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Synthesis and Structural Characterization of Bis(2-oxoimidazolyl)hydroborato Complexes: A New Class of Bidentate Oxygen-Donor Ligands

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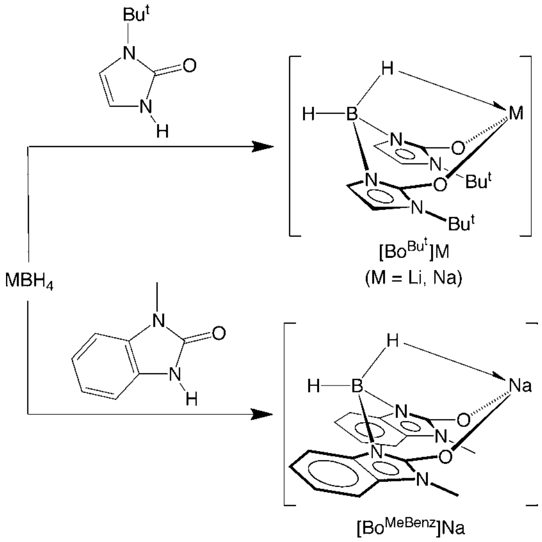
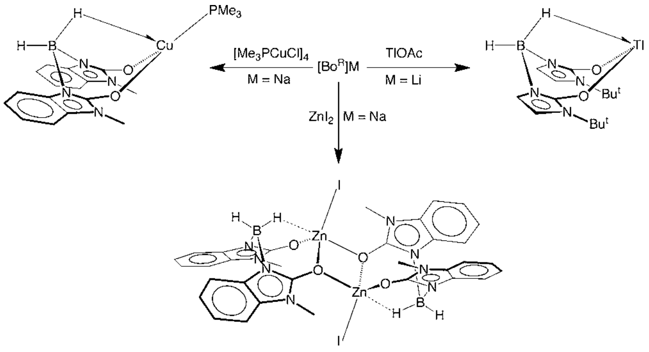
Supporting Information

ABSTRACT: A new class of bidentate ligands that feature oxygen donors, namely, the bis(2-oxo-1-*tert*-butylimidazolyl)hydroborato and bis(2-oxo-1-methylbenzimidazolyl)hydroborato ligands, $[\mathrm{Bo}^{\mathrm{Bu}^t}]$ and $[\mathrm{Bo}^{\mathrm{MeBenz}}]$, have been synthesized via the reactions of MBH_4 with 2 equiv of the respective 2-imidazolone. Chelation of $[\mathrm{Bo}^{\mathrm{Bu}^t}]$ and $[\mathrm{Bo}^{\mathrm{MeBenz}}]$ to a metal center results in a flexible eight-membered ring that is capable of adopting a "boatlike" conformation that allows for secondary M···H—B interactions.

Scheme 1. Synthesis of $[\mathrm{Bo}^{\mathrm{R}}]\mathrm{M}$ (M = Li, Na) Derivatives



Scheme 2. Synthesis of $[\mathrm{Bo}^{\mathrm{R}}]\mathrm{M}$ (M = Tl, Cu, Zn) Derivatives



Bidentate $[O_2]$ donor ligands that belong to the X_2, LX, and L_2 covalent bond classifications[1] are known for a variety of systems. For example, κ^2-carboxylate and κ^2-acetylacetonate are two commonly encountered LX donor ligands that respectively result in four- and six-membered rings upon coordination. Here, we introduce a new class of $[O_2]$ LX donor ligands that incorporate oxoimidazolyl moieties and create an eight-membered chelate ring.

We have previously described the construction of bis(mercaptoimidazolyl)hydroborato $[\mathrm{Bm}^{\mathrm{R}}]$[2] and bis(selenoimidazolyl)hydroborato $[\mathrm{Bse}^{\mathrm{R}}]$[3] ligands that respectively feature $[S_2]$ and $[Se_2]$ donor arrays, of which the former has found widespread applications.[4−6] We have now extended this series of chalcogen donor ligands to that of the lightest member and report here the synthesis of the $[O_2]$ donor counterpart, namely, the bis(oxoimidazolyl) ligand system, $[\mathrm{Bo}^{\mathrm{R}}]$ (Scheme 1). Specifically, $[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{M}$ (M = Li, Na) and $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Na}$ may be obtained by the reactions of MBH_4 (M = Li, Na) with 2 equiv of the respective 2-imidazolone (Scheme 1), an approach that is a modification of the method used for the synthesis of tris(oxoimidazolyl)hydroborato ligands.[7]

The molecular structures of several of these derivatives, namely, mononuclear $[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{Na(diglyme)}$ and dinuclear $\{[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{Li}\}_2$, $\{[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{Na}\}_2\mathrm{(diglyme)}$, and $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Na(diglyme)}\}_2$, have been determined by X-ray diffraction. In all compounds, the $[\mathrm{Bo}^{\mathrm{R}}]$ ligands chelate to the metal, forming an eight-membered ring;[8] for the dinuclear compounds, one of the oxygen atoms also serves as a bridge between the two metal centers, thereby resulting in an $[\mathrm{M}_2\mathrm{O}_2]$ core.[9]

The alkali-metal complexes, $[\mathrm{Bo}^{\mathrm{R}}]\mathrm{M}$, are useful ligand-transfer reagents for the synthesis of other derivatives. For example, the treatment of $\{[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{Li}\}_2$ with TlOAc gives $[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{Tl}$ (Scheme 2), which has been structurally characterized by X-ray diffraction, as illustrated in Figure 1. Notably, $[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{Tl}$ exists as a discrete mononuclear complex, in marked contrast to the dinuclear structure of the sulfur counterpart, $\{[\mathrm{Bm}^{\mathrm{Bu}^t}]\mathrm{Tl}\}_2$, in which one of the sulfur atoms of the $[\mathrm{Bm}^{\mathrm{Bu}^t}]$ ligand bridges the two thallium centers.[6] Furthermore, the methyl-substituted derivative $\{[\mathrm{Bm}^{\mathrm{Me}}]\mathrm{Tl}\}_\infty$ is polymeric with bridging mercaptoimidazolyl groups.[2a] The coordination geometry of thallium in $[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{Tl}$ is also supplemented by a secondary Tl···H—B interaction, which is associated with a

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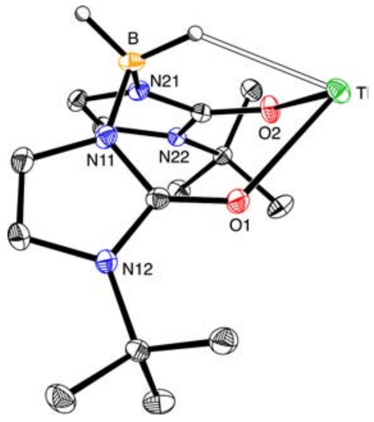


Figure 1. Molecular structure of $[\mathrm{Bo}^{\mathrm{Bu^t}}]\mathrm{Tl}$.

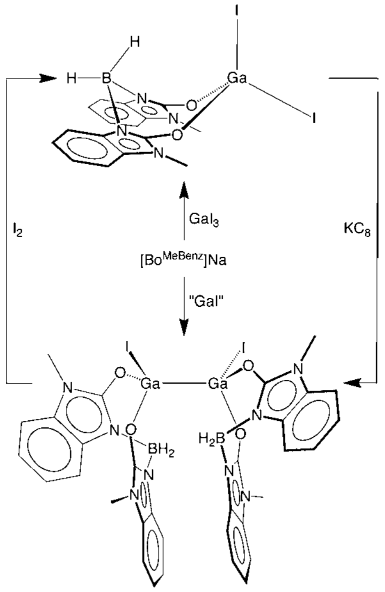
"boatlike" conformation of the $[\mathrm{Bo}^{\mathrm{Bu^t}}]$ ligand that allows the B−H group to be in the proximity of the metal center. As such, the coordination geometry more resembles that of the bis(pyrazolyl)hydroborato counterparts, $[\mathrm{Bp}^{\mathrm{R}}]\mathrm{Tl}$,[10] than that of $\{[\mathrm{Bm}^{\mathrm{R}}]\mathrm{Tl}\}_x$. It is also pertinent to contrast the mononuclear structure of $[\mathrm{Bo}^{\mathrm{Bu^t}}]\mathrm{Tl}$ with thallium(I) acetylacetonate derivatives, $\mathrm{Tl}[\mathrm{acac}^{\mathrm{R_2}}]$, which exhibit a variety of intermolecular interactions.[11]

The zinc iodide compound, $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{ZnI}\}_2$, may be obtained via the reaction of $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Na}$ with $\mathrm{ZnI_2}$ (Scheme 2). The molecular structure of $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{ZnI}\}_2$ has been determined by X-ray diffraction, thereby demonstrating that the compound is dinuclear by virtue of an oxygen atom of each $[\mathrm{Bo}^{\mathrm{MeBenz}}]$ ligand bridging the two zinc centers. Although this dinuclear structure is in marked contrast to that of the monomeric mercapto counterpart, $[\mathrm{Bm}^{\mathrm{Me}}]\mathrm{ZnI}$,[2a,b] it is similar to that of the selenium analogue, $\{[\mathrm{Bse}^{\mathrm{Me}}]\mathrm{ZnI}\}_2$.[3a,12] The overall coordination geometry about zinc can be described as a trigonal bipyramid in which the axial sites are occupied by a bridging oxygen atom and a hydrogen of the 3-center-2-electron Zn···H−B interaction ($d_{\mathrm{Zn\cdots H}} = 1.97$ Å and $d_{\mathrm{Zn\cdots B}} = 2.85$ Å).

The $[\mathrm{Bo}^{\mathrm{MeBenz}}]$ ligand is also effective for coordinating gallium, including formation of a compound that features a Ga−Ga bond. Specifically, $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Na}$ reacts with (i) $\mathrm{GaI_3}$ to give $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI_2}$ and (ii) "GaI"[13] to give dinuclear $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}\}_2$ (Scheme 3). The latter transformation is formally accompanied by disproportionation, in accordance with the previously reported reactivity of "GaI".[4b,13]

The molecular structures of $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI_2}$ and $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}\}_2$ (Figure 2) have been determined by X-ray diffraction. A noteworthy feature of both structures is that the $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Ga}$ moieties adopt a "boatlike" conformation, whereas those for $[\mathrm{Bm}^{\mathrm{R}}]\mathrm{Ga}$ in the mercapto counterparts, $[\mathrm{Bm}^{\mathrm{R}}]\mathrm{GaI_2}$ and $\{[\mathrm{Bm}^{\mathrm{R}}]\mathrm{GaI}\}_2$, are "chairlike".[4b] Another notable difference between the structures of $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}\}_2$ and $\{[\mathrm{Bm}^{\mathrm{R}}]\mathrm{GaI}\}_2$ is that, whereas the two $[\mathrm{Bm}^{\mathrm{R}}]\mathrm{GaI}$ moieties of the latter adopt a trans conformation, the two $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}$ moieties adopt an approximately eclipsed conformation in which the I−Ga−Ga−O torsion angles are 18.9° and 20.8°. Furthermore, the I−Ga−Ga−I torsion angle is 101.9°, in contrast to a value of 180° for $\{[\mathrm{Bm}^{\mathrm{R}}]\mathrm{GaI}\}_2$.[4b] Despite this conformational difference, however, the Ga−Ga bond length for $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}\}_2$ [2.3995(6) Å] is comparable to the values in the mercapto counterparts, $\{[\mathrm{Bm}^{\mathrm{Bu^t}}]\mathrm{GaI}\}_2$ [2.423(2) Å] and $\{[\mathrm{Bm}^{\mathrm{Me}}]\mathrm{GaI}\}_2$ [2.414(2) Å].[4b]

Scheme 3. Synthesis of $[\mathrm{Bo}^{\mathrm{R}}]\mathrm{Ga}$ Compounds



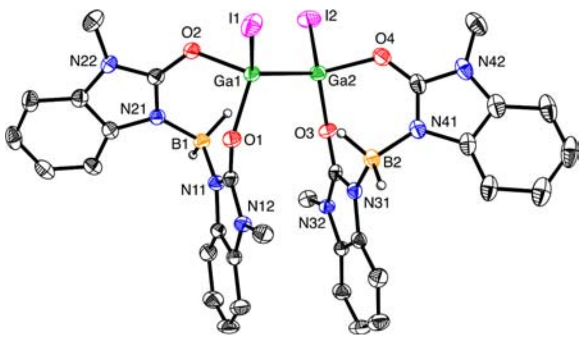


Figure 2. Molecular structure of $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}\}_2$.

Significantly, $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI_2}$ and $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}\}_2$ can be interconverted. Thus, the Ga−Ga bond of $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}\}_2$ can be cleaved by $\mathrm{I_2}$ to give $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI_2}$, while $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}\}_2$ can be regenerated by the treatment of $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI_2}$ with $\mathrm{KC_8}$ (Scheme 3).

Finally, we note that not only is the $[\mathrm{Bo}^{\mathrm{R}}]$ ligand applicable to main-group chemistry, but it is also of use in transition-metal chemistry. For example, the treatment of $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Na}$ with $[\mathrm{Me_3PCuCl}]_4$ yields $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Cu(PMe_3)}$. The molecular structure of $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Cu(PMe_3)}$ has been determined by X-ray diffraction, thereby demonstrating that the approximately trigonal-planar primary coordination sphere is supplemented by a Cu···H−B interaction ($d_{\mathrm{Cu\cdots H}} = 1.81$ Å and $d_{\mathrm{Cu\cdots B}} = 2.78$ Å) that is similar to that in the mercapto counterpart, $[\mathrm{Bm}^{\mathrm{MeBenz}}]\mathrm{Cu(PMe_3)}$ ($d_{\mathrm{Cu\cdots H}} = 1.90$ Å and $d_{\mathrm{Cu\cdots B}} = 2.75$ Å).[2c] The principal differences between the structures of $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Cu(PMe_3)}$ and $[\mathrm{Bm}^{\mathrm{MeBenz}}]\mathrm{Cu(PMe_3)}$ are that (i) the $[\mathrm{O_2CuP}]$ core deviates more from planarity than does the $[\mathrm{S_2CuP}]$ core, as is evidenced by the respective sum of the E−Cu−E and E−Cu−P angles in $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Cu(PMe_3)}$ (350.6°) and $[\mathrm{Bm}^{\mathrm{MeBenz}}]\mathrm{Cu(PMe_3)}$ (355.8°), and (ii) the difference in the two P−Cu−O bond angles (15.3°) is considerably greater than the difference in the two P−Cu−S bond angles (2.0°). Neglecting the Cu···H−B interaction, coordination of the $[\mathrm{Bo}^{\mathrm{MeBenz}}]$ ligand to copper in $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Cu(PMe_3)}$ resembles that of the β-diketonate ligands in $[\mathrm{acac}^{\mathrm{R_2}}]\mathrm{Cu(PR'_3)}$,[14] with both classes having O−Cu−O bond angles that are close to 90°. The Cu−O bond lengths in $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Cu}(\mathrm{PMe}_3)$ [2.017(2) Å and 2.073(2) Å] are, however, slightly longer than those of $[\mathrm{acac}^{\mathrm{R}_2}]\mathrm{Cu}(\mathrm{PR'}_3)$, e.g., $[\mathrm{acac}^{(\mathrm{CF}_3)_2}]\mathrm{Cu}(\mathrm{PMe}_3)$ [1.990(8) Å and 2.034(7) Å].[14]

A comparison of the structures of the $\{[\mathrm{Bo}^{\mathrm{R}}]\mathrm{M}\}$ complexes allows several observations to be made: (i) the C−O bonds are only slightly longer than those of the respective oxoimidazole;[15] (ii) in situations where one of the oxygen donors bridge two metal centers, the $\mathrm{M{-}O_{bridge}}$ bonds are slightly longer than the corresponding $\mathrm{M{-}O_{term}}$ bonds; (iii) the eight-membered ring is flexible, a feature that allows the B−H moiety to adjust its position to accommodate a 3-center-2-electron M···H−B interaction if so required to supplement the bidentate $[O_2]$ coordination. For example, the M···B distances vary from 2.78 Å for $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Cu}(\mathrm{PMe}_3)$ to 3.41 Å for $[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{Tl}$ (Table 1).

Table 1. Selected Metrical Data for $[\mathrm{Bo}^{\mathrm{R}}]\mathrm{M}$ Complexes[a]

	$d(\mathrm{M{-}O_{term}})$/Å	$d(\mathrm{M}\cdots\mathrm{B})$/Å	Δd/Å[b]
$[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Cu}(\mathrm{PMe}_3)$	2.05	2.78	0.73
$\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{ZnI}\}_2$	1.96	2.85	0.89
$[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{Tl}$	2.51	3.41	0.90
$[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{Na}(\mathrm{diglyme})$	2.25	3.20	0.95
$\{[\mathrm{Bo}^{\mathrm{Bu}^t}]\mathrm{Li}\}_2$	1.83	2.81	0.98
$\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Na}(\mathrm{diglyme})\}_2$	2.32	3.35	1.03
$\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}\}_2$	1.90	3.32	1.42
$[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}_2$	1.86	3.40	1.54

[a] Average values listed where appropriate. [b] $\Delta d = d(\mathrm{M}\cdots\mathrm{B}) - d(\mathrm{M{-}O_{term}})$.

A simple gauge of the significance of these M···H−B interactions (Δd) can be obtained by comparing the M···B distance relative to the average terminal M−O distances, i.e., $\Delta d = d(\mathrm{M}\cdots\mathrm{B}) - d(\mathrm{M{-}O_{term}})$. On this basis, the most significant M···H−B interaction is for $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{Cu}(\mathrm{PMe}_3)$ (Δd = 0.73 Å), while the least significant is for $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}_2$ (Δd = 1.54 Å). Indeed, the latter is to be expected because, in the absence of any interaction with the B−H group, the gallium centers of $[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{GaI}_2$ are four-coordinate, a common situation for gallium.[16]

In summary, a new class of bidentate LX ligands that feature two oxygen donors, namely, $[\mathrm{Bo}^{\mathrm{R}}]$, have been synthesized via the respective reactions of MBH_4 with 2 equiv of 1-*tert*-butylimidazolone and 1-methyl-2-benzimidazolinone. The $[\mathrm{Bo}^{\mathrm{R}}]$ ligands are versatile and are able to coordinate to both main-group and transition metals. Unlike for related $[\mathrm{acac}^{\mathrm{R}_2}]$ ligands, chelation of the $[\mathrm{Bo}^{\mathrm{R}}]$ ligand results in the formation of a flexible eight-membered ring that is capable of adopting a "boatlike" conformation, thereby allowing for a range of secondary M···H−B interactions to accommodate the nature of the metal center.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystallographic data (CIFs), and Cartesian coordinates for geometry-optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) An interesting difference between the structures of $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{ZnI}\}_2$ and $\{[\mathrm{Bse}^{\mathrm{Me}}]\mathrm{ZnI}\}_2$ is that the two pairs of Zn−O bond lengths pertaining to the $[\mathrm{Zn}_2\mathrm{O}_2]$ core of $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{ZnI}\}_2$ [2.008(2) and 2.201(2) Å; Δ = 0.193 Å] are much more similar than the two pairs of Zn−Se bond lengths in $\{[\mathrm{Bse}^{\mathrm{Me}}]\mathrm{ZnI}\}_2$ [2.452(1) and 2.826(1) Å; Δ = 0.374 Å].[3a] This trend is in accordance with density functional theory calculations on $\{[\mathrm{Bo}^{\mathrm{MeBenz}}]\mathrm{ZnI}\}_2$ (0.083 Å, average value) and $\{[\mathrm{Bse}^{\mathrm{Me}}]\mathrm{ZnI}\}_2$ (0.415 Å, average value).

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