N$^t$Bu)$_2$(NNMe$_2$)$_4$], Dr. Klaus Harms

Identification code  aam54
Habitus, colour  irregular, pale yellow
Crystal size 0.36 x 0.27 x 0.15 mm$^3$
Crystal system  Monoclinic
Space group  P 2$_1$/n  Z = 4
Unit cell dimensions
\[ a = 14.1548(6) \text{ Å} \quad \alpha = 90^\circ. \]
\[ b = 16.1252(5) \text{ Å} \quad \beta = 104.014(3)^\circ. \]
\[ c = 17.6329(7) \text{ Å} \quad \gamma = 90^\circ. \]
Volume 3904.9(3) Å$^3$
Cell determination  46052 peaks with Theta 1.5 to 28.2°.
Empirical formula  C$_{30}$H$_{64}$N$_8$Ta$_2$
Formula weight  898.79
Density (calculated) 1.529 Mg/m$^3$
Absorption coefficient 5.628 mm$^{-1}$
F(000) 1784
Diffractometer type  IPDS2
Wavelength 0.71073 Å
Temperature 193(2) K
Theta range for data collection 1.66 to 28.27°.
Index ranges -18<=h<=18, -21<=k<=21, -19<=l<=23
Data collection software  STOE WinXpose (X-Area)
Cell refinement software  STOE WinCell (X-Area)
Data reduction software  STOE WinIntegrate (X-Area)
Reflections collected 52482
Independent reflections 9624 [R(int) = 0.0313]
Completeness to theta = 25.00° 99.9 %
Observed reflections 7621[I>2sigma(I)]
Reflections used for refinement 9624
Extinction coefficient X = 0.00235(10)
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.3667 and 0.182
Largest diff. peak and hole 1.447 and -0.713 e.Å$^{-3}$
Solution  Direct methods
Refinement  Full-matrix least-squares on F$^2$
Treatment of hydrogen atoms  Me calculated, others located
Programs used  
SHELXS-97 (Sheldrick, 1997)
SHELXL-97 (Sheldrick, 1997)
Diamond 2.1, STOE IPDS2 software
Data / restraints / parameters 9624 / 0 / 398
Goodness-of-fit on F$^2$ 1.015
R index (all data) wR2 = 0.0811
R index conventional [I>2sigma(I)] R1 = 0.0295

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Crystal structure of [(DAD)Nb(N\textsubscript{2}Bu\textsubscript{2}Li\textsubscript{2}] 10, Dr. Klaus Harms

Identification code aam46
Habitus, colour prism, red
Crystal size 0.45 x 0.33 x 0.33 mm\textsuperscript{3}
Crystal system Monoclinic
Space group P 2\textsubscript{1}/c Z = 4
Unit cell dimensions
\begin{align*}
a &= 14.8512(12) \text{ Å} & \alpha &= 90^\circ.
\end{align*}
\begin{align*}
b &= 19.1798(12) \text{ Å} & \beta &= 108.094(9)^\circ.
\end{align*}
\begin{align*}
c &= 19.4306(15) \text{ Å} & \gamma &= 90^\circ.
\end{align*}
Volume 5261.0(7) Å\textsuperscript{3}
Cell determination 8000 peaks with Theta 1.8 to 26°.
Empirical formula C\textsubscript{42} H\textsubscript{90} Li\textsubscript{2} N\textsubscript{8} Ta\textsubscript{2}
Formula weight 1083.00
Density (calculated) 1.367 Mg/m\textsuperscript{3}
Absorption coefficient 4.189 mm\textsuperscript{-1}
F(000) 2200
Diffractometer type IPDS1
Wavelength 0.71073 Å
Temperature 193(2) K
Theta range for data collection 1.79 to 25.99°.
Index ranges -18<=h<=18, -23<=k<=23, -19<=l<=23
Data collection software STOE Expose
Cell refinement software STOE Cell
Data reduction software STOE Integrate
Reflections collected 30869
Independent reflections 10238 [R(int) = 0.0823]
Completeness to theta = 25.00° 99.9 %
Observed reflections 6917[I>2sigma(I)]
Reflections used for refinement 10238
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.537 and 0.3737
Largest diff. peak and hole 1.868 and -1.307 e.Å\textsuperscript{-3}
Solution Direct methods
Refinement Full-matrix least-squares on F\textsuperscript{2}
Treatment of hydrogen atoms H1,H2,H19,H20 refined, others riding
Programs used SHELXS-97 (Sheldrick, 1997)
SHELXL-97 (Sheldrick, 1997)
Diamond 2.1, STOE IPDS1 software
Data / restraints / parameters 10238 / 6 / 524
Goodness-of-fit on F\textsuperscript{2} 0.843
R index (all data) wR2 = 0.0737
R index conventional [I>2sigma(I)] R1 = 0.0356
Crystal structure of [(DAD)Nb(NBu)2Li(dad)] 11, Dr. Klaus Harms

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<th>Parameter</th>
<th>Value</th>
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<td>hexagonal plate, red</td>
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<td>Crystal size</td>
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<td>Space group</td>
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<td>b = 18.9399(10) Å, β = 90°.</td>
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<td>Cell determination</td>
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<td>Empirical formula</td>
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<td>Density (calculated)</td>
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<td>Data reduction software</td>
<td>STOE WinIntegrate (X-Area)</td>
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<td>Reflections collected</td>
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<td>Independent reflections</td>
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<td>Observed reflections</td>
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<td>Reflections used for refinement</td>
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<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<td>Max. and min. transmission</td>
<td>0.9849 and 0.9276</td>
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<td>Largest diff. peak and hole</td>
<td>0.391 and -0.349 e.A⁻³</td>
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<td>Solution</td>
<td>Direct methods</td>
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<td>Refinement</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Treatment of hydrogen atoms</td>
<td>Calcul. positions, fixed isotr. U's, H7, H12 located, refined</td>
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<td>Programs used</td>
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<td>SHLEXL-97 (Sheldrick, 1997)</td>
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<td>WinGX, Diamond 2.1, STOE IPDS2 software</td>
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<td>Goodness-of-fit on F²</td>
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<td>R index (all data)</td>
<td>wR2 = 0.0738</td>
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<tr>
<td>R index conventional [</td>
<td>I</td>
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</table>
Chapter IX.

Crystal structure of [Ta(N^tBu)(NH^tBu)Cl_2Py_2]_2, Dr. Klaus Harms

Identification code  merk10
Habitus, colour  plate, colourless
Crystal size  0.21 x 0.12 x 0.09 mm^3
Crystal system  Monoclinic
Space group  C c c Z = 4
Unit cell dimensions
\[ a = 11.7720(15) \, \text{Å} \quad \alpha = 90^\circ. \]
\[ b = 16.1797(14) \, \text{Å} \quad \beta = 91.122(10)^\circ. \]
\[ c = 15.9663(19) \, \text{Å} \quad \gamma = 90^\circ. \]
Volume  3040.5(6) Å^3
Cell determination  14296 peaks with Theta 2.1 to 26°.
Empirical formula  \( \text{C}_{26}\text{H}_{45}\text{Cl}_2\text{N}_4\text{O}_2\text{Ta} \)
Formula weight  697.51
Density (calculated)  1.524 Mg/m^3
Absorption coefficient  3.819 mm\(^{-1}\)
F(000)  1408
Diffractometer type  IPDS2
Wavelength  0.71073 Å
Temperature  193(2) K
Theta range for data collection 2.14 to 25.00°.
Index ranges  -13<=h<=13, -18<=k<=19, -18<=l<=18
Data collection software  STOE WinXpose (X-Area)
Cell refinement software  STOE WinCell (X-Area)
Data reduction software  STOE WinIntegrate (X-Area)
Reflections collected  9047
Independent reflections  4769 [R(int) = 0.0361]
Completeness to theta = 25.00°  99.6 %
Observed reflections  4224[I>2sigma(I)]
Reflections used for refinement  4769
Extinction coefficient  \( X = 0.00066(10) \)
Absorption correction  Integration
Max. and min. transmission  0.5457 and 0.3097
Flack parameter (absolute struct.)  0.55(3) , "racemic twin"
Largest diff. peak and hole  1.564 and -3.466 e Å\(^{-3}\)
Solution  Direct methods
Refinement  Full-matrix least-squares on F^2
Treatment of hydrogen atoms  Calculated, N-H located
Programs used  SHELXS-97 (Sheldrick, 1997)
SHELXL-97 (Sheldrick, 1997)
SHELXTL, STOE IPDS2 software
Data / restraints / parameters  4769 / 278 / 328
Goodness-of-fit on F^2  1.090
R index (all data)  wR2 = 0.1142
R index conventional [I>2sigma(I)]  R1 = 0.0441