GDCh Highlights Angewandte Chemie International Edition

Mononuclear Bismuth Compounds

International Edition: DOI: 10.1002/anie.201509234
German Edition: DOI: 10.1002/ange.201509234

Well-Defined, Mononuclear Bi^{I} and Bi^{II} Compounds: Towards Transition-Metal-Like Behavior

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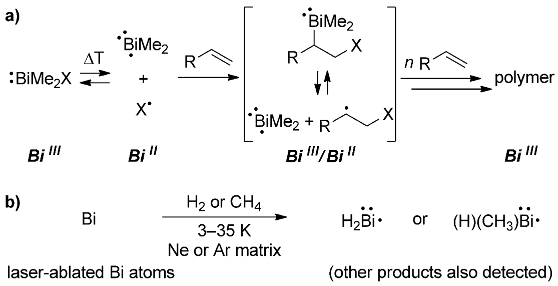
bismuth · low-valent compounds · mononuclear compounds · radicals · reactivity patterns

Heavy main-group elements commonly show oxidation states of n or $n+2$ in their mononuclear complexes ($n=1$, 2, and 3, respectively, for Group 13, 14, and 15 of the periodic table). In recent years, an increasing number of species have been reported that contradict this principle, thereby providing first glimpses of new classes of compounds.[1] Expectedly, their (physico)chemical properties clearly differ from those of traditional main-group compounds, but they remain to be fully explored. Various characteristics, such as radical ground states, the accessibility of multiple redox states, or energetically close-lying valence orbitals, offer new prospects for synthetic applications.[2]

One possibility to access main-group complexes with the metal center in an oxidation state of $<n$ is the homolytic cleavage of one or more M−X bonds (X = anionic ligand). This method is especially appealing for heavier main-group elements: In general, bond dissociation energies decrease with an increase in the atomic number of the element, providing low-energy pathways for homolytic bond cleavage processes. At the same time, low-energy pathways in principle allow for bond formation/cleavage events to proceed in a reversible manner, which generally sets the basis for catalytic applications.

Among the heaviest main-group elements, bismuth offers opportunities for synthetic chemistry as it has a low toxicity and is considerably less toxic than its neighboring elements (Pb, Sn, Sb, Te, and Po). Furthermore, for the Group 15 element bismuth, mononuclear complexes with six distinct metal-centered oxidation states should theoretically be accessible. However, the synthesis of mononuclear bismuth compounds with the metal center in an oxidation state of <3 has been challenging.[3] The difficulties encountered during the reduction of bismuth species include overreduction, disproportionation (e.g., $3\,Bi^{II}X_2 \rightarrow Bi^{0} + 2\,Bi^{III}X_3$), and oligomerization reactions (e.g., $n\,Bi^{I}X \rightarrow (Bi^{I}X)_n$).

Recently, the first examples of alleged Bi^{II} radicals as transient species in synthetic applications have been reported: Thermally activated Bi^{III} compounds, such as $BiMe_2(CMe_2CO_2Me)$ or $[Bi(C_3H_5)_2(thf)_2]^+$, act as initiators for the controlled living radical polymerization of activated olefins (Scheme 1 a).[4] Bi^{II} radicals were suggested to be the active species based on reactivity studies with trapping reagents and substoichiometric amounts of radical inhibitors. Direct IR spectroscopic evidence for the existence of the short-lived, in situ generated Bi^{II} radicals $H_2Bi^{\bullet}$ and $HMeBi^{\bullet}$ has been obtained using matrix-isolation techniques (Scheme 1 b).[5]



Scheme 1. Transient Bi^{II} species. a) Mechanism suggested for the organobismuth-mediated radical polymerization of olefins ($X=CMe_2CO_2Me$, R = electron-withdrawing group, $\Delta T \geq 333$ K). b) Matrix isolation of Bi^{II} radicals (see also Scheme 3 b).

Following these initial studies on transient Bi^{II} radicals, the first persistent bismuth-centered radical was reported by Ishida, Iwamoto, and co-workers. It was shown that these species can indeed be handled in solution at room temperature under an inert atmosphere when stabilized by a bulky supporting ligand.[6] The radical species **1** exists in a temperature-dependent equilibrium with its dimer, dibismuthane $(\mathbf{1})_2$ (Scheme 2 a). At 298 K in dilute solutions ($c = 1.0\times10^{-5}$ M), the equilibrium lies almost completely on the radical side (> 99 %). Higher temperatures favor the formation of **1** owing to the large entropic contribution to the dissociation of $(\mathbf{1})_2$ ($\Delta H = 55\ \mathrm{kJ\,mol^{-1}}$, $\Delta S = 156\ \mathrm{J\,mol^{-1}}$). Two factors limit the possibilities available to characterize radical species **1**: No EPR signal could be detected in (frozen) solutions (114–298 K), which was ascribed to strong spin–orbit coupling, and only the dimeric species, $(\mathbf{1})_2$, could be isolated from solutions containing **1** and $(\mathbf{1})_2$. Further valuable insights into the (physico)chemical properties of Bi^{II} radicals were obtained from the first isolable and fully characterized species of this kind, namely the dark red, crystalline compound **2**, which was

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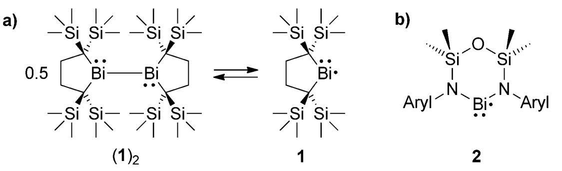
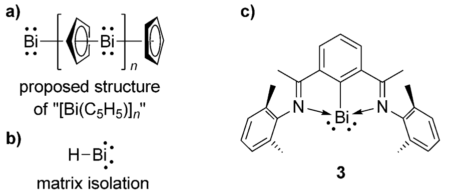


Scheme 2. a) Persistent Bi^{II} radical **1** in equilibrium with its dimer, dibismuthane $(\mathbf{1})_2$. b) The isolable Bi^{II} radical **2** (Aryl = 2,6-diisopropylphenyl).

reported by Coles and co-workers (Scheme 2b).[7] Compound **2** is stable in the solid state but shows initial signs of decomposition within 24 hours in solution at room temperature. Magnetic susceptibility measurements revealed a spin of $S = 1/2$ in the solid state and in solution, that is, **2** does not undergo dimerization. EPR spectroscopic investigations justify a description of **2** as a Bi^{II} radical with a spin density of $\rho \approx 94\,\%$ at the metal center.

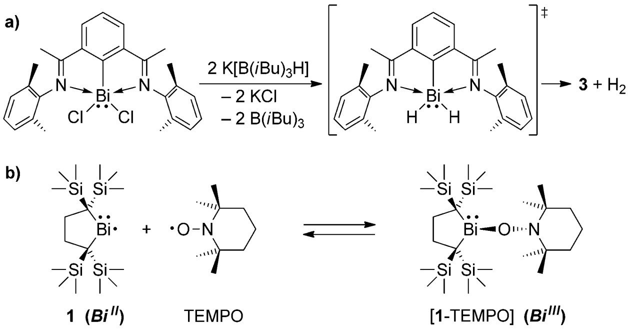
Organobismuth(I) compounds have been suggested to be stabilized by relativistic effects.[8] However, such compounds without covalent Bi–Bi bonds remained elusive for decades. A Bi^{I} compound of this class, "$[Bi(C_5H_5)]_n$", was suggested as the product resulting from the reductive elimination of $(C_5H_5)_2$ from $[Bi(C_5H_5)_3]$, but could not be satisfactorily characterized and remains ill-defined (Scheme 3a).[9] Low-temperature matrix-isolation techniques enabled the IR spectroscopic characterization of monomeric BiH (Scheme 3b).[5] The isolation of the first stable mononuclear Bi^{I} species as a deep blue crystalline material was achieved only recently by Dostál et al. (Scheme 3c).[10] The aryl diimine ligand used in this study stabilizes the Bi^{I} center both sterically (shielding of a p- and an s-type Bi-centered lone pair) and electronically (dative interactions of the imine moieties with an empty, Bi-centered p-type orbital).



Scheme 3. a) Proposed structure of ill-defined "$[Bi(C_5H_5)]_n$". b) BiH, isolated in a Ne or Ar matrix at 3–28 K (see also Scheme 1b). c) Fully characterized monomeric Bi^{I} compound **3**.

In the hands of dedicated chemists, mononuclear Bi^{I} and Bi^{II} compounds have evolved from being reactive intermediates[4] and transient species detected using matrix-isolation techniques[5] to well-defined, isolable complexes.[6,7,10] These compounds display several properties that are rather exceptional for mononuclear bismuth compounds and for traditional mononuclear main-group compounds in general:

1) Compounds **1**, **2**, and **3** are intensely colored. The radical species **1** and **2** show UV/Vis transitions that involve the metal-centered SOMO (n(Bi)→p(Bi) for **1**) or metal-to-ligand and ligand-to-metal transfer (for **2**). These transitions require the presence of valence orbitals that are relatively close in energy.
2) In the series of Bi^{I} compound **3**, the Bi^{II} compounds **1** and **2**, and a common Bi^{III} compound, the oxidation state of the metal center changes by one unit each.
3) Compound **3** is the product of a well-defined reductive elimination reaction with H_2 as the byproduct (Scheme 4a).
4) Compound **1** undergoes a reversible radical combination/homolytic bond cleavage reaction with the stable radical 2,2,6,6-tetramethyl-1-piperidinyl *N*-oxide (TEMPO; Scheme 4b). This reaction is accompanied by changes between Bi^{II} and Bi^{III} oxidation states in compounds **1** and [**1**-TEMPO].
5) Compounds **1** and **2** are paramagnetic, metal-centered radical species that can be isolated or handled in solution at room temperature.



Scheme 4. a) Reductive elimination to give **3** and H_2. b) Reversible reaction of Bi^{II} compound **1** with TEMPO to give the Bi^{III} compound [**1**-TEMPO].

The characteristics listed as (1)–(5) are traditionally associated with transition-metal species rather than with main-group compounds. Recently, it was pointed out that modern main-group chemistry has developed in a way that challenges the general validity of the traditional distinctions between the characteristics of transition-metal and main-group compounds.[2] These considerations were mainly focused on compounds containing E–E multiple bonds (E = heavy main-group element), heavy carbene analogues, and frustrated Lewis pairs. The recent developments in the field of low-valent organobismuth chemistry demonstrate that analogies can also be drawn between the characteristics of transition-metal compounds and well-defined, mononuclear bismuth complexes.

The reports describing compounds **1**–**3** are anticipated to be a starting point for the rational design and synthesis of a broader variety of low-valent, mononuclear bismuth species.[11] More detailed investigations of their fundamental reactivity patterns will be challenging tasks for future research. These include single-electron-transfer processes ($Bi^{I} \rightleftarrows Bi^{II} \rightleftarrows Bi^{III}$), the reactivity towards small molecules (e.g., CO, C_2H_4, and H_2), and oxidative-addition reactions. The reversibility of such reactions (as demonstrated in principle by the reaction in Scheme 4 b) would lay the foundation for catalysis. Irrespective of the comparison with transition-metal compounds, it is expected that these investigations will reveal new reactivity patterns and enable the development of new catalytic processes based on heavy main-group compounds.

Acknowledgements

I thank Prof. Holger Braunschweig for his support, Dr. Rian Dewhurst for helpful discussions, and the Alexander von Humboldt Foundation for funding (return fellowship).

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 484–486
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Received: October 2, 2015