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Bis(bismuth)toluene Inverted-Sandwich Complex Supported by Aminetris(phenoxide) Ligands

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The reaction of bismuth amides or alkoxides with phenolic ligand precursors yields Bi complexes of aminetris(phenoxide)s, one of which was characterized by X-ray crystallography, revealing monomeric Bi units of the tetradentate NO_3 ligand further associated via a symmetrical toluene bridge into a bis(bismuth)toluene inverted-sandwich complex. Synthesis of the analogous Sb complex suggests a markedly different geometric and electronic environment at the metal center, as evidenced by the solid-state molecular structure. Density functional theory calculations of the sandwich bismuth arene complex indicate the presence of a weak σ^*–2π interaction.

Bi plays an important role as a cocatalyst or promoter in heterogeneously catalyzed reactions,[1,2] as a component of functional materials,[3-5] as a therapeutic agent,[6] and as a Lewis acid catalyst for organic transformations.[7,8] However, despite these wide-ranging applications, well-defined and structurally characterized metalloorganic compounds of Bi are sparse in comparison to those of lighter p-block elements. This is largely due to the propensity of Bi to form polymetallic oxo species of limited solubility in organic solvents.[9] In attempting to address this problem, we have investigated aminetris(phenoxide)s as ligands to Bi. These tripodal, tetradentate ligands have recently generated considerable interest because they have been shown to provide versatile supports for a range of main-group and transition-metal centers.[10-21] Specifically in this context, they have proved useful in stabilizing monomeric complexes of metals that normally have a propensity to oligomerize.[18] Herein we report the first application of aminetris(phenoxide) ligands to Bi and Sb chemistry,[22] resulting in the structural characterization of an isolated Bi "inverted-sandwich" complex, which is well-defined and hydrocarbon-soluble.

Treatment of a toluene solution of $[Bi(OBu^t)_3]$ with an equimolar amount of tris(3,5-dimethyl-2-hydroxybenzyl)-amine (**1**) resulted in the formation of the corresponding bismuth aminetris(phenoxide) (**3**). Compound **3** could be isolated and characterized as a solid but decomposes rapidly in solution, limiting its potential usefulness and the extent to which it could be characterized. A similar reaction using the more sterically demanding ligand **2** in a dichloromethane solution yielded compound **4** in near-quantitative yield, which could be characterized fully in solution but did not yield X-ray-quality crystals (Scheme 1).[23] The reaction of **2** with $[Bi(NMe_2)_3]$ in a toluene solution yielded a crystalline solid amenable to single-crystal X-ray diffraction, which revealed a toluene adduct, $[(\mathbf{4})_2 \cdot C_7H_8]$.[24]

At the molecular level, the structure of $[(\mathbf{4})_2 \cdot C_7H_8]$ (Figure 1) is consistent with previously reported metal aminetris-

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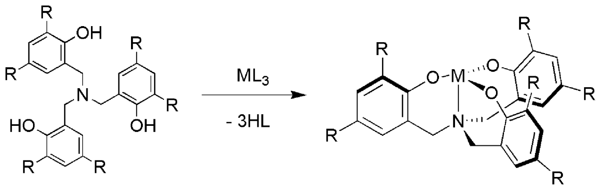
Scheme 1. Synthesis of Tris(phenoxy)aminobismuth and -antimony Complexes



1 (R = Me)
2 (R = Bu^t)

3 (R = Me, M = Bi, L = OBu^t)
4 (R = Bu^t, M = Bi, L = NMe_2 or OBu^t)
5 (R = Bu^t, M = Sb, L = NEt_2)

(phenoxide) complexes.[10−19] The ligand adopts a tripodal, tetradentate, C_3-symmetric (noncrystallographic), propeller-like arrangement around the metal center, which itself lies only 0.319 Å above the plane of the three O atoms, resulting in a pseudo-trigonal-bipyramidal coordination geometry. The Bi−OAr bond distances (average, 2.173 Å) are longer than those found in the simple homoleptic bismuth aryloxide $[Bi(OC_6H_3\text{-}2,6\text{-}Me_2)_3]$[25] (average, 2.091 Å) but similar to the nonbridging Bi−OAr distances in a recently reported bismuth oxoaryloxide calixarene complex (average, 2.175 Å).[9] The open metal faces of two of these monomeric fragments are bridged by a toluene molecule, which is symmetrically π-bonded to each Bi center in a hexahapto fashion to give an inverted-sandwich complex. A few examples of similar μ-η^6:η^6-arene bridging have been reported previously for Bi in $[(BiCl_3)_2{\cdot}C_6Me_6]_\infty$,[26,27] $[(BiBr_3)_2{\cdot}C_6Me_6]_\infty$,[27] and $[Bi_2(O_2CCF_3)_4{\cdot}C_6Me_6]_\infty$.[28] However, in all of these cases, the bridges lead to polymeric supramolecular structures, and to our knowledge, this bridging mode is unique within an isolated, molecular complex. In this respect, $[(\mathbf{4})_2{\cdot}C_7H_8]$ more closely resembles the structures of $[(CpV)_2{\cdot}C_7H_8]$[29] and an inverted-sandwich U complex $[\{(R_2N)_2U\}_2{\cdot}C_7H_8]$ reported by Cummins et al.[30] In the latter compound, the authors propose a model of back-bonding from the metal 6d and 5f orbitals into the arene lowest unoccupied molecular orbitals (LUMOs), suggesting a significant contribution from $[U^{4+}-(arene)^{4-}-U^{4+}]$. This model is supported by a small but significant elongation in the C−C(aryl) bond distances in the complex. More recently, 10-π-electron benzene, $[(C_6H_6)^{4-}]$, has been predicted to be stable within the inverted-sandwich complex $[Ba^{2+}-(C_6H_6)^{4-}-Ba^{2+}]$.[31] Despite the structural similarity of $[(\mathbf{4})_2{\cdot}C_7H_8]$ to the U complex, it is unlikely that there is a significant contribution to Bi−arene bonding from $[Bi^{5+}-(C_7H_8)^{4-}-Bi^{5+}]$, there is no significant elongation of the C−C bond lengths within the toluene moiety (average toluene C−C distances, 1.378 and 1.438 Å, for $[(\mathbf{4})_2{\cdot}C_7H_8]$ and $[\{(R_2N)_2U\}_2{\cdot}C_7H_8]$, respectively), and the Bi−arene distance is long [Bi···(arene centroid) distances, 3.263(4) and 3.07(2) Å for $[(\mathbf{4})_2{\cdot}C_7H_8]$ and $[(BiCl_3)_2{\cdot}C_6Me_6]_\infty$, respectively].

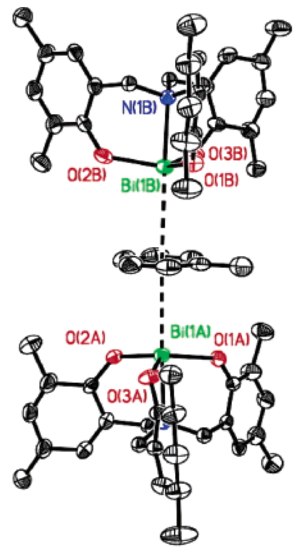


Figure 1. ORTEP diagram of complex $[(\mathbf{4})_2{\cdot}C_7H_8]$ with thermal ellipsoids at the 50% probability level. H atoms, methyls of the Bu^t groups, and ligand disorder (the structure is disordered such that both *P* and *M* enantiomers of the ligand are superimposed on the same position) are omitted for clarity. Selected bond distances (Å) and angles (deg): Bi(1)−O(1) 2.214(6), Bi(1)−O(2) 2.127(7), Bi(1)−O(3) 2.179(6), Bi(1)−N(1) 2.360(3), Bi(1)−(centroid) 3.263(4), O(1)−Bi(1)−O(2) 119.3(3), O(1)−Bi(1)−O(3) 121.3(1), O(2)−Bi(1)−O(3) 112.5(3), O(1)−Bi(1)−N(1) 80.2(2), O(2)−Bi(1)−N(1) 81.9(2), O(3)−Bi(1)−N(1) 81.8(2).

The interesting structural features of $[(\mathbf{4})_2{\cdot}C_7H_8]$ prompted investigation of the corresponding Sb analogue. $[Sb(NEt_2)_3]$ undergoes amine elimination upon the addition of **2** to afford antimony aminetris(phenoxide) (**5**; Scheme 1). X-ray diffraction analysis of white blocks of **5** (Figure 2) reveals a markedly different metal geometry from $[(\mathbf{4})_2{\cdot}C_7H_8]$; the Sb center resides in a seesaw environment consistent with valence-shell electron-pair repulsion theory for a 10-electron core with a stereochemically active lone pair. The O atoms reside in a T-shaped arrangement about the Sb center, with the trans oxides adopting a pseudolinear arrangement [165.74(4)°]. Toluene coordination to Sb is not observed in the solid state, and no solvent is present in the unit cell. The contrasting metal geometries of $[(\mathbf{4})_2{\cdot}C_7H_8]$ and **5** are attributed to the diffuse nature of the Bi lone-pair electrons versus the Sb complex. The solid-state molecular structure of **5** is not retained in solution, as indicated by the equivalent phenoxide environments in the ^1H NMR spectrum, even upon cooling to −90 °C. Similarly, Kol and co-workers have recently reported a dibenzyltris(phenoxy)aminotantalum complex possessing octahedral crystal geometry that becomes C_{3v} symmetric in solution owing to a highly fluxional process on the NMR time scale.[32]

To further characterize the nature of the bonding within $[(\mathbf{4})_2{\cdot}C_7H_8]$, density functional theory (DFT) molecular and

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(24) The NMR data of the toluene sandwich complex do not indicate that the toluene coordination is retained in solution; the chemical shifts of the toluene component in the ^1H NMR spectrum are identical with those of free toluene in solution. See the Supporting Information.

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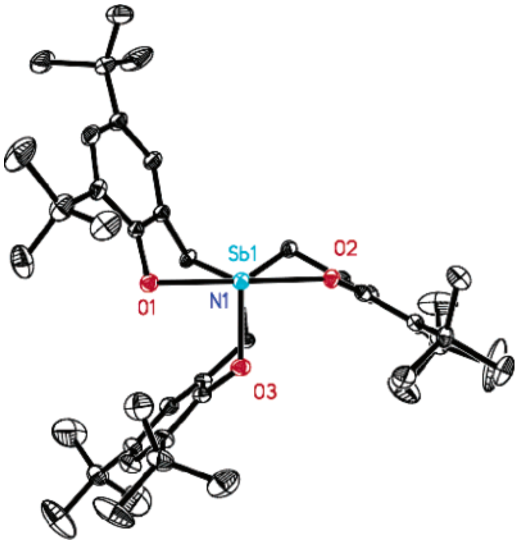
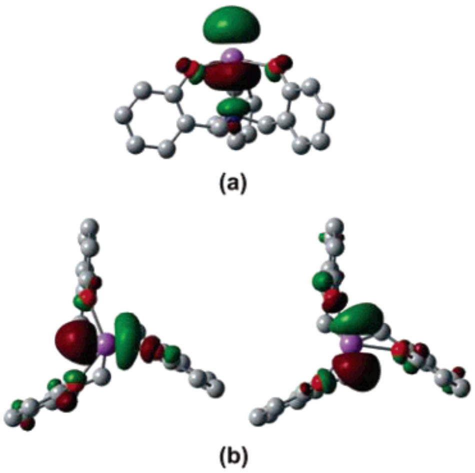


Figure 2. ORTEP diagram of complex **5** with thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sb(1)−O(1) 2.096(1), Sb(1)−O(2) 2.142(1), Sb(1)−O(3) 1.978(1), Sb(1)−N(1) 2.233(1), O(1)−Sb(1)−O(2) 165.74(4), O(1)−Sb(1)−O(3) 92.10(4), O(2)−Sb(1)−O(3) 88.53(4), O(1)−Sb(1)−N(1) 83.64(4), O(2)−Sb(1)−N(1) 82.12(4), O(3)−Sb(1)−N(1) 89.09(4).


(a)

(b)

Figure 3. LUMO (a) and LUMO+1/2 (b) MO plots for **6**.

electronic structure calculations were performed on a simplified model compound, **6**, in which the Bu^t groups of **4** were replaced by H atoms and benzene was substituted for toluene.[23] The calculated structure of **6** closely reproduced the molecular geometry of **4** within the X-ray structure of $[(\mathbf{4})_2{\cdot}C_7H_8]$. Examination of the molecular orbitals of **6** indicates the highest occupied MO (HOMO) to be ligand-based (as are HOMO−1 and HOMO−2), which is consistent with the “lone pair” of Bi being significantly lowered in energy, a phenomenon attributed to relativistic effects upon the 6s orbital.[33] The LUMO (Figure 3) is of *a* symmetry, is largely localized on the metal, and is antibonding with respect to the Bi−N and Bi−O interactions. This is consistent with the σ^* acceptor orbital model, which has been used to explain the Lewis acidity of heavy p-block elements.[34] The LUMO+1 and LUMO+2 orbitals (Figure 3) are a degenerate pair of *e* symmetry, predominantly of metal p character. Thus, the first three unoccupied MOs are of the correct symmetries to interact with the three occupied MOs of benzene, providing a $\sigma + 2\pi$ mechanism for the arene binding interaction. Indeed, calculation of the benzene adduct, $[\mathbf{6}{\cdot}C_6H_6]$, under C_3 symmetry, reproduces the hexahaptometal arene coordination found in the solid state. The binding energy of this adduct is estimated to be 3.0 kcal mol^{-1}, which is similar in magnitude to the value of 7.4 kcal mol^{-1} recently reported for a related $[AsCl_3{\cdot}C_6H_6]$ adduct.[35] Finally, the inverted-sandwich structure of $[(\mathbf{4})_2{\cdot}C_7H_8]$ is again closely reproduced when modeled as $[(\mathbf{6})_2{\cdot}C_6H_6]$ under D_3 symmetry. The overall stabilization energy due to the μ-η^6:η^6 interaction is estimated to be 5.2 kcal mol^{-1}. The metal−centroid distance in this adduct is longer than that found in the solid state, suggesting that the strength of the interaction may be somewhat underestimated, although both are consistent with a relatively weak $\sigma + 2\pi$ interaction between the arene donor and the metal acceptor, such as has been observed previously for heavy p-block arene complexes.[36]

In conclusion, we have prepared and structurally characterized the first tripodal tris(phenoxy)aminobismuth and -antimony complexes. The crystallographic observation of a unique molecular toluene inverted-sandwich complex is reproduced by DFT calculations, which also confirm that the arene forms a relatively weak $\sigma + 2\pi$ complex with the Bi centers involving LUMOs of *a* and *e* symmetry on Bi-suitable π HOMOs of toluene. By contrast, the analogous Sb complex possesses a stereochemically active lone pair and does not feature arene coordination in the solid state.

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Supporting Information Available: Experimental details for the synthesis of complexes **3**−**5**, NMR spectroscopic data, DFT analysis, and X-ray crystallographic data including collection parameters and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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