Monovalent indium in a sulfur-rich coordination environment: synthesis, structure and reactivity of *tris*(2-mercapto-1-*tert*-butylimidazolyl)hydroborato indium, $[Tm^{Bu^t}]In$†

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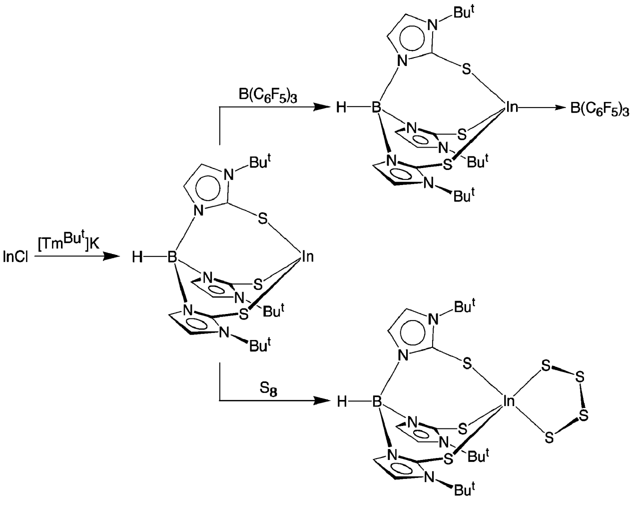
$[Tm^{Bu^t}]In$, the first structurally-characterized monovalent indium compound that features a sulfur-rich coordination environment, has been synthesized *via* treatment of InCl with $[Tm^{Bu^t}]K$; in contrast to the thallium counterpart, the lone pair of $[Tm^{Bu^t}]In$ is a site of reactivity, thereby allowing formation of $[Tm^{Bu^t}]In \rightarrow B(C_6F_5)_3$ and $[Tm^{Bu^t}]In(\kappa^2\text{-}S_4)$ upon treatment with $B(C_6F_5)_3$ and S_8, respectively.

The *tris*(2-mercapto-1-R-imidazolyl)hydroborato ligand system, $[Tm^R]$, has been shown to provide a suitable ligand platform for investigating the reactivity of metal centers in a sulfur-rich coordination environment.[1,2] In this regard, although a variety of thallium(I) complexes $[Tm^R]Tl$ have been reported as convenient reagents to introduce $[Tm^R]$ ligands to other metal centers, the application of $[Tm^R]$ ligands to the lighter Group 13 elements has received virtually no attention. Indeed, the trivalent indium complex $\{[Tm^{Me}]_2In\}I$ is the only *tris*(2-mercapto-1-R-imidazolyl)hydroborato derivative for the other Group 13 elements.[3] Herein, we report the application of the $[Tm^{Bu^t}]$ ligand to the chemistry of indium, and thereby demonstrate how the chemistry of monovalent indium in a sulfur-rich coordination environment differs considerably from that of thallium.

The monovalent indium complex $[Tm^{Bu^t}]In$ may be readily obtained *via* treatment of InCl with $[Tm^{Bu^t}]K$ (Scheme 1). The molecular structure of $[Tm^{Bu^t}]In$ has been determined by X-ray diffraction,† as illustrated in Fig. 1, which demonstrates that it exists as a discrete mononuclear complex with a trigonal pyramidal indium center.

The observed structure of $[Tm^{Bu^t}]In$ is significant because the thallium counterpart[4] does *not* adopt such a structure and exists as a dinuclear compound $\{[Tm^{Bu^t}]Tl\}_2$,† in which the $[Tm^{Bu^t}]$ ligand bridges two thallium centers (Fig. 2).[5,6] The nonisostructural nature of $[Tm^{Bu^t}]In$ and $\{[Tm^{Bu^t}]Tl\}_2$ is noteworthy because *tris*(pyrazolyl)hydroborato analogues, $[Tp^{RR'}]In$ and $[Tp^{RR'}]Tl$, are invariably isostructural, with mononuclear trigonal pyramidal geometries.[7–9] Another interesting aspect of $[Tm^{Bu^t}]In$ is that, while monovalent indium compounds are reasonably common, structurally characterized mononuclear derivatives are rare and are limited to ligands that feature C, N, O and P donors.[10,11] As such, $[Tm^{Bu^t}]In$ is the first structurally characterized example of a monovalent indium compound with a sulfur-rich environment.



Scheme 1

Molecular orbital calculations indicate that the HOMO of $[Tm^{Bu^t}]In$ is occupied by the indium(I) lone pair that has predominantly indium 5s (46%) and $5p_z$ (32%) character. The observed reactivity of $[Tm^{Bu^t}]In$ is also in accord with an indium based HOMO. For example, $[Tm^{Bu^t}]In$ serves as a Lewis base towards $B(C_6F_5)_3$, thereby forming the adduct $[Tm^{Bu^t}]In \rightarrow B(C_6F_5)_3$ (Scheme 1) that has been structurally characterized by X-ray diffraction (Fig. 3).†[12]

A comparison of the In–B bond length in $[Tm^{Bu^t}]In \rightarrow B(C_6F_5)_3$ [2.374(2) Å] with the corresponding lengths in the two other complexes that feature $In \rightarrow B(C_6F_5)_3$ interactions, namely $[Ar^{dipp}]In \rightarrow B(C_6F_5)_3$ [2.298(2) Å][13,14] and $[Ar^{trip}]In \rightarrow B(C_6F_5)_3$ [2.322(2) Å],[13,14] indicates that $[Tm^{Bu^t}]In$ is a less effective electron pair donor than either $[Ar^{dipp}]In$ or $[Ar^{trip}]In$

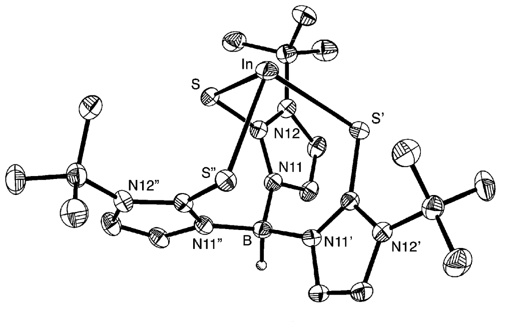


Fig. 1 Molecular structure of $[Tm^{Bu^t}]In$ (20% thermal ellipsoids). The molecule resides on a crystallographic three-fold axis.

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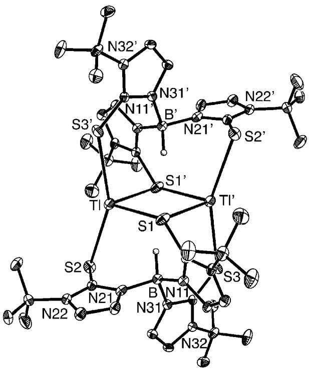


Fig. 2 Molecular structure of $\{[\mathrm{Tm^{Bu^t}}]\mathrm{Tl}\}_2$ (20% thermal ellipsoids). The dimeric molecule resides on a crystallographic inversion center.

which feature monocoordinate indium. In addition to the variation in In–B bond lengths, the degree of pyramidal distortion of the $\mathrm{B(C_6F_5)_3}$ ligand also provides a means to compare the magnitude of the $\mathrm{In \rightarrow B(C_6F_5)_3}$ interactions. While a variety of methods have been proposed for quantifying structural distortions of four-coordinate compounds,[15] a simple indication is provided by the deviation of the $\mathrm{B(C_6F_5)_3}$ ligand from planarity, as indicated by the magnitude of Σ(C–B–C).[16] On the basis of this criterion, $[\mathrm{Tm^{Bu^t}}]$In is also considered to be the less effective electron pair donor, with $[\mathrm{Tm^{Bu^t}}]\mathrm{In \rightarrow B(C_6F_5)_3}$ having the value closest to 360°, *viz.*: $[\mathrm{Tm^{Bu^t}}]\mathrm{In \rightarrow B(C_6F_5)_3}$ [347.9°], $[\mathrm{Ar^{dipp}}]\mathrm{In \rightarrow B(C_6F_5)_3}$ [339.4°],[14] and $[\mathrm{Ar^{trip}}]\mathrm{In \rightarrow B(C_6F_5)_3}$ [337.8°].[14]

The degree of pyramidal distortion also provides a convenient means to compare the magnitude of the $\mathrm{M \rightarrow B(C_6F_5)_3}$ interaction for compounds of different metals for which the M → B bond lengths differ due to the different covalent radii of M. In this regard, it is interesting to note that the only structurally characterized $\mathrm{M \rightarrow B(C_6F_5)_3}$ complexes listed in the Cambridge Structural Database[17] are for the Group 13 metals, for which the largest value of Σ(C–B–C) is observed for $\mathrm{Cp^*Ga \rightarrow B(C_6F_5)_3}$ [342.2°].[18] Furthermore, for nonmetals, Σ(C–B–C) for $\mathrm{L \rightarrow B(C_6F_5)_3}$ varies from 324.9° to 343.1°, with the largest value being for $\mathrm{MeCN \rightarrow B(C_6F_5)_3}$ [343.1°].[19,20] The value of Σ(C–B–C) for $\mathrm{MeCN \rightarrow B(C_6F_5)_3}$ lies between the values for the indium complexes $[\mathrm{Ar^{trip}}]\mathrm{In \rightarrow B(C_6F_5)_3}$ and $[\mathrm{Tm^{Bu^t}}]\mathrm{In \rightarrow B(C_6F_5)_3}$, thereby indicating how the Lewis basicity of a monovalent indium center is effectively modulated by the coordination environment. As such, it is evident that In(I) may function as either a better or worse Lewis base than acetonitrile, depending on the nature of the coordination environment around indium.

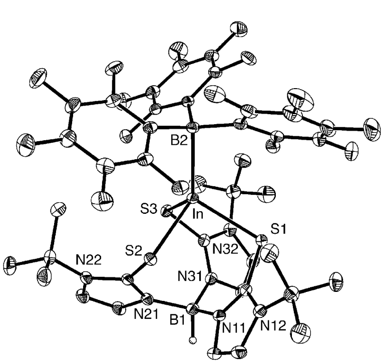


Fig. 3 Molecular structure of $[\mathrm{Tm^{Bu^t}}]\mathrm{In \rightarrow B(C_6F_5)_3}$ (20% thermal ellipsoids).

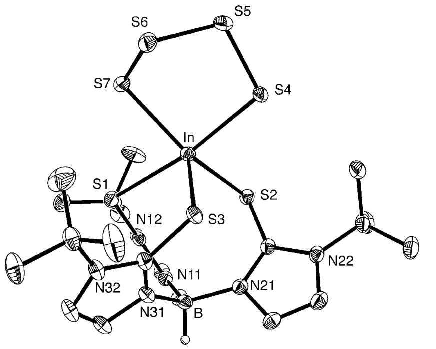
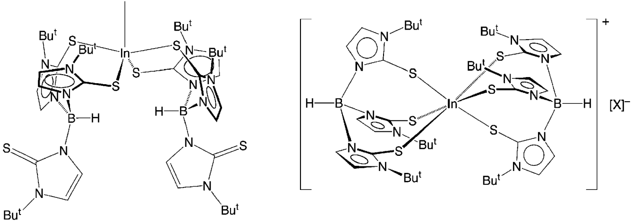


Fig. 4 Molecular structure of $[\mathrm{Tm^{Bu^t}}]\mathrm{In}(\kappa^2\text{-}\mathrm{S_4})$ (20% thermal ellipsoids).

A further illustration of the availability of the indium lone pair of $[\mathrm{Tm^{Bu^t}}]$In is provided by the observation that treatment with sulfur results in the formation of the tetrasulfido complex $[\mathrm{Tm^{Bu^t}}]\mathrm{In}(\kappa^2\text{-}\mathrm{S_4})$, as illustrated in Scheme 1. The molecular structure of $[\mathrm{Tm^{Bu^t}}]\mathrm{In}(\kappa^2\text{–}\mathrm{S_4})$ has been determined by X-ray diffraction (Fig. 4),† thereby demonstrating that the coordination geometry of indium is trigonal bipyramidal.[21] As expected for such a geometry, the In–S bonds in the axial positions are longer than those in the equatorial positions.[22] Specifically, the axial In–S(4) bond of the $\{\mathrm{In}(\kappa^2\text{-}\mathrm{S_4})\}$ moiety is 2.571[1] Å, while the equatorial In–S(7) bond is 2.509[1] Å;[23] likewise, the axial In–S(1) bond of the $\{[\mathrm{Tm^{Bu^t}}]\mathrm{In}\}$ moiety is 2.6414(7) Å, while the equatorial In–S(2) and In–S(3) bonds are 2.5903(7) and 2.5070(7) Å, respectively.

The formation of $[\mathrm{Tm^{Bu^t}}]\mathrm{In \rightarrow B(C_6F_5)_3}$ and $[\mathrm{Tm^{Bu^t}}]\mathrm{In}(\kappa^2\text{-}\mathrm{S_4})$ upon treatment of $[\mathrm{Tm^{Bu^t}}]$In with $\mathrm{B(C_6F_5)_3}$ and $\mathrm{S_8}$, respectively, is also noteworthy because the thallium analogue does not exhibit such reactivity. This difference is, nevertheless, in accord with the notion that thallium typically shows a greater tendency to exist in the monovalent state, a phenomenon that is often expressed in terms of the so-called "inert pair effect".[24]

In addition to the trivalent indium complexes that feature one $[\mathrm{Tm^{Bu^t}}]$ ligand, derivatives with two $[\mathrm{Tm^{Bu^t}}]$ ligands, namely $\{[\mathrm{Tm^{Bu^t}}]_2\mathrm{In}\}\mathrm{X}$ (X = Cl, I, $\mathrm{N_3}$, $[\mathrm{InCl_4}]$), have also been isolated. Interestingly, X-ray diffraction studies† demonstrate that the $\{[\mathrm{Tm^{Bu^t}}]_2\mathrm{In}\}\mathrm{X}$ complexes adopt two types of structural motifs (Fig. 5) that differ according to whether or not X coordinates to the indium center. If X coordinates, the two $[\mathrm{Tm^{Bu^t}}]$ ligands bind in a κ^2-manner such that the indium center of $[\kappa^2\text{-}\mathrm{Tm^{Bu^t}}]_2\mathrm{InX}$ is five coordinate. Conversely, if X does not coordinate, the $[\mathrm{Tm^{Bu^t}}]$ ligands adopt a κ^3-coordination mode such that the indium center of $\{[\kappa^3\text{-}\mathrm{Tm^{Bu^t}}]_2\mathrm{In}\}^+\mathrm{X}^-$ is six coordinate.[25] Structurally characterized examples of



X = Cl, $\mathrm{N_3}$

X = Cl, I, $[\mathrm{InCl_4}]$

Fig. 5 Structural motifs for $[\mathrm{Tm^{Bu^t}}]_2\mathrm{InX}$.

Table 1 Experimental and calculated In–S bond lengths for the $[\mathrm{Tm^{Bu^t}}]$–In interaction in various derivatives

	$d(\mathrm{In–S})$/Å (expt.)	$d(\mathrm{In–S})$/Å (calc.)
$[\mathrm{Tm^{Bu^t}}]\mathrm{In}$	2.7493(6), 2.7493(6), 2.7493(6)	2.855, 2.855, 2.855
$[\mathrm{Tm^{Bu^t}}]\mathrm{In} \rightarrow \mathrm{B(C_6F_5)_3}$	2.5487(5), 2.5709(6), 2.5856(5)	2.640, 2.635, 2.635
$[\mathrm{Tm^{Bu^t}}]\mathrm{In}(\kappa^2\text{-}\mathrm{S_4})$	2.5070(7), 2.5903(7), 2.6415(7)	2.593, 2.618, 2.772
$\{[\mathrm{Tm^{Bu^t}}]_2\mathrm{In}\}[\mathrm{I}]$	2.6405(8)	2.624–2.672; 2.654 (av.)[a]

[a] Values for $\{[\mathrm{Tm^{Bu^t}}]_2\mathrm{In}\}^+$.

$\{[\kappa^3\text{-}\mathrm{Tm^{Bu^t}}]_2\mathrm{In}\}^+\mathrm{X}^-$ have been obtained for X = Cl and I, $[\mathrm{InCl_4}]$, while structurally characterized examples of $[\kappa^2\text{-}\mathrm{Tm^{Bu^t}}]_2\text{-}\mathrm{InX}$ have been obtained for X = Cl and $\mathrm{N_3}$. Interestingly, both forms have been structurally characterized for X = Cl.

Other than the different coordination modes adopted by the $[\mathrm{Tm^{Bu^t}}]$ ligand, the most interesting feature concerned with the structures of the various $\{[\mathrm{Tm^{Bu^t}}]\mathrm{In}\}$ derivatives pertains to the In–S bond lengths, as summarized in Table 1. Specifically, the In–S bond lengths in monovalent $[\mathrm{Tm^{Bu^t}}]\mathrm{In}$ are distinctly longer than those in all the trivalent derivatives.[26] Thus, the addition of both $\mathrm{B(C_6F_5)_3}$ and sulfur to monovalent $[\mathrm{Tm^{Bu^t}}]\mathrm{In}$ is accompanied by a considerable shortening of the In–S bond lengths, a trend that is reproduced by DFT calculations. On the basis of calculations by Green and Suter on related [Tp]Ga and [Tp]GaE (E = O, S, Se, Te) complexes,[27] the origin of the shortening of the In–S bond lengths may be attributed to the fact that the indium lone pair orbital in $[\mathrm{Tm^{Bu^t}}]\mathrm{In}$ possesses some In–S antibonding character. Thus, removal of electron density from this orbital upon either coordination of $\mathrm{B(C_6F_5)_3}$ or oxidative addition of a S–S bond reduces the antibonding interaction with the sulfur atoms of the $[\mathrm{Tm^{Bu^t}}]$ ligand and thereby shortens the In–S bonds.

In summary, $[\mathrm{Tm^{Bu^t}}]\mathrm{In}$, the first monovalent indium compound that features a sulfur-rich coordination environment has been synthesized. The facile formation of $[\mathrm{Tm^{Bu^t}}]\mathrm{In} \rightarrow \mathrm{B(C_6F_5)_3}$ and $[\mathrm{Tm^{Bu^t}}]\mathrm{In}(\kappa^2\text{-}\mathrm{S_4})$ demonstrates that the indium lone pair of $[\mathrm{Tm^{Bu^t}}]\mathrm{In}$ is a site of reactivity, in marked contrast to the inertness of the thallium counterpart.

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