A Dibismuthane with Olefin Functional Groups: Towards Tridentate Hybrid Chalcogen/Olefin Ligands

Felix Geist,[a] Sebastián Martínez,[a] Jacqueline Ramler,[a] Kai Oberdorf,[a] Lisa Brändler,[b] Sascha Reith,[a] and Crispin Lichtenberg*[a]

Bis[dibenzobismepine], a dibismuthane composed of two bismepine units (R$_2$Bi–BiR$_2$), was synthesized and fully characterized (R$_2$=(C$_6$H$_4$CH)$_2$). Reactions of this dibismuthane with diphenyl dichalcogenides, dibenzoylperoxide, and elemental chalcogens have been investigated. All products of these reactions have been isolated and fully characterized, including a series of compounds R$_2$Bi–E–BiR$_2$ (E=O–Te). These species contain two olefin units of the bismepine moieties and a chalcogen atom as potential coordination sites. The potential of these species to act as hybrid tridentate chalcogen/olefin ligands with bismuth atoms as structure-determining elements in the backbone has been investigated by theoretical approaches, aiming at the complexation of Co^I, Rh^I, Ir^I and Ni^0, Pd^0, Pt^0. The analytical techniques applied in this work include heteronuclear and 2D NMR spectroscopy, elemental analysis, single-crystal X-ray diffraction analysis, and DFT calculations.

Introduction

The coordination of olefin moieties to transition metal atoms plays an important role in many processes such as the polymerization,[1] hydrogenation,[2] and functionalization of unsaturated hydrocarbons.[3] In most of these processes, the olefin ligand is activated by the transition metal center through coordination, undergoes a chemical transformation and subsequently dissociates from the metal. Olefin ligands also play an important role in catalyst precursors for asymmetric catalysis and in precursors for the synthesis of various transition metal complexes. The latter approach benefits from the lability of olefin ligands and their facile replacement by other ligands through ligand exchange reactions and from the removal of volatile olefins such as ethylene providing an additional driving force.[4] The potential application of olefin ligands as spectator ligands which stay coordinated to the metal atom during the catalytic process and influence the catalytic properties of the complex has only more recently moved into the focus of research activities. Most of this work has focused on chiral diene ligands and their application in asymmetric catalysis due to the higher stability of diolefin complexes in comparison to mono-olefin complexes.[5] A variety of Rh and Ir complexes with chiral diene ligands derived from bicyclic hepta- or octadienes (Scheme 1; I) have been synthesized and used in asymmetric catalysis, for example the asymmetric addition of organoboron reagents to enones[6] or imines.[7] The combination of olefins with heteroatom-containing functional groups, mainly amines and phosphanes (Scheme 1; II), has led to new classes of ligands. While the heteroatom ensures sufficiently strong binding to the metal atom, the olefin unit can be used to introduce chirality and fine-tune the electronic properties of the metal center. In this context, it is important to note that the (de-)coordination of electron-accepting olefin ligands can also respond to the varying electronic needs of a transition metal center in the different steps of a catalytic cycle. This class of ligands has shown promising results in the rhodium-catalyzed asymmetric conjugate addition of arylboronic acids to α,β-unsaturated carbonyl compounds, in some cases even outperforming established phosphane-based ligands.[8] Although less examples are known for sulfur-containing olefin hybrid ligands, they have also shown promising results in similar reactions.[9] In addition to catalysis, research of diolefin ligands and their coordination properties has led to remarkable findings in other fields of molecular chemistry: rhodium complexes with
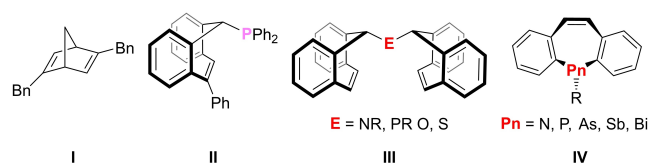
[a] F. Geist, Dr. S. Martínez, Dr. J. Ramler, Dr. K. Oberdorf, S. Reith,
Prof. Dr. C. Lichtenberg
Department of Chemistry
Philipps-University Marburg
Hans-Meerwein-Straße 4
35043 Marburg (Germany)
E-mail: crispin.lichtenberg@chemie.uni-marburg.de

[b] L. Brändler
Institute of Inorganic Chemistry
Julius-Maximilians-University Würzburg
Am Hubland
97074 Würzburg (Germany)

Scheme 1. Selected diolefin and hybrid olefin/E ligands (I–III) and group 15 dibenzoheteropines (IV).

EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202300415

Chemistry Europe
European Chemical
Societies Publishing

amine-bridged diolefin ligands based on tropolone of the type trop$_2$NR (R=H, Me; trop = 5H-dibenzo[a,d]cylo-hepten-5-yl; Scheme 1; **III**) have enabled the first isolation of a stable metal aminyl radical complex[10] and the heterolytic splitting of H$_2$ across a Rh—N bond.[11] Further variations of this ligand motif have been reported (Scheme 1, **III**; E=PR, O, S).[12]

Based on these results, dibenzoheteropines containing group 15 elements could be an interesting class of hybrid olefin ligands (**IV**, Scheme 1). While the coordination of the olefin moiety of dibenzoazepines to various main group and transition metals has been investigated,[13] coordination compounds of their heavier homologues have remained rare. In the case of dibenzophosphepines, coordination of the olefin moiety to Rh has been observed,[14] while for dibenzoarsepines only the coordination to Au through the arsenic atom has been described.[15] Coordination compounds of dibenzostibepines have remained elusive. The first coordination compounds involving dibenzobismepines were only recently described by our group. The reaction of a cationic dibenzobismepine with a pyrazolide substituted Os^{II} complex led to a Lewis acid/base adduct between the bismepine and one nitrogen atom of the pyrazolide ligand, however no interactions between the bismepine fragment and the Os atom were observed due to steric bulk.[16] More recently we have shown that neutral dibenzobismepines can act as rigid, ditopic arene donors towards Tl$^+$, ligating the soft Lewis acid Tl$^+$ through arene→Tl$^+$ bonding, supported by weak olefin→Tl$^+$ interactions. DFT calculations showed that the incorporation of Bi (instead of N—Sb) into the heteropine ligand framework makes the coordination more favorable through electronic factors.[17] The potential to fine-tune the character of ligands by incorporating bismuth atoms, which do not directly interact with the central atom, has previously been shown in studies by the groups of Wright and García-Rodríguez using tripodal tris(pyridyl)[18–20] and tris(quinolyl)[21] ligands. Coinage metal complexes of those ligands have shown interesting properties, such as unusual coordination modes,[21] novel supramolecular assemblies,[20] and an increased radical contribution in the Cu(I) catalyzed aziridination of alkenes.[18] With these results in mind, we became interested in the synthesis of novel dibenzobismepines which allow for the facile installation of a set of functional groups, thereby creating a new family of potential hybrid olefin/heteroatom ligands.

Results and Discussion

A set of dibenzobismepines, including a dinuclear bismepine, halobismepines, and cationic bismepines, have recently been described by our group,[22] including the investigation of their soft Lewis acidity[23] and their exploitation as rigid, ditopic arene donor ligands.[17] Our next goal was the synthesis of bis[dibenzobismepine] (**2**), a dibismuthane featuring two dibenzobisempine units (for a Lewis formula see Scheme 2). Two olefin moieties and four arene groups, potential donor functionalities towards metal centers, and a weak bismuth-bismuth bond, which allows for further functionalization, make this
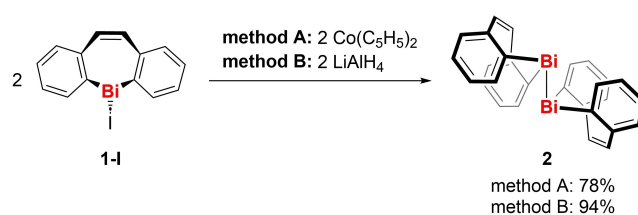

Scheme 2. Synthesis of dibismuthane 2.

compound an interesting starting point to further explore the potential of bismepines in coordination chemistry. The reduction of alkoxy substituted diarylbismuth compounds using phenylsilane, which was recently employed in the synthesis of a similar dibismuthane,[24] proved unsuccessful for the preparation of **2**. Similarly, attempts to reduce the iodine substituted bismepine **1-I** with a triethylborohydride salt (LiBHEt$_3$, Super-Hydride®), a strategy that had been successful for the synthesis of some dibismuthanes,[25,26] did not yield the desired product. The ^{1}H NMR spectrum of the crude reaction mixture showed a set of signals for the dibenzobismepine backbone in the aromatic region and one set of signals in the aliphatic region, which was assigned to a bismuth-bound ethyl group. This indicates that an ethyl group, instead of a hydride, was transferred from the borate anion to the bismuth atom. This uncommon reactivity of triethylborohydride salts has previously been observed in rare cases, for example in the reaction of [BiCl{Mo(CO)$_3$Cp}$_2$] with KBHEt$_3$.[27]

The reduction of iodobismepine **1-I** with lithium aluminium hydride or cobaltocene gave access to bis[dibenzobismepine] (**2**), which could be isolated in good to excellent yields as an orange solid (Scheme 2). ^{1}H NMR spectra of **2** in THF-d$_8$ and CD$_2$Cl$_2$ show the expected signal pattern for the benzo groups and one singlet in the olefinic region for the two olefin units. ^{13}C NMR spectra of **2** are in agreement with the suggested structure. The resonance of the ipso-carbon atoms shows significant broadening, which can be attributed to quadrupolar line broadening induced by the neighboring ^{209}Bi nucleus. Dibismuthane **2** crystallizes in the monoclinic space group P2$_1$/c with Z = 4 (Figure 1).

The crystal structure of **2** shows the two dibenzobismepine units in the expected boat conformation and the bismuth atoms in trigonal-pyramidal coordination geometries. In contrast to other dibismuthanes, **2** does not show thermochromic behavior in the solid state which may be explained by the absence of intermolecular Bi···Bi interactions.[28] The bismuth-bismuth bond length of 2.901(7) Å is at the lower end of the range of Bi–Bi distances reported for other aryl substituted dibismuthanes (2.986(7)–3.087(3) Å).[24,26,29] Short Bi1···C7/C8 distances of 3.38(1)–3.403(9) Å, which is ca. 10% below the sum of the van der Waals radii (3.77 Å),[30] suggest weak Bi···olefin interactions, which have previously been described for halobismepines **1-X** (X=Cl, Br, I).[22]

Dibismuthanes are known to react with diorganodichalcogenides with cleavage of the two element-element bonds and formation of a bismuth-chalcogen bond.[31–34,35] Reactions
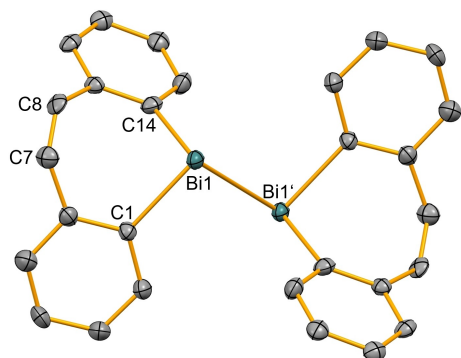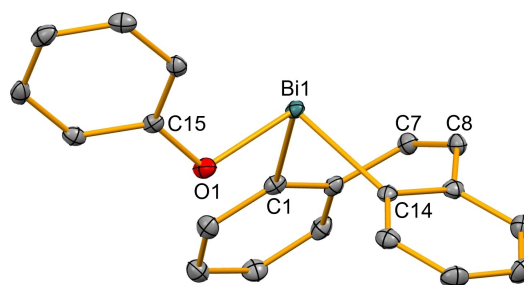
Figure 1. a) Molecular structure of **2** in the solid state. Displacement ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), interatomic distances (Å), and bond angles (deg): Bi1–Bi1′, 2.9801(7); Bi1–C1, 2.259(9); Bi1–C14, 2.268(9); Bi1⋯C7, 3.38(1); Bi1⋯C8, 3.403(9); C1–Bi1–C14, 90.4(3); C1–Bi1–Bi1′, 94.7(2).

between dibismuthane **2** and diphenyl dichalcogenides PhE–EPh (E=S, Se, Te) led to a series of phenyl chalcogenide-substituted bismepines (**3-E**, E=S, Se, Te). To complete the series, the analogous phenoxy-substituted bismepine **3-O** was prepared by salt elimination of halobismepine **1-I** with potassium phenolate. Compounds **3-E** were isolated in moderate to good yields as white (E=O), pale yellow (E=S, Se) or orange (E=Te) solids and fully characterized.
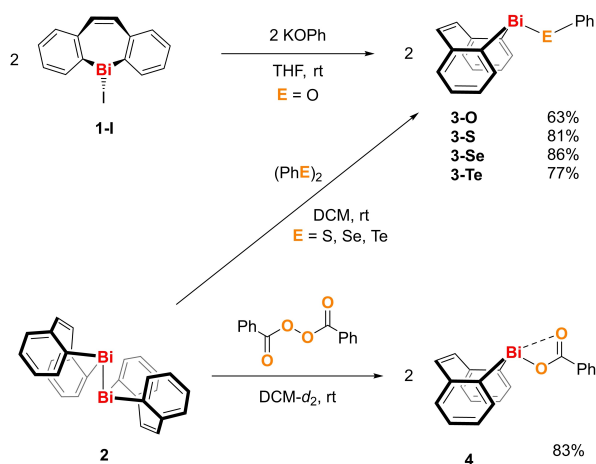
Scheme 3. Syntheses of compounds **3-E** (E=O, S, Se, Te) and **4**.

While reactions between dibismuthanes and diorgano dichalcogenides have been described for a variety of differently substituted compounds,[31–34] the analogous reaction between a dibismuthane and a peroxide has not been reported, yet, to the best of our knowledge. Addition of dibenzoyl peroxide to a solution of **2** resulted in an immediate discoloration of the previously orange solution and NMR spectroscopic analysis revealed the selective formation of a new bismepine species. Layering of the solution with *n*-pentane and storage at −30 °C led to the formation of colorless crystals which were identified as the benzoate-substituted bismepine **4** (Scheme 3). Compound **4** was isolated in a good yield (83%) and fully characterized. The ^{1}H and ^{13}C NMR spectra of compounds **3-E** and **4** are in agreement with the suggested structures. The ^{77}Se NMR spectrum of **3-Se** shows a singlet at 175.70 ppm and the ^{125}Te NMR spectrum of **3-Te** shows a singlet at 170.17 ppm. These chemical shifts are similar to those reported for the related compounds [Bi(C$_6$H$_4$CH$_2$)$_2$S(EPh)] (E=Se, 183.70 ppm; E=Te, 141.10 ppm).[24] Like dibismuthane **2**, compounds **3-E** crystallize in the monoclinic space group $P2_1/c$ with Z=4 (**3-O** is shown as a representative example in Figure 2). Selected bonding parameters are summarized in Table 1. The molecular structures of compounds **3-E** show the bismuth atoms in trigonal-pyramidal coordination geometries (C–Bi–C/E, 85.72(7)–93.40(7)°), when weak Bi⋯olefin and Bi⋯arene interactions are not taken into consideration (*vide infra*). The Bi–C bond lengths are in the range of 2.203(8)–2.2362(19) Å, which is similar to those in previously reported dibenzobismepines.[22]
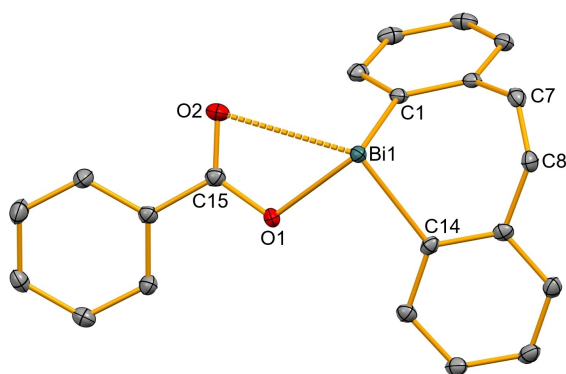

Figure 2. Molecular structure of **3-O** in the solid state as a representative example of compounds **3-E** (for graphical representations of the molecular structures of **3-S**, **3-Se**, and **3-Te**, see Supp. Inf.). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and one lattice bound benzene molecule are omitted for clarity. Bond parameters are summarized in Table 1.

Table 1. Summary of the bonding parameters in compounds **3-E** and **4** (bond lengths and interatomic distances in angstroms, angles in degrees).

	3-O	3-S	3-Se	3-Te	4
Bi1–E1	2.1460(13)	2.5420(19)	2.6686(7)	2.8559(2)	2.2097(15)
Bi1⋯E2	–	–	–	–	2.883(2)
Bi1–C1	2.2362(19)	2.203(8)	2.248(6)	2.250(3)	2.242(2)
Bi1–C14	2.2316(18)	2.243(7)	2.232(6)	2.248(3)	2.244(2)
Bi1⋯C7	3.283(2)	3.359(8)	3.404(7)	3.425(4)	3.191(2)
Bi1⋯C8	3.258(2)	3.387(8)	3.383(7)	3.410(3)	3.206(2)
C1–Bi1–C14	85.72(7)	90.3(3)	90.5(2)	91.10(11)	87.83(8)
C1–Bi1–E1	90.46(6)	93.13(18)	93.36(15)	93.40(7)	99.42(7)

The Bi–E bond lengths in compounds **3-E** are similar to those in previously reported aryl-substituted bismuth chalcogenides.[24,32,36] Weak intramolecular interactions between the bismuth atoms and olefin moieties are suggested by Bi···C7/C8 distances of 3.258(2) to 3.425(4) Å. These distances are slightly larger than those in halobismepines **1-X** (3.20–3.25 Å)[22] and steadily increase with increasing atomic number of the chalcogen atom in **3-E**, reflecting the decreasing ability of the σ*(Bi–E) orbital to effectively accept electron density from the olefin donor. In addition to intramolecular Bi···olefin interactions, intermolecular Bi···arene interactions can be found in the solid state structures of compounds **3-E**. In **3-O**, the bismuth atom is coordinated by one benzo group of a neighboring dibenzobismepine unit (Bi1···ct(C1′–C6′), 3.371 Å; ct indicates the centroid of a benzo group) and the phenoxy group of an additional molecule (Bi1···ct(C15″–C20″), 3.700 Å), leading to the formation of a three-dimensional coordination polymer in the solid state (see Supp. Inf.). **3-S**, **3-Se** and **3-Te** are isostructural and show interactions between the bismuth atom and one arene group of a neighboring dibenzobismepine unit (Bi1···ct(C1′–C6′), 3.513–3.572 Å), which leads to the formation of dimeric structures (a graphical representation can be found in the supporting information).

Compound **4** crystallizes in the orthorhombic space group *Pbca* (Z = 8). Its molecular structure in the solid state is shown in Figure 3, and selected bonding parameters are presented in Table 1. The benzoate group in **4** acts as a strongly asymmetric bidentate ligand with one Bi–O bond being considerably shorter (Bi1–O1, 2.2097(15) Å) than the other (Bi1–O2, 2.883(2) Å). The Bi1···C7/8 distances in **4** (3.191(2)/3.206(2) Å) are the shortest found for dibenzobismepines so far. Each bismuth atom in the solid state structure of **4** is additionally coordinated by the oxygen atom O1′ of a neighboring molecule (Bi1···O1′; 3.308 Å) and one benzo unit (Bi1···ct(C1″–C6″; 3.565 Å) of another neigboring molecule, which leads to the formation of a one dimensional coordination polymer along the crystallographic *a*-axis (for details see Supp. Inf.). In the ¹H NMR spectrum of **4**, the resonances assigned to the protons of the benzoate ligands are slightly broadened which might be due to a fluxional coordination of the benzoate ligand in solution.
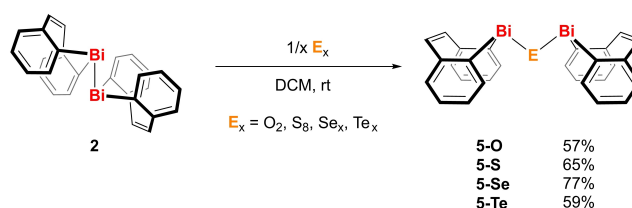
The reaction of dibismuthanes with elemental chalcogens usually leads to the insertion of one chalcogen atom into the bismuth-bismuth bond, which has been used for the synthesis of a variety of differently substituted chalcogen-bridged bismuth compounds.[33,37] More recently, the generation of a peroxo species[38] and the insertion of sulfur chains S_n (n = 3, 5) into the bismuth-bismuth bond have also been described.[26] The reluctance of aryl-substituted dibismuthanes to react with elemental tellurium has previously been noted.[32,33] Remarkably, simple exposure of a solution of dibismuthane **2** to air gave analytically pure **5-O** (Scheme 4). Along these lines, addition of stoichiometric amounts of elemental sulfur, (grey) selenium and tellurium completed this series of dinuclear bismepine complexes (**5-E**) containing a Bi–E–Bi unit (E = O, S, Se, Te; Scheme 4).
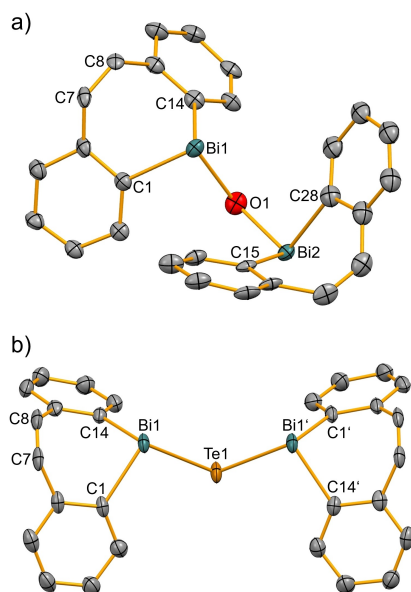
When an excess of S_8 (3 equiv.) was added to a solution of **2** in CD_2Cl_2, ¹H NMR spectroscopy revealed the formation of **5-S** as the only product. No signs for the insertion of multiple sulfur atoms into the Bi–Bi bond could be found. While a lack of reaction between Ph_2Bi–$BiPh_2$ and Te and a rapid degradation of Mes_2Bi–Te–$BiMes_2$ have previously been reported, both of these observations could not be made during the synthesis and analysis of **5-Te**.[32,39] Compounds **5-E** were isolated in moderate yields as white (E = O, S), pale yellow (E = Se) or yellow (E = Te) solids and fully characterized. The ¹H and ¹³C NMR spectra of the insertion products show resonances typical of a benzo group and a singlet in the olefinic region, which suggests an apparent C_{2v} symmetry in solution. In contrast to compounds **3-Se** and **3-Te**, the expected ⁷⁷Se and ¹²⁵Te NMR resonances of **5-Se** and **5-Te** could not be detected via standard 1D- or more sensitive 2D- (¹H,⁷⁷Se)- or (¹H,¹²⁵Te)-HMQC experiments. This can be rationalized by the expectedly small $^4J_{HX}$ coupling (X = Se, Te) and once again by the presence of two adjacent ²⁰⁹Bi nuclei, which induce significant quadrupolar line broadening.

Single-crystals of compounds **5-E** were obtained by recrystallization from benzene/*n*-pentane (E = O, S) or THF/*n*-pentane (E = Se, Te) solvent mixtures at −30 °C. The molecular structures of **5-O** and **5-Te** are shown in Figure 4, and selected bonding parameters are given in Table 2. Compound **5-O** crystallizes in the triclinic space group $P\bar{1}$ with Z = 2. **5-S** crystallizes in the monoclinic space group $P2_1/n$ with Z = 4. Compounds **5-Se** and **5-Te** are isostructural and crystallize in the monoclinic space group *C2/c* (Z = 4). All bismuth atoms in compounds **5-E** show a trigonal pyramidal coordination geometry (C–Bi–C/E, 86.3(5)–96.38(13)°). The Bi–E–Bi units are bent with the Bi–E–Bi angle successively decreasing from 129.5(6)° (E = O) to 96.90(13)° (E = Te). Together with the varying Bi–E bond lengths, which are

Figure 3. Molecular structure of **4** in the solid state. Displacement ellipsoids are shown at the 50 % level. Hydrogen atoms are omitted for clarity. Bond parameters are summarized in Table 1.

Scheme 4. Synthesis of chalcogen bridged bismepines **5-E**.

5-O	57%
5-S	65%
5-Se	77%
5-Te	59%

$E_x = O_2, S_8, Se_x, Te_x$

1/x E_x

DCM, rt

EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202300415

Chemistry
Europe
European Chemical
Societies Publishing

Figure 4. Molecular structures of compounds **5-O** (a) and **5-Te** (b) in the solid state. Displacement ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity. Bond parameters are summarized in Table 2.

Table 2. Summary of the bonding parameters in compounds **5-E** (bond lengths and interatomic distances in angstroms, angles in degrees).

	5-O	5-S	5-Se	5-Te
Bi1–E1	2.104(14)	2.5326(12)	2.6686(7)	2.8666(5)
Bi1–C1	2.244(19)	2.244(4)	2.251(8)	2.260(5)
Bi1–C14	2.298(19)	2.246(4)	2.257(8)	2.262(5)
Bi1···C7	3.33(2)	3.359(5)	3.249(8)	3.251(5)
Bi1···C8	3.35(2)	3.358(5)	3.250(8)	3.256(5)
Bi1–E1–Bi2/Bi1′	129.5(6)	104.80(4)	98.53(4)	96.90(13)
C1–Bi1–E1	92.8(6)	92.54(11)	96.0(2)	96.38(13)

similar to those in related compounds of the type $(R_2Bi)_2E$,[39,40] this gives a broad set of geometric parameters, which should provide a valuable platform for the future exploration of **5-E** as ligands towards transition metal atoms (*vide infra*).

The Bi–C bond lengths in compounds **5-E** closely resemble those in the starting material **2** and other previously reported dibenzobismepines.[22,23] Interatomic Bi1···C7/C8 distances of 3.249(8)–3.359(5) Å suggest the presence of weak Bi···olefin interactions. The main difference between the molecular solid state structures of **5-O** and its heavier homologues is the orientation of the two dibenzobismepine units. When viewed along an axis through the two bismuth atoms, the orientation of the carbon substituents at bismuth can be described as *anti*-periplanar in **5-O** or *syn*-periplanar in compounds **5-S**, **5-Se** and **5-Te**. A similar trend has been described for the analogous mesityl-substituted compounds $(Mes_2Bi)_2E$ (E=O, S, Se; Mes = 2,4,6-$Me_3C_6H_2$), where it was attributed to different intermolecular interactions.[39] Similarly, the intermolecular interactions in the solid state structures of compounds **5-E** are quite diverse. In **5-O**, one bismuth atom is coordinated by the oxygen atom of a

neighboring molecule (Bi1–O1′, 3.405 Å), while the second bismuth atom is coordinated by two arene units of a third molecule (Bi2···ct(C15′/23′–C20′/28′), 3.460/3.423 Å), leading to the formation of a one-dimensional coordination polymer along the crystallographic *a*-axis (Supp. Inf.). The solid state structure of **5-S** shows dimeric motifs, which are formed through two arene-arene interactions between neighboring molecules (Supp. Inf.). In the isostructural compounds **5-Se** and **5-Te** each bismuth atom is coordinated by the chalcogen atom of a neighboring molecule, which leads to the formation of one-dimensional coordination polymers along the crystallographic *b*-axes (Supp. Inf.).
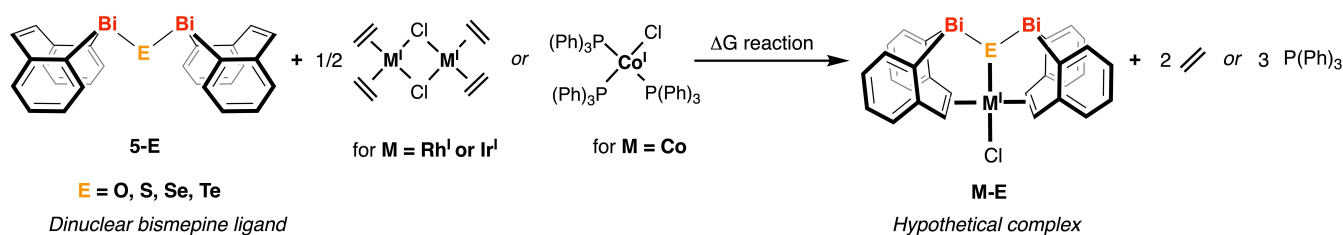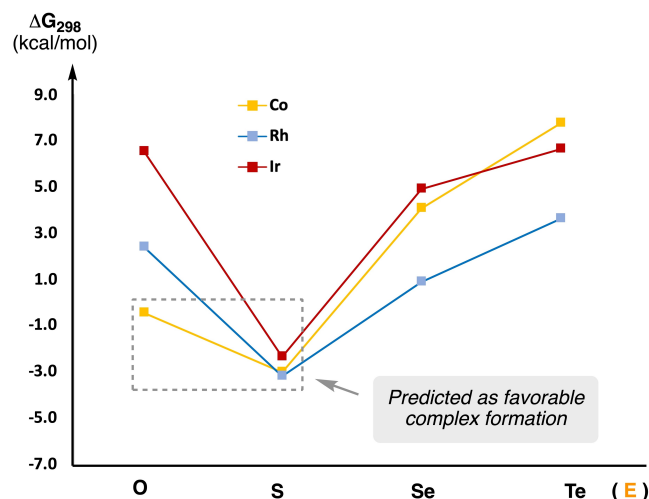
Density Functional Theory Studies

In order to evaluate the feasibility of the dinuclear bismepine compounds **5-E** to act as ligands in transition metal complexes, we performed a computational investigation, aiming at the identification of suitable combinations of such bismuth-based ligands and transition metals. We commenced the study considering the formation of hypothetical complexes from commercially available transition metal precursors of the series Co[I], Rh[I] and Ir[I], as detailed in the reaction equation presented in Figure 5a. Our study shows that the formation of Co, Rh, and Ir chlorido complexes with the sulfur-containing dinuclear bisme-pine **5-S** is thermodynamically favorable (Figure 5b,d). More-over, we predict that the formation of the complex **Co-O** from **5-O** and the cobalt precursor is slightly favorable. The remaining combinations of group 9 metal precursors and ligands **5-E** did not lead to thermodynamically favorable product formation according to the reactions shown in Fig-ure 5a. It should be noted, however, that the removal of ethylene as a volatile by-product gives an additional handle to push the reactions towards the desired complex formation, when starting from the proposed rhodium and iridium precursors.

In order to gain insights into the factors making **5-S** the most promising ligand in the series that was investigated, we studied electronic and geometric parameters. The M–E inter-action energies were investigated by second order perturbation analyses within the context of NBO studies, but did not show a clear trend, i.e. the M–S interaction energies were not more favorable than the other M–E interaction energies (E=O, Se, Te; Supp. Inf.). This makes the M–E interactions as electronic parameters unlikely to be decisive for the trends observed in thermodynamic stabilities. In order to evaluate the relevance of geometric parameters during complex formation, we deter-mined the energy that is necessary to bring each ligand from its ground state conformation to the conformation it adopts in the metal complex (i.e. the preparation energy of the ligand). Here, the results show a minimum of preparation energy being required for **5-S** in each series of metal complexes (Figure 5c and Supp. Inf.).
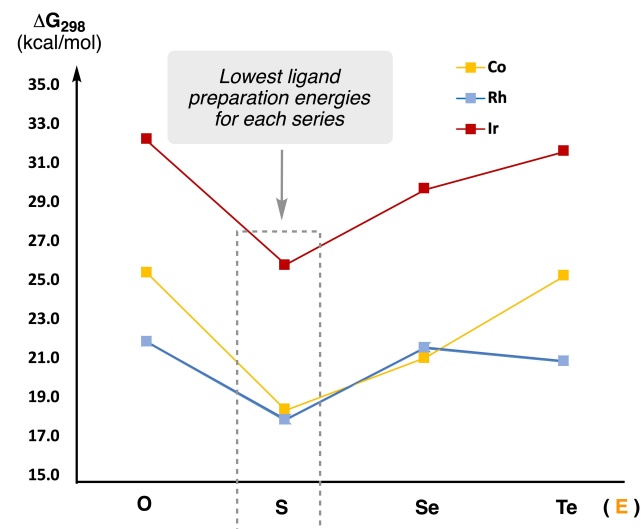
In addition, we investigated the thermodynamic parameters for the formation of a series of hypothetical Ni, Pd, and Pt complexes featuring the bismepine ligands **5-E** in a similar

EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202300415

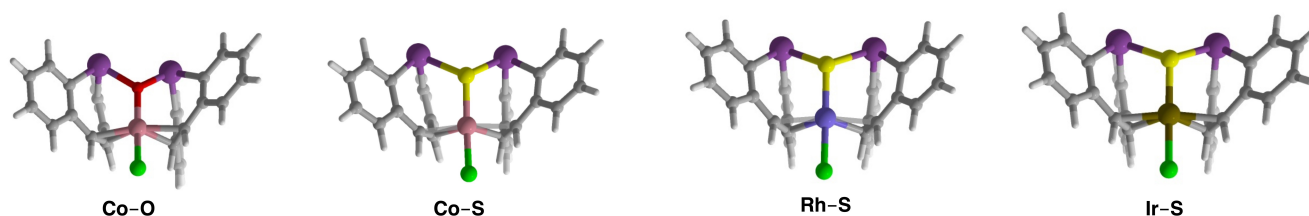**Chemistry Europe**
European Chemical Societies Publishing

Figure 5. Evaluation of dinuclear bismepine compounds **5-E** as ligands in transition metal complexes of Co, Rh and Ir.

approach. However, our study predicts that in most cases the ligands will react via oxidative addition of a Bi–E bond to the group 10 metal center instead of forming the targeted compounds.[41] Therefore, combinations of the bismuth ligands **5-E** and electron rich Ni, Pd, or Pt centers do not appear to be promising without further modifications, if the ligand framework is meant to be kept intact (see Supp. Inf. for details).

Conclusions

In summary, bis[dibenzobismepine], a dibismuthane featuring two dibenzobismepine units with olefinic functional groups has been synthesized and fully characterized. Reactions between the dibismuthane and diphenyl dichalcogenides, as expected,

led to a series of phenyl chalcogenide-substituted bismepines, which was completed by rational synthesis of the phenoxy-substituted derivate *via* salt elimination. We have shown for the first time that this reactivity pattern can be expanded to peroxides, furnishing a benzoate substituted bismepine. Exposure of bis[dibenzobismepine] to air or reactions with the elemental chalcogens sulfur, selenium and tellurium led to the insertion of one chalcogen atom into the bismuth-bismuth bond. The resulting products $(R_2Bi)_2E$ (**5-E**) were isolated and fully characterized (E$=$O–Te; $R_2Bi=$ dibenzobismepinyl). Their potential as hybrid tridentate olefin/chalcogen ligands towards transition metals of group 9 and 10 was explored by DFT calculations. As a result, we predict that in the series of compounds **5-E**, the sulfur species **5-S** is a privileged ligand for the complexation of Co^I, Ir^I, and Rh^I due to its geometric

Eur. J. Inorg. Chem. **2023**, *26*, e202300415 (6 of 10)

© 2023 The Authors. European Journal of Inorganic Chemistry published by Wiley-VCH GmbH

EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202300415

Chemistry Europe
European Chemical
Societies Publishing

parameters, promising the experimental accessibility of such complexes. It is anticipated that these findings will inspire the design, synthesis, and utilization of transition metal complexes exploiting these and related ligands with uncommon structural motifs.

Experimental Section

All air- and moisture sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in gloveboxes containing an atmosphere of purified argon. Solvents were degassed and purified according to standard laboratory procedures.

NMR spectra were recorded on Bruker instruments operating at 400 or 500 MHz with respect to ^1H. ^1H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using the residual ^1H and ^{13}C chemical shifts of the solvent as a secondary standard. ^{77}Se and ^{125}Te NMR chemical shifts are reported relative to $SeMe_2$ (plus 5% C_6D_6) and $TeMe_2$ (plus 5% C_6D_6) as external standards. NMR spectra were recorded at ambient temperature (typically 300 K), if not otherwise noted. Elemental analyses were performed on a Vario Micro Cube by Elementar Analysesysteme GmbH. Crystal data were collected either on a Bruker Apex II diffractometer with a CCD area detector and a multi-mirror monochromator or on a Bruker D8-QUEST diffractometer with a CCD area detector and multi-mirror monochromator using MoKα radiation (λ = 0.71073 Å). The respective solid-state structures were solved using intrinsic phase methods (ShelXT), refined with the ShelX software package and developed using Fourier techniques.[42] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions.

Deposition Numbers 2278294 (for **2**), 2278295 (for **3-O**), 2278296 (for **3-S**), 2278297 (for **3-Se**), 2278298 (for **3-Te**), 2278299 (for **4**), 2278300 (for **5-O**), 2278301 (for **5-S**), 2278302 (for **5-Se**), 2278303 (for **5-Te**), 2278304 (for **SI-1**), and 2278305 (for **SI-2**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

The images of the solid-state structures were created with the Mercury software. Compound **1-I** was synthesized according to a modified literature procedure (a detailed protocol can be found in the supporting information).[22] The following labeling scheme was used for reporting NMR chemical shifts:
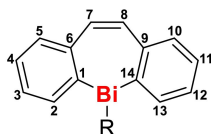
Bis[dibenzobismepine] (2): *Method A:* **1-I** (150 mg, 292 μmol) was dissolved in THF (8 mL), the solution cooled to −78 °C and a solution of $LiAlH_4$ (13 mg, 350 μmol) in THF (5 mL) was added dropwise. The reaction mixture was stirred for 1 h at −78 °C, slowly warmed to ambient temperature, and the solvent was removed under reduced pressure. The residue was dissolved in toluene (10 mL), filtrated, layered with *n*-pentane (10 mL) and stored at −30 °C. After a week the product had precipitated as an orange solid which was isolated by filtration, washed with *n*-pentane (3× 2 mL) and dried in vacuo. **Yield**: 88 mg (114 μmol, 78%). *Method B:* **1-I** (500 mg, 973 μmol) was dissolved in THF (8 mL) and a solution of cobaltocene (184 mg, 973 μmol) in THF (3 mL) was added. The

reaction mixture was filtered, the filtrate layered with *n*-pentane (11 mL) and stored at −30 °C. After 16 h the product had precipitated as an orange solid which was isolated by filtration, washed with *n*-pentane (3×4 mL) and dried in vacuo. **Yield**: 355 mg (458 μmol, 94%). ^1H **NMR** (400 MHz, THF-d_8): δ = 6.59 (s, 4H, *H*-7, *H*-8), 7.04–7.12 (m, 8H, *H*-3, *H*-4, *H*-11, *H*-12), 7.19 (dd, 4H, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.8 Hz, *H*-5, *H*-10), 7.90 (dd, 4H, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 2.0 Hz, *H*-2, *H*-13) ppm. ^1H **NMR** (400 MHz, CD_2Cl_2): δ = 6.62 (s, 4H, *H*-7, *H*-8), 7.10–7.18 (m, 8H, *H*-3, *H*-4, *H*-11, *H*-12), 7.24 (dd, 4H, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 2.0 Hz, *H*-5, *H*-10), 7.93 (dd, 4H, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.9 Hz, *H*-2, *H*-13) ppm. $^{13}C\{^1H\}$ **NMR** (101 MHz, THF-d_8): δ = 127.77 (s, *C*-4, *C*-11), 128.92 (s, *C*-3, *C*-12), 131.15 (s, *C*-5, *C*-10), 136.96 (s, *C*-7, *C*-8), 139.67 (s, *C*-2, *C*-13), 142.32 (br, *C*-1, *C*-14), 147.45 (s, *C*-6, *C*-9) ppm. $^{13}C\{^1H\}$ **NMR** (101 MHz, CD_2Cl_2): δ = 127.81 (s, *C*-4, *C*-11), 128.94 (s, *C*-3, *C*-12), 130.90 (s, *C*-5, *C*-10), 136.75 (s, *C*-7, *C*-8), 139.50 (s, *C*-2, *C*-13), 141.83 (br, *C*-1, *C*-14), 147.00 (s, *C*-6, *C*-9) ppm. **Elemental analysis**: Anal. calc. (%) for $C_{28}H_{20}Bi_2$ (774.43 g/mol): C 43.43, H 2.60; found: C 43.07, H 2.44.

5-Phenoxy-5*H*-dibenzo[*b,f*]bismepine (3-O): At 0 °C, THF (6 mL) was added to a mixture of phenol (30 mg, 321 μmol) and potassium hydride (13 mg, 321 μmol). The resulting suspension was brought to room temperature, stirred for 2 h, and filtrated onto a solution of **1-I** (150 mg, 292 μmol) in THF (10 mL). The reaction mixture was stirred for 3 h at room temperature, filtrated and all volatiles were removed under reduced pressure. The residue was extracted with toluene (12 mL), the solution layered with *n*-pentane (12 mL) and stored at −30 °C. After 2 d white colorless needles had precipitated which were isolated by filtration and dried in vacuo. **Yield**: 88 mg (184 μmol, 63%). ^1H **NMR** (401 MHz, C_6D_6): δ = 6.55 (s, 2H, *H*-7, *H*-8), 6.87–6.95 (m, 3H, *H*-4, *H*-11, PhO-H^{para}), 6.99–7.04 (m, 2H, PhO-H^{ortho}), 7.22 (dd, 2H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.0 Hz, *H*-5, *H*-10), 7.26–7.31 (m, 2H, PhO-H^{meta}), 7.36 (ddd, 2H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, *H*-3, *H*-12), 8.36 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, *H*-2, *H*-13) ppm. $^{13}C\{^1H\}$ **NMR** (101 MHz, C_6D_6): δ = 119.38 (s, PhO-C^{para}), 120.66 (s, PhO-C^{ortho}), 127.63 (s, *C*-4, *C*-11), 129.97 (s, PhO-C^{meta}), 131.29 (s, *C*-7, *C*-8), 132.26 (s, *C*-5, *C*-10), 132.34 (s, *C*-3, *C*-12), 133.02 (s, *C*-2, *C*-13), 139.81 (s, *C*-6, *C*-9), 164.37 (s, PhO-C^{ipso}), 178.11 (s, *C*-1, *C*-14) ppm. **Elemental analysis**: Anal. calc. (%) for $C_{20}H_{15}BiO$ (480.32 g/mol): C 50.01, H 3.15; found: C 50.18, H 3.22.

5-Phenylthio-5*H*-dibenzo[*b,f*]bismepine (3-S): Diphenyl disulfide (7 mg, 32 μmol) was added to solution of **2** (25 mg, 32 μmol) in dichloromethane (6 mL). The reaction mixture was stirred at ambient temperature for 3 h and then layered with *n*-pentane (6 mL). After 16 h at ambient temperature, the product had precipitated as a pale yellow crystalline solid, which was isolated by filtration, washed with *n*-pentane (4×2 mL) and dried in vacuo. **Yield**: 26 mg (52 μmol, 81%). ^1H **NMR** (400 MHz, CD_2Cl_2): δ = 6.99 (s, 2H, *H*-7, *H*-8), 7.16–7.21 (m, 1H, PhS-H^{para}), 7.25–7.34 (m, 4H, PhS-C^{meta}, *H*-4, *H*-11), 7.46 (dd, 2H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.0 Hz, H-5, H-10), 7.55 (ddd, 2H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, *H*-3, *H*-12), 7.58–7.62 (m, 2H, PhS-H^{ortho}), 8.67 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, *H*-2, *H*-13) ppm. $^{13}C\{^1H\}$ **NMR** (101 MHz, CD_2Cl_2): δ = 126.77 (s, PhS-C^{para}), 127.97 (s, *C*-4, *C*-11), 129.22 (s, PhS-C^{meta}), 131.48 (s, *C*-5, *C*-10), 132.35 (s, *C*-3, *C*-12), 132.70 (s, *C*-7, *C*-8), 135.11 (s, PhS-C^{ortho}), 135.84 (s, *C*-2, *C*-13), 136.07 (s, PhS-C^{ipso}), 141.09 (s, *C*-6, *C*-9), 160.10 (s, *C*-1, *C*-14) ppm. **Elemental analysis**: calc. (%) for $C_{20}H_{15}BiS$ (496.38 g/mol): C 48.39, H 3.05, S 6.46; found: C 48.51, H 3.09, S 6.49.

5-Phenylseleno-5*H*-dibenzo[*b,f*]bismepine (3-Se): Diphenyl diselenide (8 mg, 26 μmol) was added to solution of **2** (20 mg, 26 μmol) in dichloromethane-d_2 (0.5 mL). After 1 h at ambient temperature, small amounts of a pale yellow solid had precipitated, which were dissolved by addition of THF (0.5 mL). The reaction mixture was filtered, layered with *n*-pentane (1 mL) and stored at −30 °C. After 3 d the product had precipitated as a pale yellow solid which was isolated by filtration, washed with *n*-pentane (2×2 mL) and dried in

EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202300415

Chemistry Europe
European Chemical
Societies Publishing

vacuo. **Yield**: 24 mg (44 μmol, 86%). **^{1}H NMR** (400 MHz, CD$_2$Cl$_2$): $\delta =$ 7.00 (s, 2H, H-7, H-8), 7.21–7.26 (m, 3H, PhSe-$H^{\text{meta,para}}$), 7.31 (ddd, 2H, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.3$ Hz, H-4, H-11), 7.45 (dd, 2H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.1$ Hz, H-5, H-10), 7.49 (ddd, 2H, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.3$ Hz, H-3, H-12), 7.69–7.74 (m, 2H, PhSe-H^{ortho}), 8.75 (dd, 2H, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.0$ Hz, H-2, H-13) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$): $\delta = 127.23$ (s, PhSe-C^{para}), 127.32 (s, C-4, C-11), 127.97 (s, PhSe-C^{ipso}), 129.38 (s, PhSe-C^{meta}), 131.18 (s, C-5, C-10), 132.40 (s, C-3, C-12), 133.09 (s, C-7, C-8), 137.00 (s, PhSe-C^{ortho}), 137.47 (s, C-2, C-13), 141.29 (s, C-6, C-9), 155.20 (s, C-1, C-14) ppm. **^{77}Se NMR** (76 MHz, CD$_2$Cl$_2$): $\delta = 175.70$ (s) ppm. **Elemental analysis**: calc. (%) for C$_{20}$H$_{15}$BiSe (543.29 g/mol): C 44.22, H 2.78; found: C 44.23, H 2.88.

5-Phenyltelluro-5H-dibenzo[b,f]bismepine (3-Te): Diphenyl ditelluride (13 mg, 32 μmol) was added to a solution of **2** (25 mg, 32 μmol) in dichloromethane (6 mL). After 2 min at ambient temperature the reaction mixture was filtered, layered with n-pentane (7 mL) and stored at −30 °C. After 16 h the product had precipitated in the form of an orange crystalline solid which was isolated by filtration, washed with n-pentane (4×2 mL) and dried in vacuo. **Yield**: 29 mg (49 μmol, 77%). **^{1}H NMR** (400 MHz, CD$_2$Cl$_2$): $\delta =$ 7.00 (s, 2H, H-7, H-8), 7.12–7.18 (m, 2H, PhTe-H^{meta}), 7.23–7.28 (m, 1H, PhTe-H^{para}), 7.30–7.38 (m, 4H, H-3, H-4, H-11, H-12), 7.43–7.46 (m, 2H, H-5, H-10), 7.87–7.91 (m, 2H, PhTe-H^{ortho}), 8.82–8.85 (m, 2H, H-2, H-13) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$): $\delta = 104.58$ (s, PhTe-C^{ipso}), 127.95 (s, PhTe-C^{para}), 128.07 (s, C-4, C-11), 129.53 (s, PhTe-C^{meta}), 130.75 (s, C-5, C-10), 132.23 (s, C-3, C-12), 134.22 (s, C-7, C-8), 140.63 (s, C-2, C-13), 141.92 (s, PhTe-C^{ortho}), 142.01 (s, C-6, C-9), 146.83 (s, C-1, C-14) ppm. **^{125}Te NMR** (158 MHz, CD$_2$Cl$_2$): $\delta = 170.17$ (s) ppm. **Elemental analysis**: calc. (%) for C$_{20}$H$_{15}$BiTe (591.92 g/mol): C 40.58, H 2.55; found: C 40.35, H 2.60.

5H-Dibenzo[b,f]bismepin-5-yl benzoate (4): Dibenzoyl peroxide (7 mg, 32 μmol) was added to a solution of **2** (25 mg, 32 μmol) in dichloromethane-d_2 (0.8 mL), resulting in a color change from orange to pale yellow. The reaction mixture was filtered, layered with n-pentane (1.6 mL) and stored at −30 °C. After 16 h colorless crystals had precipitated and were isolated by filtration, washed with n-pentane (2 mL), and dried in vacuo. **Yield**: 27 mg (53 μmol, 83%). **^{1}H NMR** (500 MHz, CD$_2$Cl$_2$): $\delta = 7.02$ (s, 2H, H-7, H-8), 7.29 (ddd, 2H, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.3$ Hz, H-4, H-11), 7.50 (t$_{\text{broad}}$, 2H, $^3J_{HH} = 7.5$ Hz, Ph$^{\text{meta}}$), 7.54 (dd, 2H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.0$ Hz, H-5, H-10), 7.59 (t$_{\text{broad}}$, 1H, $^3J_{HH} = 7.4$ Hz, Ph$^{\text{para}}$), 7.66 (ddd, 2H, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.3$ Hz, H-3, H-12), 8.22 (d$_{\text{broad}}$, $^3J_{HH} = 7.4$ Hz, Ph$^{\text{ortho}}$), 8.26 (dd, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.0$ Hz, H-2, H-13) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD$_2$Cl$_2$): $\delta = 127.93$ (s, C-4, C-11), 128.69 (s, Ph$^{\text{meta}}$), 130.82 (s, Ph$^{\text{ortho}}$), 131.52 (s, C-7, C-8), 132.37 (Ph$^{\text{ipso}}$), 132.79 (s, Ph$^{\text{para}}$), 132.84 (s, C-3, C-12), 132.93 (s, C-5, C-10), 134.09 (s, C-2, C-13), 140.50 (s, C-6, C-9), 172.90 (s, C^{carbonyl}) 179.20 (s, C-1, C-14) ppm. **Elemental analysis**: calc. (%) for C$_{21}$H$_{15}$O$_2$Bi (508.33 g/mol): C 49.62, H 2.97; found: C 49.76, H 3.26.

Bis[dibenzobismepine]oxide (5-O): In a J. Young NMR tube **2** (12 mg, 155 μmol) was dissolved in dichloromethane-d_2 (0.4 mL). The screw cap was removed and air was pushed through the solution using a syringe with a long needle (approximately 3× 10 mL). The J. Young NMR tube was closed and stored for 1 h at ambient temperature upon which a complete discoloration of the previously yellow solution was observed. The solution was filtered, layered with n-pentane (1 mL) and stored at −30 °C. After 16 h a white solid had precipitated which was isolated by filtration, washed with n-pentane (3×1 mL) and dried in vacuo. **Yield**: 7 mg (89 μmol, 57%). **^{1}H NMR** (401 MHz, C$_6$D$_6$): $\delta = 6.64$ (s, 4H, H-7, H-8), 6.98 (ddd, 4H, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.3$ Hz, H-4, H-11), 7.26 (dd, 4H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.0$ Hz, H-5, H-10), 7.36 (ddd, 4H, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.2$ Hz, H-3, H-12), 8.45 (dd, 4H, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.1$ Hz, H-2, H-13) ppm. **^{13}C{^{1}H} NMR** (101 MHz,

C$_6$D$_6$): $\delta = 127.46$ (s, C-4, C-11), 131.23 (s, C-3, C-12), 131.81 (s, C-7, C-8), 131.88 (s, C-5, C-10), 132.44 (s, C-2, C-13), 140.89 (s, C-6, C-9), 175.50 (br, C-1, C-14, detected via ^{1}H-^{13}C-HMBC) ppm. **Elemental analysis**: calc. (%) for C$_{28}$H$_{20}$Bi$_2$O (790.43 g/mol): C 42.55, H 2.55; found.: C 42.21, H 2.21.

Bis[dibenzobismepine]sulfide (5-S): Elemental sulfur (1 mg, 31 μmol) was added to a solution of **2** (25 mg, 32 μmol) in dichloromethane (6 mL). The reaction mixture was stirred at ambient temperature for 10 min, during which the product precipitated as a white solid. The product was isolated by filtration, washed with n-pentane (3×4 mL) and dried in vacuo. **Yield**: 17 mg (21 μmol, 65%). **^{1}H NMR** (400 MHz, C$_6$D$_6$): $\delta = 6.64$ (s, 4H, H-7, H-8), 6.99 (t, 4H, $^3J_{HH} = 7.5$ Hz, H-4, H-11), 7.16–7.21 (m, 4H, H-5, H-10, overlaps with solvent residual signal), 7.27 (t, 4H, $^3J_{HH} = 7.3$ Hz, H-3, H-12), 8.98 (d, 4H, $^3J_{HH} = 7.3$ Hz, H-2, H-13) ppm. **^{13}C{^{1}H} NMR** (101 MHz, C$_6$D$_6$): $\delta = 127.60$ (s, C-4, C-11), 131.03 (s, C-5, C-10), 132.06 (s, C-3, C-12), 132.60 (s, C-7, C-8), 136.15 (s, C-2, C-13), 141.27 (s, C-6, C-9), 160.10 (s, C-1, C-14, detected via ^{1}H-^{13}C-HMBC) ppm. **Elemental analysis**: calc. (%) for C$_{28}$H$_{20}$Bi$_2$S (806.49 g/mol): C 41.70, H 2.52, S 3.98; found: C 41.55, H 2.62, S 4.16.

Bis[dibenzobismepine]selenide (5-Se): **2** (20 mg, 26 μmol) and grey selenium (2 mg, 26 μmol) were suspended in dichloromethane (5 mL). The reaction mixture was stirred at ambient temperature for 3 h, which led to the precipitation of the product as a pale yellow solid. The product was isolated by filtration, washed with dichloromethane (2 mL), n-pentane (2×4 mL) and dried in vacuo. **Yield**: 17 mg (20 μmol, 77%). **^{1}H NMR** (400 MHz, THF-d_8): $\delta = 6.96$ (s, 4H, H-7, H-8), 7.19–7.25 (m, 4H, H-4, H-11) 7.33–7.39 (m, 8H, H-3, H-5, H-10, H-12), 8.79–8.84 (m, 4H, H-2, H-13) ppm. **^{13}C{^{1}H} NMR** (101 MHz, THF-d_8): $\delta = 127.80$ (s, C-4, C-11), 131.03 (s, C-5, C-10), 132.26 (s, C-3, C-12), 133.26 (s, C-7, C-8), 137.97 (s, C-2, C-13), 141.92 (s, C-6, C-9), 155.66 (s, C-1, C-14) ppm. A ^{77}Se NMR signal could not be detected via ^{77}Se NMR or ^{1}H-^{77}Se HMBC experiments. **Elemental analysis**: calc. (%) for C$_{28}$H$_{20}$Bi$_2$Se (853.39 g/mol): C 39.41, H 2.36; found: C 39.68, H 2.48.

Bis[dibenzobismepine]telluride (5-Te): Elemental tellurium (5 mg, 39 μmol) was added to a solution of **2** (30 mg, 39 μmol) in dichloromethane (8 mL). The reaction mixture was stirred at ambient temperature for 2 d, filtrated and layered with n-pentane (8 mL). After 16 h the product had precipitated in the form of yellow, crystalline needles which were isolated by filtration, washed with n-pentane (3×2 mL) and dried in vacuo. **Yield**: 21 mg (23 μmol, 59%). **^{1}H NMR** (400 MHz, THF-d_8): $\delta = 6.97$ (s, 4H, H-7, H-8), 7.21–7.27 (m, 8H, H-3, H-4, H-11, H-12) 7.32–7.38 (m, 4H, H-5, H-10), 8.90–8.96 (m, 4H, H-2, H-13) ppm. **^{13}C{^{1}H} NMR** (101 MHz, THF-d_8): $\delta = 127.89$ (s, C-4, C-11), 130.68 (s, C-5, C-10), 132.54 (s, C-3, C-12), 134.05 (s, C-7, C-8), 141.50 (s, C-2, C-13), 142.15 (s, C-6, C-9), 147.82 (s, C-1, C-14) ppm. A ^{125}Te NMR signal could not be detected via ^{125}Te NMR or ^{1}H-^{125}Te HMBC experiments. **Elemental analysis**: calc. (%) for C$_{28}$H$_{20}$Bi$_2$Te (902.03 g/mol): C 37.28, H 2.23; found: C 37.32, H 2.41.

Computational details: All DFT calculations[43] were performed with the *Gaussian16* suite of programs.[44] Geometries were optimized with the M06-L[45] functional including Grimme's dispersion correction GD3[46] and the basis sets def2-SVP[47,48] (for C, H, O and S atoms) and LANL2DZ (for Bi, Co, Rh, Ir, Ni, Pd, Pt, Se and Te atoms).[49] Stationary points were probed through vibrational analysis. Gibbs free energy corrections were performed under standard conditions (298.15 K, 1.0 atm). Single point energy calculations including the effect of dichloromethane as a solvent were performed with the M06-L functional,[45] the SMD solvation model,[50] Grimme's dispersion correction GD3,[46] the basis sets def2-TZVP[47,48] (for C, H, O and S atoms) and LANL2DZ (for Bi, Co,

Rh, Ir, Ni, Pd, Pt, Se and Te atoms).[49] NBO calculations were performed using the program version NBO 7.[51]

Supporting Information

The authors have cited additional references within the Supporting Information.[52–59]

Acknowledgements

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

[1] a) C. Chen, *Nat. Chem. Rev.* **2018**, *2*, 6–14; b) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; c) D. Takeuchi, *Dalton Trans.* **2010**, *39*, 311–328.
[2] a) J. Wen, F. Wang, X. Zhang, *Chem. Soc. Rev.* **2021**, *50*, 3211–3237; b) S. Kraft, K. Ryan, R. B. Kargbo, *J. Am. Chem. Soc.* **2017**, *139*, 11630–11641.
[3] a) M. Beller, J. Seayad, A. Tillack, H. Jiao, *Angew. Chem. Int. Ed.* **2004**, *43*, 3368–3398; b) R. I. McDonald, G. Liu, S. S. Stahl, *Chem. Rev.* **2011**, *111*, 2981–3019.
[4] a) C. Amatore, A. Jutand, *Coord. Chem. Rev.* **1998**, *178–180*, 511–528; b) A. L. Clevenger, R. M. Stolley, J. Aderibigbe, J. Louie, *Chem. Rev.* **2020**, *120*, 6124–6196; c) T. van Tran, Z.-Q. Li, O. Apolinar, J. Derosa, M. V. Joannou, S. R. Wisniewski, M. D. Eastgate, K. M. Engle, *Angew. Chem. Int. Ed.* **2020**, *59*, 7409–7413; d) L. Nattmann, R. Saeb, N. Nöthling, J. Cornella, *Nat. Catal.* **2020**, *3*, 6–13.
[5] a) C. Defieber, H. Grützmacher, E. M. Carreira, *Angew. Chem. Int. Ed.* **2008**, *47*, 4482–4502; b) F. Glorius, *Angew. Chem. Int. Ed.* **2004**, *43*, 3364–3366; c) X. Feng, H. Du, *Asian J. Org. Chem.* **2012**, *1*, 204–213.
[6] a) Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakai, N. Miyaura, *J. Am. Chem. Soc.* **1998**, *120*, 5579–5580; b) T. Hayashi, K. Ueyama, N. Tokunaga, K. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 11508–11509.
[7] a) N. Tokunaga, Y. Otomaru, K. Okamoto, K. Ueyama, T. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2004**, *126*, 13584–13585; b) Y. Otomaru, N. Tokunaga, R. Shintani, T. Hayashi, *Org. Lett.* **2005**, *7*, 307–310; c) Z.-Q. Wang, C.-G. Feng, M.-H. Xu, G.-Q. Lin, *J. Am. Chem. Soc.* **2007**, *129*, 5336–5337.
[8] a) E. Piras, F. Läng, H. Rüegger, D. Stein, M. Wörle, H. Grützmacher, *Chem. Eur. J.* **2006**, *12*, 5849–5858; b) R. Shintani, W.-L. Duan, T. Nagano, A. Okada, T. Hayashi, *Angew. Chem. Int. Ed.* **2005**, *44*, 4611–4614; c) W.-L. Duan, H. Iwamura, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2007**, *129*, 2130–2138.
[9] a) X. Feng, B. Wei, J. Yang, H. Du, *Org. Biomol. Chem.* **2011**, *9*, 5927–5929; b) G. Chen, J. Gui, L. Li, J. Liao, *Angew. Chem. Int. Ed.* **2011**, *50*, 7681–7685; c) G. Chen, J. Gui, P. Cao, J. Liao, *Tetrahedron* **2012**, *68*, 3220–3224; d) F. Xue, X. Li, B. Wan, *J. Org. Chem.* **2011**, *76*, 7256–7262.
[10] T. Büttner, J. Geier, G. Frison, J. Harmer, C. Calle, A. Schweiger, H. Schönberg, H. Grützmacher, *Science* **2005**, *307*, 235–238.
[11] P. Maire, T. Büttner, F. Breher, P. Le Floch, H. Grützmacher, *Angew. Chem. Int. Ed.* **2005**, *44*, 6318–6323.
[12] a) C. Lichtenberg, J. Bloch, T. L. Gianetti, T. Büttner, J. Geier, H. Grützmacher, *Dalton Trans.* **2015**, *44*, 20056–20066; b) F. F. Puschmann, J. Harmer, D. Stein, H. Rüegger, B. de Bruin, H. Grützmacher, *Angew. Chem. Int. Ed.* **2010**, *49*, 385–389; c) F. F. Puschmann, H. Grützmacher, B. de Bruin, *J. Am. Chem. Soc.* **2010**, *132*, 73–75.
[13] a) A. Herrera, A. Grasruck, F. W. Heinemann, A. Scheurer, A. Chelouan, S. Frieß, F. Seidel, R. Dorta, *Organometallics* **2017**, *36*, 714–720; b) S. Frieß, A. Herrera, A. Linden, F. W. Heinemann, R. Dorta, *J. Organomet. Chem.* **2019**, *898*, 120876; c) I. Heuermann, B. Heitmann, R. Stichauer, D. Duvinage, M. Vogt, *Organometallics* **2019**, *38*, 1787–1799; d) G. Mora, S. van Zutphen, C. Thoumazet, X. F. Le Goff, L. Ricard, H. Grützmacher, P. Le Floch, *Organometallics* **2006**, *25*, 5528–5532; e) E. Drinkel, A. Briceño, R. Dorta, R. Dorta, *Organometallics* **2010**, *29*, 2503–2514; f) B. Freitag, H. Elsen, J. Pahl, G. Ballmann, A. Herrera, R. Dorta, S. Harder, *Organometallics* **2017**, *36*, 1860–1866.
[14] V. Lyaskovskyy, R. J. A. van Dijk-Moes, S. Burck, W. I. Dzik, M. Lutz, A. W. Ehlers, J. C. Slootweg, B. de Bruin, K. Lammertsma, *Organometallics* **2013**, *32*, 363–373.
[15] I. Kawashima, H. Imoto, M. Ishida, H. Furuta, S. Yamamoto, M. Mitsuishi, S. Tanaka, T. Fujii, K. Naka, *Angew. Chem. Int. Ed.* **2019**, *58*, 11686–11690.
[16] J. Ramler, K. Radacki, J. Abbenseth, C. Lichtenberg, *Dalton Trans.* **2020**, *49*, 9024–9034.
[17] J. Ramler, L. Wüst, A. Rempel, L. Wolz, C. Lichtenberg, *Organometallics* **2021**, *40*, 832–837.
[18] A. J. Plajer, A. L. Colebatch, F. J. Rizzuto, P. Pröhm, A. D. Bond, R. García-Rodríguez, D. S. Wright, *Angew. Chem. Int. Ed.* **2018**, *57*, 6648–6652.
[19] Á. García-Romero, A. J. Plajer, D. Miguel, D. S. Wright, A. D. Bond, C. M. Álvarez, R. García-Rodríguez, *Inorg. Chem.* **2020**, *59*, 7103–7116.
[20] J. E. Waters, G. Berger, A. J. Peel, R. García-Rodríguez, A. D. Bond, D. S. Wright, *Chem. Eur. J.* **2021**, *27*, 12036–12040.
[21] Á. García-Romero, J. E. Waters, R. B. Jethwa, A. D. Bond, A. L. Colebatch, R. García-Rodríguez, D. S. Wright, *Inorg. Chem.* **2023**, *62*, 4625–4636.
[22] J. Ramler, K. Hofmann, C. Lichtenberg, *Inorg. Chem.* **2020**, *59*, 3367–3376.
[23] J. Ramler, C. Lichtenberg, *Chem. Eur. J.* **2020**, *26*, 10250–10258.
[24] J. Ramler, I. Krummenacher, C. Lichtenberg, *Chem. Eur. J.* **2020**, *26*, 14551–14555.
[25] R. J. Schwamm, M. Lein, M. P. Coles, C. M. Fitchett, *Angew. Chem. Int. Ed.* **2016**, *55*, 14798–14801.
[26] T. Dunaj, K. Dollberg, C. Ritter, F. Dankert, C. Hänisch, *Eur. J. Inorg. Chem.* **2021**, *2021*, 870–878.
[27] W. Clegg, N. A. Compton, R. Errington, G. A. Fisher, N. C. Norman, N. Wishart, *J. Organomet. Chem.* **1990**, *399*, C21–C25.
[28] R. E. v H Spence, D. P. Hsu, S. L. Buchwald, *Organometallics* **1992**, *11*, 3492–3493.
[29] a) L. Balázs, H. J. Breunig, E. Lork, *Z. Naturforsch. B* **2005**, *60*, 180–182; b) F. Calderazzo, A. Morvillo, G. Pelizzi, R. Poli, *J. Chem. Soc. Chem. Commun.* **1983**, 507; c) K. H. Whitmire, J. M. Cassidy, *Acta Crystallogr. Sect. C* **1992**, *48*, 917–919.
[30] M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. A* **2009**, *113*, 5806–5812.
[31] M. Wieber, I. Sauer, *Z. Naturforsch. B* **1984**, *39*, 1668–1670.
[32] F. Calderazzo, A. Morvillo, G. Pelizzi, R. Poli, F. Ungari, *Inorg. Chem.* **1988**, *27*, 3730–3733.
[33] M. Wieber, I. Sauer, *Z. Naturforsch. B* **1987**, *42*, 695–698.
[34] A. J. Ashe, E. G. Ludwig, *J. Organomet. Chem.* **1986**, *308*, 289–296.
[35] a) S. Heimann, A. Kuczkowski, D. Bläser, C. Wölper, R. Haack, G. Jansen, S. Schulz, *Eur. J. Inorg. Chem.* **2014**, *2014*, 4858–4864; b) W.-W. Du Mont, T. Severengiz, H. J. Breunig, D. Müller, *Z. Naturforsch. B* **1985**, *40*, 848–849.
[36] a) G. G. Briand, A. Decken, N. M. Hunter, G. M. Lee, J. A. Melanson, E. M. Owen, *Polyhedron* **2012**, *31*, 796–800; b) J. Ramler, J. Schwarzmann, A. Stoy, C. Lichtenberg, *Eur. J. Inorg. Chem.* **2022**, *2022*, e202100934; c) P. Šimon, R. Jambor, A. Růžička, L. Dostál, *Organometallics* **2013**, *32*, 239–248.
[37] a) H. J. Breunig, D. Müller, *Z. Naturforsch. B* **1986**, *41*, 1129–1132; b) H. J. Breunig, L. Königsmann, E. Lork, M. Nema, N. Philipp, C. Silvestru, A.

Soran, R. A. Varga, R. Wagner, *Dalton Trans.* **2008**, 1831–1842; c) S. Heimann, D. Bläser, C. Wölper, S. Schulz, *Organometallics* **2014**, *33*, 2295–2300; d) H. Suzuki, T. Ikegami, *Product Class 3: Bismuth Compounds in Science of synthesis* (Ed.: I. Fleming), Thieme, Stuttgart, New York, NY **2002**.

[38] L. Balazs, H. J. Breunig, E. Lork, A. Soran, C. Silvestru, *Inorg. Chem.* **2006**, *45*, 2341–2346.

[39] H. J. Breunig, K. H. Ebert, R. E. Schulz, M. Wieber, I. Sauer, *Z. Naturforsch. B* **1995**, *50*, 735–744.

[40] H. Breunig, I. Ghesner, E. Lork, *J. Organomet. Chem.* **2002**, *664*, 130–135.

[41] The oxidative addition of Bi–Cl and Bi–C bonds to Pt(0) has previously been reported: a) H. Braunschweig, P. Brenner, P. Cogswell, K. Kraft, K. Schwab, *Chem. Commun.* **2010**, *46*, 7894–7896; b) S. Shimada, X.-B. Wang, M. Tanaka, *Chem. Commun.* **2020**, *56*, 15216–15219.

[42] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122; b) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.

[43] C. J. Cramer, D. G. Truhlar, *Phys. Chem. Chem. Phys.* **2009**, *11*, 10757–10816.

[44] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16 Rev. C.01*, **2016**.

[45] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157–167.

[46] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.

[47] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[48] D. Andrae, U. Huermann, M. Dolg, H. Stoll, H. Preu, *Theor. Chim. Acta* **1990**, *77*, 123–141.

[49] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310.

[50] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

[51] a) E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comput. Chem.* **2019**, *40*, 2234–2241; b) F. Weinhold, C. R. Landis, E. D. Glendening, *Int. Rev. Phys. Chem.* **2016**, *35*, 399–440.

[52] M. Giannerini, M. Fañanás-Mastral, B. L. Feringa, *J. Am. Chem. Soc.* **2012**, *134*, 4108–4111.

[53] X. Zhang, Y. Yang, Y. Liang, *Tetrahedron Lett.* **2012**, *53*, 6406–6408.

[54] B. Quillian, Y. Wang, P. Wei, C. S. Wannere, P. v R Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 13380–13381.

[55] a) T. Matsumoto, H. Takamine, K. Tanaka, Y. Chujo, *Org. Lett.* **2015**, *17*, 1593–1596; b) I. Kawashima, H. Imoto, M. Ishida, H. Furuta, S. Yamamoto, M. Mitsuishi, S. Tanaka, T. Fujii, K. Naka, *Angew. Chem. Int. Ed.* **2019**, *58*, 11686–11690; c) S. Ito, T. Kuwabara, Y. Ishii, *Organometallics* **2020**, *39*, 640–644; d) T. Tsuda, S.-M. Choi, R. Shintani, *J. Am. Chem. Soc.* **2021**, *143*, 1641–1650; e) V. Lyaskovskyy, R. J. A. van Dijk-Moes, S. Burck, W. I. Dzik, M. Lutz, A. W. Ehlers, J. C. Slootweg, B. de Bruin, K. Lammertsma, *Organometallics* **2013**, *32*, 363–373; f) A. Caruso, M. A. Siegler, J. D. Tovar, *Angew. Chem. Int. Ed.* **2010**, *49*, 4213–4217.

[56] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[57] S. Grimme, J. Antony, S. Ehrlich, H. A. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104–154119.

[58] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213–222.

[59] a) T. H. Dunning Jr, P. J. Hay, *Modern Theoretical Chemistry*, Ed. H. F. Schaefer III, Vol. 3, Plenum, New York **1977**, 1–28; b) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270–283; c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310.