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Bismuth in Dynamic Covalent Chemistry: Access to a Bowl-Type Macrocycle and a Barrel-Type Heptanuclear Complex Cation

Andreas Stoy, Malte Jürgensen, Christina Millidoni, Chantsalmaa Berthold,
*Jacqueline Ramler, Sebastián Martínez, Magnus R. Buchner, and Crispin Lichtenberg**

Abstract: Dynamic covalent chemistry (DCvC) is a powerful and widely applied tool in modern synthetic chemistry, which is based on the reversible cleavage and formation of covalent bonds. One of the inherent strengths of this approach is the perspective to reversibly generate in an operationally simple approach novel structural motifs that are difficult or impossible to access with more traditional methods and require multiple bond cleaving and bond forming steps. To date, these fundamentally important synthetic and conceptual challenges in the context of DCvC have predominantly been tackled by exploiting compounds of lighter p-block elements, even though heavier p-block elements show low bond dissociation energies and appear to be ideally suited for this approach. Here we show that a dinuclear organometallic bismuth compound, containing $BiMe_2$ groups that are connected by a thioxanthene linker, readily undergoes selective and reversible cleavage of its Bi–C bonds upon exposure to external stimuli. The exploitation of DCvC in the field of organometallic heavy p-block chemistry grants access to unprecedented macrocyclic and barrel-type oligonuclear compounds.

*T*he concept of dynamic covalent chemistry (DCvC) is widely exploited in chemical research, covering fields such as (in)organic synthesis, polymerization catalysis, pharmaceutical chemistry, and protein folding.[1–3] DCvC is located between the realm of molecular chemistry with strong and static covalent bonds and supramolecular chemistry, which relies on labile and relatively weak non-covalent interactions. DCvC relates to chemical transformations that are reversible under conditions of equilibrium control and rely on the reversible formation and breaking of covalent bonding within molecules.[2–5]

A large majority of dynamic covalent transformations involve only lighter main group elements found in the second and third row of the periodic table. In contrast to that, DCvC that is based on heavier p-block elements ($n \geq 4$) is less explored. This is somewhat surprising since covalent bonds involving heavier p-block elements remain strong enough to enable the straightforward handling and isolation of the corresponding compounds,[6] but tend to be significantly weaker than covalent bonds between second and third row elements.[7] These characteristics bear a tremendous potential for heavier p-block elements in DCvC, as demonstrated by dynamic covalency of molecular and macromolecular compounds with Se–Se, Se–N, Te–Te, Pn–S (Pn = As-Bi), and Pn–Pn′ bonds, for instance.[5,8–11] This has enabled remarkable applications such as self-healing polymers and inhibitors of thiol-mediated cytosolic delivery.[9–11] In contrast to these pioneering findings, one of the core strengths of DCvC that offers new starting points for future developments has only scarcely been exploited with the incorporation of heavier p-block elements: the construction, interconversion, and detailed investigation of new structural motifs, which are difficult or even impossible to access with more traditional synthetic strategies. In this respect, bismuth is especially appealing, since its covalent bonds are among the weakest in main group chemistry,[12–14] and the low toxicity of its compounds have been suggested to grant the status of a "green element".[15] Furthermore, it offers three sites for covalent bonding in its favored oxidation state of +III, enabling the construction of ring *and* cage motifs, as opposed to the heaviest synthetically relevant representatives of group 13 (Tl(I)), group 14 (Pb(II)), group 16 (Te(II)).

In the context of the reversible cleavage and formation of covalent Bi–C bonds, ligand scrambling in organobismuth compounds has been described,[16] comproportionation reactions have been exploited,[17] and condensation reactions that liberate $BiMe_3$ with concomitant Bi–C bond formation have been reported.[18] However, these reactions lack detailed investigations towards the crucial stimuli-responsive and selective reversibility of Bi–C bond cleavage/formation and the construction of complex molecular scaffolds. Importantly, the exploitation and detailed investigation of organometallic compounds of heavier p-block elements ($n \geq 4$) with the dynamic formation/cleavage of E–C bonds towards the design of complex molecular architectures

[*] Dr. A. Stoy, C. Millidoni, C. Berthold, Dr. J. Ramler, Dr. S. Martínez,
Dr. M. R. Buchner, Prof. Dr. C. Lichtenberg
Department of Chemistry, Philipps-University Marburg
Hans-Meerwein-Str. 4, 35032 Marburg (Germany)
E-mail: crispin.lichtenberg@uni-wuerzburg.de

M. Jürgensen
Institute of Inorganic Chemistry, Julius-Maximilians-University
Würzburg
Am Hubland, 97074 Würzburg (Germany)

featuring new structural motifs has—to the best of our knowledge—not been reported to date.

In this work we present a dinuclear organometallic bismuth compound, which is highly susceptible to DCvC, when exposed to external stimuli, thereby granting access to novel macrocyclic and barrel-like oligonuclear compounds.

Well-defined dinuclear bismuth compunds containing an organic linker are relatively rare and represent tri-aryl species, with only a few exceptions.[17–19] We identified the literature-known thioxanthene derivative **TXBr₂**[20] as a promising starting point for this project (Scheme 1). **TXBr₂** was subjected to metal-halide exchange, followed by reaction with BiMe₂Cl to furnish the dinuclear thioxanthene-bridged bismuth compound **1** as a colorless, air and moisture sensitive powder in excellent yields of 96% (Scheme 1a—top; for definition of TX see Scheme 1b). NMR spectroscopic analyses in solution indicate a C_{2v}-symmetry of **1**. The low homolytic bond dissociation energies of Bi–Me bonds in radical reactions[12–14] and the potential of bismuth-bound methyl groups to undergo dynamic exchange via polar reaction pathways[21] prompted us to screen the behavior of **1** in the presence of potential templating agents (Supp. Inf.).

Indeed, addition of the soft Lewis acid Tl⁺ (introduced as TlBArF) to a solution of **1** in 1,2-difluorobenzene (DFB) at room temperature induced the facile formation of the macrocyclic thallium complex **2** as a beige-brown powder in 67% isolated yield (Scheme 1a—right, (BArF=B-(3,5-(CF₃)₂C₆H₃)₄). The formation of **2** is accompanied by the liberation of two equivalents of BiMe₃, as confirmed by NMR spectroscopy. So the overall reaction is realized by the cleavage of four Bi–C bonds and the formation of four new Bi–C bonds. The templating TlBArF moiety can be extracted from **2** simply by washing the compound with acetonitrile at room temperature to give the free heterocycle **3** as a colorless powder in excellent 92% isolated yield (Scheme 1a—bottom). Thus, the Tl⁺ cation is only necessary for the pre-coordination of the bismuth-decorated thioxanthene moieties during the formation of the heterocycle, but is not essential for its stability, and the formation of **2** represents a template-assisted cyclization reaction (for a screening of the reactivity of other Lewis acids towards **1**, see the Supp. Inf.).[22] It should be noted that the coordination of Tl⁺ by the heterocycle is reversible: **2** is easily prepared by treating **3** with a stoichiometric amount of TlBArF in DFB (Scheme 1a—bottom). Furthermore, quantum chemical calculations suggest that the formation of **3** from **1** is thermodynamically favored by $\Delta G = -4.5$ kcal/mol (see Supp. Inf.), but most likely kinetically hindered, because **1** does not form **3**, even at elevated temperatures of 100°C in solution. To our surprise, **2** and **3** proved to be air and moisture stable for weeks, whereas **1** rapidly decomposes under atmospheric conditions. So in terms of stability, **2** and **3** (with two aryl and one alkyl group per bismuth atom) parallel the behavior of air and moisture stable BiPh₃,[23] while **1** (bearing one aryl and two alkyl groups per bismuth atom) is more reminiscent of the pyrophoric BiMe₃. Due to the C_{2v}-symmetric nature of **2** and **3**, their ¹H NMR and ¹³C NMR spectra are similar to that of **1**, notable differences being the smaller relative intensity of the signal for the bismuth-bound methyl group and a more pronounced low-field shift of the CH-units in the ¹H NMR spectrum ($\Delta\delta$ approx. +0.2 and +0.5 ppm, respectively; for details see Supp. Inf.). The methyl groups of CMe₂ moieties in the ligand backbone in **3** are magnetically inequivalent, indicating a non-planar, bowl-shaped geometry of the macrocycle. This behavior does not change in the temperature range of +25°C to +100°C. Thus, a rapid inversion of the bowl-shaped molecule does not take place in this temperature window, which is further supported by quantum chemical calculations (see Supp. Inf.). Analytical data for **2** and **3** (mass spectrometry, (VT–)NMR spectroscopy, elemental analysis) and their facile interconversion indicate that their respective composition in the solid state is also maintained in solution.

In order to evaluate the capability of **3** to coordinate large and soft cations, this heterocycle was treated with [BiMe₂(SbF₆)] in dichloromethane (DCM) at room temperature, resulting in a spontaneous color change to an intense red solution. After workup, red micro-crystals of **4-Bi** could be isolated in 29% yield (Scheme 1b—top right) after optimization of the reaction conditions (Supp. Inf.). Compound **4-Bi** consists of a heptanuclear complex cation with eight thioxanthene-diyl units with a molecular weight of 4215.3 g/mol, which could be verified by high resolution
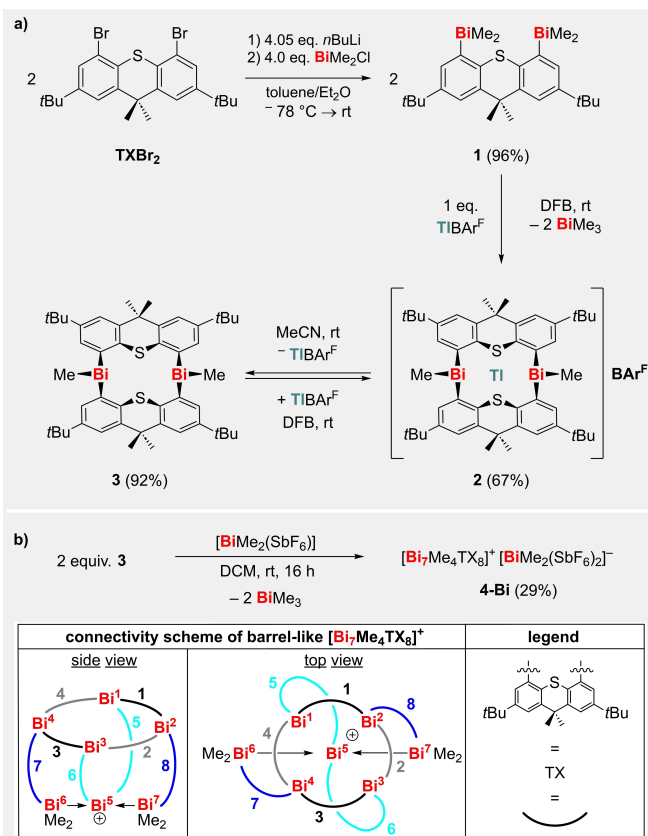
Scheme 1. a) Synthesis of compounds **1**, **2** and **3**. b) Synthesis of **4-Bi**. All TX moieties are labeled with numbers 1–8 and identical colors to indicate symmetry-equivalence (for details see Supp. Inf.). BArF=B-(3,5-(CF₃)₂C₆H₃)₄).

mass spectrometric analyses in a double-ionization approach; a connectivity Scheme is presented in Scheme 1b (bottom). The formation of **4-Bi** is remarkable, given the fact that at least eleven Bi–C bonds are broken and at least eleven Bi–C bonds are formed in this reaction. Despite the complex constitution of **4-Bi**, the NMR spectra of this compound allow for the unambiguous assignment of the relevant spin systems, since there is little signal overlap due to the absence of strong signal broadening and because the individual resonances cluster in blocks that do not interfere with each other. The protons of aromatic groups resonate as sufficiently resolved doublets in a wide range of 8.68–5.80 ppm in the ^{1}H NMR spectrum. All *t*Bu- and methyl moieties are detected as singlets in the range of 0.14 to 1.98 ppm. Alongside the resonances of **4-Bi**, signals of solvent molecules are reproducibly detected when dissolving single-crystals of **4-Bi** in CD_2Cl_2, indicating that up to twelve solvent molecules co-crystallize in or with the macromolecule, emphasizing the accessibility of the void in compound **4-Bi** for smaller molecules (see below). Additionally, VT NMR studies were carried out to evaluate a possible dynamic behavior in solution, but no significant change of the ^{1}H NMR spectrum could be observed within the scanned temperature range from $+23\,°C$ to $+100\,°C$. Thus, NMR spectroscopic analyses in conjunction with mass spectrometric data indicate that the composition of **4-Bi** in the solid state is essentially maintained in solution.

The intense red color of **4-Bi** prompted us to further characterize the substance by UV/Vis-spectroscopy, showing that the color is attributed to a main absorption band at $\lambda_{max} = 397$ nm and a less pronounced shoulder at $\lambda = 460$ nm (Figure S31). TD-DFT calculations suggest a dominant HOMO-11→LUMO+1 transition (32% contribution, Supp. Inf.) to be responsible for the main absorption band at $\lambda_{max} = 397$ nm. The LUMO+1 of **4-Bi** is predominantly constituted of a p-type atomic orbital of the (formally) cationic bismuth atom Bi5, whereas the HOMO-11 shows main contributions by s-type atomic orbitals of the bismuth atoms Bi3 and Bi7 (see Supp. Inf. for further details).

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ as a typical molecular compound (Figure 1, left). Based on distance criteria, it forms weak intermolecular Bi⋯S contacts (3.699(1) Å, which is 4% below the sum of the van der Waals radii). This results in a dimeric arrangement and a bisphenoidal coordination geometry of the bismuth atoms, underlining their tendency to interact with soft donors (Figure S23). No distinct Bi–Bi interactions are observed as the Bi1⋯Bi2 distance of 5.2330(9) Å clearly exceeds the sum of the covalent radii of the corresponding atoms. All Bi–C bond lengths in the molecule are identical within limits of the threefold standard deviation (2.257(4)–2.266(3) Å). The angle between the Ph1- and Ph2-plane (41.9°) emphasizes the overall butterfly like shape of the molecule.

In a similar fashion, **2** crystallizes in the monoclinic space group $P2_1/m$ with two molecules in the asymmetric unit, confirming a bowl-type structure with the Tl(I) atom in the center (Figure 1—middle). Most likely, the dominating forces that lead to this constitution are i) the strong pyramidalization of the bismuth atoms due to their hybridization defect ($\Sigma_{Bi} = 282.6(2)°$), which induces an acute angle between the idealized planes of the aryl rings (plane^{Ph1}/plane^{Ph2}, 75.84°) and ii) interactions between Tl$^+$ and the soft donors of the macrocycle, i.e. arene rings (average Tl⋯Ph^{centroid}, 3.715 Å), S atoms (average Tl⋯S, 3.193 Å), and Bi atoms (Tl⋯Bi, 4.098 Å).[24] These Tl-donor interactions are likely to be also crucial for the templating effect of this ion in the synthesis of **2** and are further supported by NBO analyses, which yield significant interaction energies for the Tl⋯arene ($\Sigma = 43.93$ kcal mol^{-1}), Tl⋯S ($\Sigma = 27.99$ kcal mol^{-1}), and Tl⋯Bi contacts ($\Sigma = 16.5$ kcal mol^{-1}; see Supp. Inf. for further details). The coordination sphere of the Tl atom in **2**
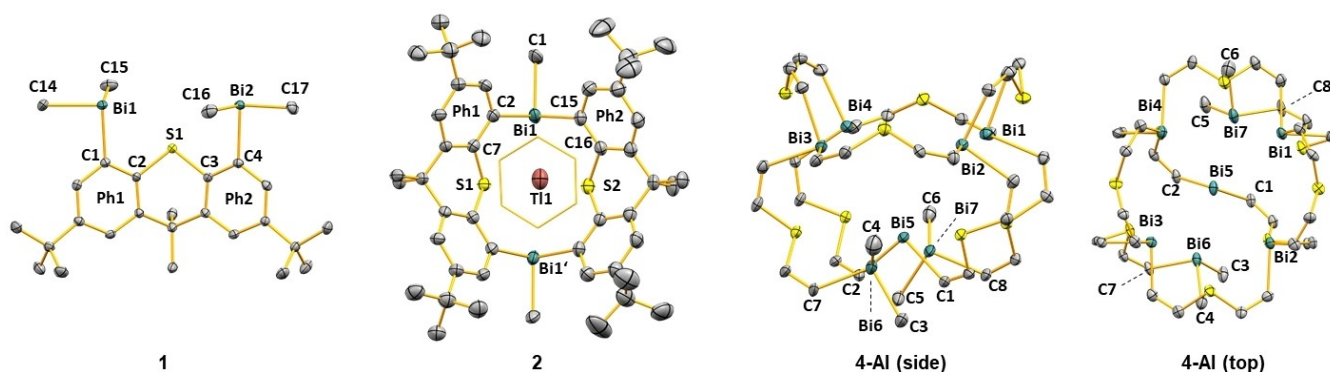

Figure 1. Molecular structure of $(BiMe_2)_2TX$ (**1**), $[(BiMe)_2TX_2Tl][BAr^F]$ (**2**) and $[Bi_7Me_4TX_8][AlCl_4]$ (**4-Al**) in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, the BAr^F anion (in the case of **2**), the $[AlCl_4]^-$ anion and most of the organic backbone elements of the used TX ligands (in the case of **4-Al**) are omitted for clarity. The coordinated benzene molecule (in the case of **2**) is shown as a wireframe. For the dimeric arrangement of **1** in the solid state arising from weak intermolecular interactions, see the Supporting Information. Selected bond lengths (Å), interatomic distances (Å), and angles (°): **1)** Bi1⋯Bi2, 5.2330(9); Bi1–C1, 2.258(2); Bi1–C14, 2.257(4); Bi1–C15, 2.253(4); Bi2–C4, 2.266(3); Bi2–C16, 2.256(3); Bi2–C17, 2.257(3); C14–Bi1–C1, 92.0(1); C1–Bi1–C15, 95.4(1); C15–Bi1–C14, 92.9(1); **2)** Bi1–C1, 2.260(7); Bi1–C2, 2.279(5); Bi1–C15, 2.281(5); C1–Bi1–C2, 94.2(2); C2–Bi1–C15, 93.7(2); C15–Bi1–C1, 94.7(2); **4-Al)** Bi6–Bi5, 3.3264(8); Bi7–Bi5, 3.2017(8); Bi5–C1, 2.251(6); Bi5–C2, 2.246(6); C1–Bi5–C2, 96.7(2); Bi6–Bi5–Bi7, 151.983(14). (Further bonding parameters are discussed in the Supp. Inf.; in the case of compound **1**, only a single molecule of the dimeric structure is shown.)

is saturated by a benzene molecule with a Tl-centroid distance of 3.129 Å. These results underscore previous findings about the crucial role of Tl-arene interactions in the context of complex formation and self-assembly.[25,26] The Bi–C bond lengths in **2** are within limits of error identical to those in **1**, showing that the electronic structure of the bismuth atoms is only weakly influenced by the macrocyclization. Furthermore, no directional bonding interactions between the anion and cation can be observed and a large Bi⋯Bi-distance of 5.4325(7) Å excludes relevant Bi–Bi-bonding.[27]

The quality of single-crystal X-ray diffraction data of **4-Bi** does not allow a discussion of bonding parameters, but serves as a proof of connectivity (Supp. Inf.). Changing the counteranion in **4-Bi**, [BiMe$_2$(SbF$_6$)$_2$]$^-$, for [AlCl$_4$]$^-$ gave compound **4-Al**, for which crystallographic data of sufficient quality could be obtained (Supp. Inf). Compound **4-Al** crystallizes in the triclinic space group $P\bar{1}$ (Figure 1—right), revealing the structure of an unprecedented heptanuclear organometallic bismuth complex cation. While a range of oligonuclear bismuth-containing clusters[28] and ligand-stabilized chains of up to four bismuth atoms have been reported,[29] compound **4-Al** is best described as a molecular complex, albeit two Bi→Bi donor/acceptor interactions are present (see below). The global structure of complex **4-Al** resembles that of an open barrel and is analyzed using the connectivity scheme in Scheme 1b. The upper rim is built of four bismuth atoms (Bi1–4) and four TX ligands (TX1–4), forming a 24-membered Bi$_4$TX$_4$ ring with a diameter of approximately 8.2 Å. Each of the bismuth atoms Bi1–4 is linked to an additional TX ligand. These ligands TX5–8 are part of the side walls of the barrel. Two of the TX ligands in the side wall (TX5,6) are connected through a bismuth atom (Bi5) to form a cationic [BiTX$_2$]$^+$ motif. The other two TX ligands in the side wall (TX7,8) are terminated by BiMe$_2$ units (with the bismuth atoms Bi6 and Bi7). Overall, the side walls of the barrel are thus constructed of four 19-membered heterocycles (4×Bi$_4$TX$_3$). The bottom of the barrel is formed by the three bismuth atoms Bi5–7. They form the unprecedented structural motif of a Bi→Bi←Bi unit, in which the bismuth atom Bi5 of a cationic [BiR$_2$]$^+$ unit is stabilized by two dative R$_3$Bi→BiR$_2$ interactions, with Bi6 and Bi7 acting as Lewis bases. The volume of the void inside the barrel-like structure amounts to ca. 350 Å^3 (approximated by an idealized cylinder; Supp. Inf.). The Bi–C bonds (2.190(8)—2.256(6) Å) and angles between idealized planes of arene groups within TX ligands (41.7–60.4°) show moderate variations, most likely due to the geometric constraints induced by the formation of the five macrocycles in compound **4-Al**, which are connected through bismuth bridgehead atoms. The two dative bonds in the Bi→Bi←Bi motif measure 3.2017(8) Å and 3.3264(8) Å, respectively, and are significantly longer than that in the only other example of a Bi→Bi donor acceptor interaction, recently reported for [Me$_3$Bi→BiMe$_2$(SbF$_6$)] (3.0005-(11) Å).[21] These differences are attributed i) to a non-linear arrangement of the bismuth atoms of the Bi$_3$ unit in **4-Al** (151.983(14)°) due to geometric constraints and ii) to the presence of two bismuth-based donors in **4-Al** populating

one vacant p-orbital of the central bismuth atom. The unexpected asymmetry of this new structural motif is ascribed to a subtle counterion effect: the shorter Bi→Bi bond involves the bismuth-based donor, which is spatially close to the counteranion. This effect was reproduced for different counteranions in DFT calculations (Supp. Inf.), and thus we suggest a Coulomb-enhanced donor-acceptor interaction.

The low-energy profiles that have been reported for some Bi–C bond cleavage steps[12–14,21,30] suggest that the reactions leading to compounds **3** and **4-Bi** may be in the regime of reversibility. Thus, the factors that influence the potential interconversion of compounds **1**, **3**, and **4-Bi** were investigated. In the formation of **3** from **1** (via **2**), two equivalents of BiMe$_3$ are eliminated (see above). Thus, an excess of 30 equivalents of BiMe$_3$ was added to **3**, which indeed induced the formation of **1** in 85% yield as determined by NMR spectroscopy, the remaining 15% being starting material **3** (Scheme 2—right). Surprisingly, the addition of 1 mol% [BiMe$_2$(SbF$_6$)] to compound **1** in benzene solution gave compound **3** in up to 42% spectroscopic yield (qualitatively identical results were obtained, when larger amounts of [BiMe$_2$(SbF$_6$)] were added; see Supp. Inf.). Addition of 30 equiv. BiMe$_3$ to this mixture gave **1** in >99% spectroscopic yield, indicating that the interconversion of **1** and **3** is not generally blocked under these conditions. These findings also indicate a pronounced solvent effect in these reactions: in the presence of [BiMe$_2$-(SbF$_6$)], **1** is transformed into **3** in benzene, but **4-Bi** is synthesized from **3** in the presence of [BiMe$_2$(SbF$_6$)] in DCM (see Supp. Inf. for further details). In addition, compound **1** also gives **4-Bi** in the presence of [BiMe$_2$-(SbF$_6$)], when DCM is chosen as the solvent, suggesting that **3** is an intermediate in this case (Scheme 2—left). The formation of **4-Bi** from **1** or **3** liberates BiMe$_3$ as well, as confirmed by NMR spectroscopy; so the reverse reaction was also investigated in this case. Reaction of **4-Bi** with
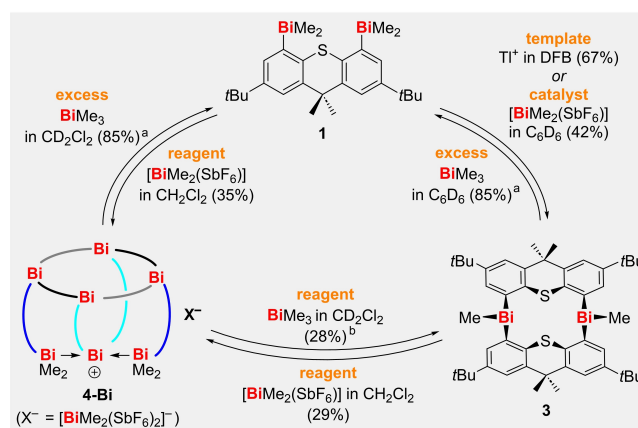
Scheme 2. Dynamic covalent relationship between **1**, **3**, and **4-Bi**. The values given in parenthesis with the non-deuterated or deuterated solvents indicate the yield of isolated compound and the spectroscopic yield, respectively. a: compound **3** is the only other major TX-containing component. b: compound **4-Bi** is the only other major TX-containing component.

6.2 equiv. of $BiMe_3$ in DCM gives a mixture containing **4-Bi** and **3** in a molar ratio 72:28 after 2 d at room temperature, with only minor amounts of thioxanthene-containing side products according to NMR spectroscopy. Using an excess of 140 equiv. $BiMe_3$ under otherwise identical conditions gives full conversion of **4-Bi** to compounds **1** (85%) and **3** (15%) with minor amounts of side products according to ^1H NMR spectroscopy. The sequence of elementary reactions related to the interconversion of **1**, **3**, and **4-Bi** is certainly complex, and its full elucidation is beyond the scope of this contribution. Nevertheless, the previously reported facile methyl exchange in compound $[Me_3Bi{\rightarrow}BiMe_2(SbF_6)]$[21] makes the viability of polar reaction pathways in the presence of $[BiMe_2(SbF_6)]$ reasonable. At the same time, facile homolytic bond dissociations of bismuth species have been reported,[31–34] which led us to monitor transformations involving **1** and $[BiMe_2(SbF_6)]$ by EPR spectroscopy. Indeed, the reaction of **1** with $[BiMe_2(SbF_6)]$ in DCM or benzene in the presence of phenyl-*N-tert*-butyl-nitrone as a spin trap allowed for the detection of a radical species, which could be related to the transfer of a methyl and/or aryl radical (Supp. Inf.). Thus, we tentatively suggest that in the complex sequence of reactions leading to **3** and **4-Bi**, both polar and radical type Bi–C bond cleavage steps may be involved.

In summary, we have presented a bifunctional organometallic bismuth(III) compound, which is highly susceptible to the reversible formation and cleavage of Bi–C bonds, opening up the field of dynamic covalent chemistry with bismuth compounds. These reactions can be controlled by external stimuli such as the addition/removal of i) the template Tl^+, ii) the reagent/catalyst $[BiMe_2(SbF_6)]$ and iii) the starting material/by-product $BiMe_3$. These approaches have granted access to a 24-membered dinuclear bismacycle (capable of coordinating Tl^+) and an unprecedented cationic heptanuclear bismuth complex with a barrel-like structure consisting of >200 non-hydrogen atoms. The controlled and reversible interconversion of these compounds under mild conditions suggests potential future applications for host–guest chemistry and switchable catalysis.

Supporting Information

The authors have cited additional references within the Supporting Information.[35–62]

Acknowledgements

Conflict of Interest

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.

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