# Benzannulated Tris(2-mercapto-1-imidazolyl)hydroborato Ligands: Tetradentate $\mathbf{K}^{4}-\mathrm{S}_{3} \mathrm{H}$ Binding and Access to Monomeric Monovalent Thallium in an [ $S_{3}$ ] Coordination Environment 

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#### Abstract

The benzannulated tris(mercaptoimidazolyl)borohydride sodium complex, [ $\left.\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{B}} \mathrm{Benz}\right] \mathrm{Na}$, has been synthesized via the reaction of $\mathrm{NaBH}_{4}$ with 1-tert-butyl-1,3-dihydro- 2 H -benzimidazole-2thione, while $\left[\mathrm{Tm}^{\text {MeBenz }}\right] \mathrm{K}$ has been synthesized via the reaction of $\mathrm{KBH}_{4}$ with 1-methyl-1,3-dihydro- 2 H -benzimidazole-2-thione. The molecular structures of the solvated adducts, $\left\{\left[\mathrm{Tm}^{\mathrm{But}}{ }^{\mathrm{Benz}}\right] \mathrm{Na}(\mathrm{THF})\right\}_{2}(\mu-\mathrm{THF})_{2}$ and $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}$, have been determined by X-ray diffraction, which demonstrates that the $\left[\mathrm{Tm}^{\mathrm{R}}\right]$ ligands in these complexes adopt different coordination modes to that in $\left\{\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Na}\right\}_{2}(\mu-\mathrm{THF})_{3}$. Specifically, while the $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right]$ ligand of the sodium complex $\left\{\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Na}\right\}_{2}(\mu-\mathrm{THF})_{3}$ adopts a $\mathrm{k}^{3}-S_{3}$ coordination mode, the potassium complex $\left[\mathrm{Tm}^{\text {MeBenz }}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}$ adopts a most uncommon inverted $\kappa^{4}-S_{3} H$ coordination mode in which the potassium binds to all three sulfur donors and the hydrogen of the B-H group in a linear $\mathrm{K} \cdot \cdot \cdot \mathrm{H}-\mathrm{B}$ manner. Furthermore, the $\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{t}} \mathrm{Benz}}\right]$ ligand of  flexibility of this ligand system. The monovalent thallium compounds, $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ and [ $\left.\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{t}} \mathrm{Benz}}\right] \mathrm{Tl}$, have been obtained via the corresponding reactions of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Na}$ and [ $\left.\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{B}} \mathrm{Benz}\right]$ Na with TlOAc. X-ray diffraction demonstrates that the three sulfur donors of the [ $\left.\mathrm{Tm}^{\mathrm{RBenz}}\right]$ ligands of both $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ and $\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{t} \text { Benz }}\right] \mathrm{Tl}$ chelate to thallium. This coordination mode is in marked contrast to that in other $\left[\mathrm{Tm}^{\mathrm{R}}\right] \mathrm{Tl}$ compounds, which exist as dinuclear molecules wherein two of the sulfur donors coordinate to different thallium centers. As such, this observation provides further evidence that benzannulation promotes $\mathrm{k}^{3}-S_{3}$ coordination in this system.


## INTRODUCTION

Tris(mercaptoimidazolyl)hydroborato ligands, $\left[\mathrm{Tm}^{\mathrm{R}}\right]$ (Figure 1), ${ }^{1,2}$ represent a popular class of $\mathrm{L}_{2} \mathrm{X}^{3}\left[S_{3}\right]$ donors that have found widespread applications. For example, we have utilized these ligands to model aspects of zinc enzymes with sulfur-rich active sites ${ }^{4}$ and the mechanism of action of the protolytic cleavage of $\mathrm{Hg}-\mathrm{C}$ bonds by organomercurial lyase $(\operatorname{MerB}) .{ }^{5}$ One of the reasons for extensive use of these ligands is that they may be readily modified by incorporation of different 1-R substituents, thereby allowing facile modification of the steric and electronic properties of the ligand system. ${ }^{6,7}$ Moreover, with the synthesis of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Na}$, we recently reported that benzannulation of this ligand system is also possible (Figure 1) and that such derivitization has an impact on the coordination mode adopted by the ligand. ${ }^{8}$ Here, we report the synthesis of a more sterically demanding benzannulated ligand, namely [ $\left.\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{Benz}}\right]$, and demonstrate how it allows the isolation of the first monomeric monovalent $\left[\mathrm{Tm}^{\mathrm{R}}\right]$ thallium compound that features $\kappa^{3}-S_{3}$ coordination.

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## RESULTS AND DISCUSSION

Our previous studies have demonstrated that benzannulated [ $\left.\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Na}$ may be synthesized via the reaction of $\mathrm{NaBH}_{4}$ with three equivalents of 1-methyl-1,3-dihydro- 2 H -benzimidazole-2-thione. ${ }^{8}$ In order to obtain a more sterically demanding variant of this ligand, we have now extended this method to the synthesis of [ $\left.\mathrm{Tm}^{B u^{t} \operatorname{Benz}}\right] \mathrm{Na}$ (Scheme 1), which features bulky t-butyl substituents. The molecular structure of the THF adduct $\left\{\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{t}} \mathrm{Benz}}\right] \mathrm{Na}(\mathrm{THF})\right\}_{2}(\mu-\mathrm{THF})_{2}$ has been determined by X-ray diffraction, as illustrated in Figure 2. The impact of the t-butyl substituents is manifested by the $\left[\mathrm{Tm}^{B u^{t} \text { Benz }}\right]$ derivative adopting a different type of structure than that of the $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right]$ derivative (Figure 3). Specifically, while both complexes are dinuclear and each sodium is attached to three THF molecules, $\left\{\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Na}\right\}_{2}(\mu-\mathrm{THF})_{3}$ features sodium centers that are triply bridged, whereas $\left.\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{B}} \mathrm{Benz}\right] \mathrm{Na}(\mathrm{THF})\right\}_{2}(\mu-\mathrm{THF})_{2}$ features sodium centers that are attached to one terminal and two bridging THF ligands. Accompanying this difference in THF coordination modes, the $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right]$ and $\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{t}} \mathrm{Benz}}\right]$ ligands adopt different conformations in their respective sodium complexes. Thus, whereas the [ $\mathrm{Tm}^{\mathrm{MeBenz}}$ ] ligand possesses a 0:3 conformation ${ }^{9}$ in which the three thione moieties point away from the $\mathrm{B}-\mathrm{H}$ group, such that the ligand binds in a $\kappa^{3}-S_{3}$ manner, the [ $\left.\mathrm{Tm}^{\mathrm{Bu}}{ }^{\text {lenzen }}\right]$ ligand adopts an inverted 3:0 conformation in which the three thione moieties point towards the $\mathrm{B}-\mathrm{H}$ group and the ligand binds in a $\kappa^{3}-S_{2} H$ manner.

The $\kappa^{3}-S_{2} H$ coordination mode of $\left.\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{t}} \mathrm{Benz}\right] \mathrm{Na}(\mathrm{THF})\right\}_{2}(\mu-\mathrm{THF})_{2}$ is characterized by two $\mathrm{Na}-\mathrm{S}$ bond lengths of 2.945(3) $\AA$ and 3.078(3) $\AA,{ }^{10}$ and a $\mathrm{Na} \cdot \cdots \cdot \mathrm{H}-\mathrm{B}$ distance of 2.12(5) $\AA$. While the $\mathrm{Na}-\mathrm{S}$ bond lengths are comparable to those in $\left\{\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Na}\right\}_{2}(\mu-\mathrm{THF})_{3}$ and its bis(mercaptoimidazolyl) counterpart, $\left\{\mu-\left[\mathrm{Bm}^{\mathrm{MeBenz}}\right] \mathrm{Na}(\mathrm{THF})_{2}\right\}_{2}$, as summarized in Table 1 , the $\mathrm{Na} \bullet \bullet \cdot \mathrm{H}-\mathrm{B}$ distance $[2.12(5) \AA$ ] is short by comparison to those in $\{\mu-$ $\left.\left[\mathrm{Bm}^{\mathrm{MeBenz}}\right] \mathrm{Na}(\mathrm{THF})_{2}\right\}_{2}[2.45(2) \AA$ and 2.48(2) $\AA] .{ }^{8}$ Furthermore, the mean $\mathrm{Na} \bullet \bullet \bullet \mathrm{H}$ distance in structurally characterized compounds listed in the Cambridge Structural Database is $2.45 \AA .{ }^{11}$ Thus, it is evident that the $\mathrm{Na} \bullet \bullet \bullet \mathrm{H}-\mathrm{B}$ interaction in $\left\{\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{B}} \mathrm{Benz}\right] \mathrm{Na}(\mathrm{THF})\right\}_{2}(\mu-\mathrm{THF})_{2}$ must be considered significant. ${ }^{12}$ Another noteworthy feature of $\left\{\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{B}} \mathrm{Benz}\right] \mathrm{Na}(\mathrm{THF})\right\}_{2}(\mu-\mathrm{THF})_{2}$ is that the bridging and terminal $\mathrm{Na}-\mathrm{THF}$ bond distances are similar (Table 1).

Although there are relatively few structurally characterized $\left[\mathrm{Tm}^{\mathrm{R}}\right] \mathrm{M}$ alkali metal derivatives, ${ }^{1 b, 8,13,14}$ it is evident that there exists a variety of structural types, which are influenced by the composition of the crystal. For example, (i) the aqua complex $\left[\mathrm{Tm}^{\mathrm{Me}}\right] \mathrm{Na} \cdot 4.5 \mathrm{H}_{2} \mathrm{O}$ is composed of discrete $\left[\mathrm{Tm}^{\mathrm{Me}}\right]^{-}$anions (i.e. $\kappa^{0}$ ) that exhibit a 3:0 conformation, ${ }^{1 \mathrm{~b}}$ (ii) the DMF adduct, $\left\{\left[\mathrm{Tm}^{\mathrm{Me}}\right] \mathrm{Na}(\mu-\mathrm{DMF})\right\}_{2}$, is dinuclear, featuring a [ $\mathrm{Tm}^{\mathrm{Me}}$ ] ligand that binds in a $\mathrm{k}^{3}-\mathrm{S}_{2} \mathrm{H}$ manner with a 3:0 conformation, ${ }^{13}$ and (iii) the mixed solvate of composition $\left[\mathrm{Tm}^{\mathrm{Me}}\right] \mathrm{Na} \bullet 3.25 \mathrm{H}_{2} \mathrm{O} \bullet 0.5 \mathrm{DMF}$ possesses an uncoordinated $\left[\mathrm{Tm}^{\mathrm{Me}}\right]^{-}$ anion and a $\kappa^{1}$-coordinated ligand, both of which adopt a 3:0 conformation. ${ }^{13}$

In contrast to there being several structurally characterized sodium complexes, $\left[\mathrm{Tm}^{\mathrm{R}}\right] \mathrm{Na}$, there is only one potassium derivative listed in the Cambridge Structural Database, ${ }^{11}$ namely [ $\left.\mathrm{Tm}^{\mathrm{Me}}\right] \mathrm{K} \cdot 4 \mathrm{H}_{2} \mathrm{O}$, which possesses a polymeric structure in which each [ $\left.\mathrm{Tm}^{\mathrm{Me}}\right]$ ligand bridges two potassium centers. ${ }^{14}$ It is, therefore, significant that we have also determined the molecular structure of the potassium complex, $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}$, (Figure 4) which may be synthesized via the reaction of $\mathrm{KBH}_{4}$ with three equivalents of 1-methyl-1,3-dihydro- 2 H -benzimidazole-2-thione in THF, followed by crystallization from acetone (Scheme 1).

The molecular structure of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}$ exhibits several interesting features. Firstly, and in marked contrast to the polymeric structure of $\left[\mathrm{Tm}^{\mathrm{Me}}\right] \mathrm{K} \cdot 4 \mathrm{H}_{2} \mathrm{O}$,
$\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}$ exists as a discrete monomeric species, with a seven-coordinate capped octahedral geometry, in which an acetone ligand ${ }^{15}$ is located trans to each sulfur donor. Secondly, the $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right]$ ligand coordinates in a $\kappa^{4}-S_{3} H$ manner, with average $\mathrm{K}-\mathrm{S}$ and $\mathrm{K} \cdot \bullet \cdot \mathrm{H}-\mathrm{B}$ interactions of $3.37 \AA$ and $2.42 \AA$, respectively (Table 2).

The tetradentate $\kappa^{4}-S_{3} H$ coordination mode is most uncommon, ${ }^{16}$ with the only other structurally characterized $\left[\kappa^{4}-S_{3} H-\mathrm{Tm}^{\mathrm{R}}\right]$ compound being the $2: 1$ lead complex, $\left[\mathrm{Tm}{ }^{\mathrm{Ph}}\right]_{2} \mathrm{~Pb}$, which exhibits both $\kappa^{4}-S_{3} H$ and $\kappa^{3}-S_{3}$ modes. ${ }^{17}$ Despite the dearth of compounds that feature $\left[\kappa^{4}-S_{3} H-\mathrm{Tm}^{\mathrm{R}}\right.$ ] ligands, $\kappa^{4}-S_{3} H$ coordination modes have, nevertheless, been reported for other ligand systems. ${ }^{18,19,20}$ Such complexes, however, do not exist as discrete mononuclear species, but are either dinuclear or polymeric. Bond lengths associated with these $\mathrm{M}\left[\mathrm{S}_{3} \mathrm{HB}\right]$ moieties are summarized in Table 3, from which it is evident that [ $\left.\mathrm{Tm}^{\text {MeBenz }}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}$ possesses $\mathrm{K}-\mathrm{S}$ and $\mathrm{K} \cdot \bullet \cdot \mathrm{H}-\mathrm{B}$ interactions that are comparable to those of the other potassium compounds that feature $\kappa^{4}-S_{3} H$ interactions.

Significantly, the $\mathrm{K} \cdot \bullet \cdot \mathrm{H}-\mathrm{B}$ interactions in these $\kappa^{4}-S_{3} H$ complexes are distinctly shorter than in other borohydride compounds that possess either tridentate $\kappa^{3}-H_{3}$ or bidentate $\kappa^{2}-$ $\mathrm{H}_{2}$ coordination modes, ${ }^{3 \mathrm{c}}$ as illustrated by the bond length data for crown ether complexes of $\mathrm{KBH}_{4}{ }^{21,22,23,24}$ and $\mathrm{K}\left[\mathrm{H}_{2} \mathrm{BR}_{2}\right]^{22,25}$ (Table 4 and Table 5). For example, the $\mathrm{K} \cdot \cdots \mathrm{H}$ distance in $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}$ is $0.36 \AA$ shorter than the average value of $2.78 \AA$ for structurally characterized crown ether complexes of $\mathrm{KBH}_{4}$ listed in the Cambridge Structural Database. ${ }^{11}$ The shortness of the $\mathrm{K} \cdot \cdots \cdot \mathrm{H}$ interactions in these $\kappa^{4}-S_{3} H$ complexes is undoubtedly linked to the geometrical constraints that enforce a linear $\mathrm{K} \bullet \bullet \mathrm{H}-\mathrm{B}$ geometry, whereas the tridentate $\kappa^{3}-H_{3}$ or bidentate $\kappa^{2}-H_{2}$ coordination modes can accommodate longer $\mathrm{K} \bullet \bullet \mathrm{H}$ distances. It is, therefore, evident that the $\mathrm{K} \bullet \bullet \cdot \mathrm{H}-\mathrm{B}$ interaction is an important component of the bonding of the $\kappa^{4}-S_{3} H$ ligand.

While the $\left[\mathrm{Tm}^{\mathrm{R}}\right]$ ligands are normally synthesized as their alkali metal derivatives, $\left[\mathrm{Tm}^{\mathrm{R}}\right] \mathrm{M}$ $(\mathrm{M}=\mathrm{Li}, \mathrm{Na}, \mathrm{K})$, the thallium derivatives $\left[\mathrm{Tm}^{\mathrm{R}}\right] \mathrm{Tl}$ are also of considerable synthetic utility due to the driving force provided by precipitation of TIX or decomposition of TIR. 26,27,28,29 For this reason, we have synthesized $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ and $\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{B}}{ }^{\mathrm{Benz}}\right] \mathrm{Tl}$ via the reactions of the respective sodium salt $\left[\mathrm{Tm}^{\text {RBenz }}\right] \mathrm{Na}$ with TlOAc, as illustrated in Scheme 2.

The molecular structures of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ (Figure 5) and $\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{t}} \mathrm{Benz}}\right] \mathrm{Tl}$ (Figure 6) have been determined by X-ray diffraction, thereby demonstrating that the [ $\mathrm{Tm}^{\text {RBenz }}$ ] ligands chelate to the thallium centers with Tl-S bond lengths in the range $2.90 \AA-3.11 \AA$ (Table 6 ). These bond lengths are comparable to those in other monovalent compounds, such as the crown thioether complex, $\left[\left\{\kappa^{3}-\left(\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{~S}\right)_{3}\right\} \mathrm{Tl}\right]\left[\mathrm{PF}_{6}\right],{ }^{30}$ and the dinuclear complexes $\left\{\left[\mathrm{Tm}^{\mathrm{Ph}}\right] \mathrm{Tl}\right\}_{2}{ }^{26}$ and $\left\{\left[\mathrm{Tm}^{\mathrm{But}}\right] \mathrm{Tl}\right\}_{2},{ }^{31}$ but are distinctly longer than those in trivalent $\left\{\left[\mathrm{Tm}^{\mathrm{Me}}\right]_{2} \mathrm{Tl}\right\}\left[\mathrm{TII}_{4}\right]^{32}$ and $\left\{\left[\mathrm{Tm}^{\mathrm{Ph}}\right]_{2} \mathrm{Tl}\right\}\left[\mathrm{ClO}_{4}\right]^{26}$ (Table 7).

While each of the sulfur atoms of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ chelate to the thallium center, one of the sulfur atoms also interacts with the thallium of an adjacent molecule, with a $\mathrm{Tl} \bullet \bullet \mathrm{S}$ distance of $3.37 \AA$ (Figure 7). ${ }^{33}$ In addition, the thallium also exhibits a secondary interaction with a benzo moiety of an adjacent molecule, although the Tl $\bullet \bullet \mathrm{C}$ distances ( $3.37-3.89 \AA$ ) are significantly longer than both (i) the Tl-C bonds in monovalent thallium compounds ( $2.31 \AA$ $-2.49 \AA)^{34}$ and (ii) the mean Tl $\bullet \bullet \mathrm{C}$ distance ( $3.31 \AA$ ) for compounds listed in the Cambridge Structural Database that feature Tl-arene interactions. ${ }^{11,35}$

In marked contrast to the structure of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$, the bulkier t-butyl derivative, $\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{B}} \mathrm{Benz}\right] \mathrm{Tl}$, is a discrete mononuclear species in the solid state, and the closest interaction of the thallium is with a benzene molecule of crystallization that is symmetrically located between two molecules of $\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{Benz}}\right] \mathrm{Tl}$, as illustrated in Figure 8. The $\mathrm{Tl} \cdot \bullet \bullet \mathrm{C}$
distances for the interaction with the benzene molecule ( $3.66 \AA$ ) are longer than those involving the benzo groups of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ and, as such, the contact between $\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{t}} \mathrm{Benz}}\right] \mathrm{Tl}$ and benzene is not considered to represent a significant bonding interaction. In this regard, density functional theory (DFT) geometry optimization of the benzene adduct $\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{B}} \mathrm{Benz}\right] \mathrm{Tl}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)$ results in the benzene dissociating from the thallium. On the other hand, geometry optimization calculations on $\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{B}} \mathrm{Benz}\right] \mathrm{Tl}$ reproduce well the experimental structure (Figure 9). For example, the calculated Tl-S bond lengths of [ $\left.\mathrm{Tm}^{\mathrm{But}}{ }^{\mathrm{Benz}}\right] \mathrm{Tl}$ (2.898 $\AA, 2.901 \AA$, and $2.902 \AA$ ) compare favorably to those of the experimental structure ( 2.892 A).

The observation that both benzannulated compounds, $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ and $\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{t}} \mathrm{Benz}}\right] \mathrm{Tl}$, exhibit chelation of the sulfur donors is noteworthy because other $\left[\mathrm{Tm}^{\mathrm{R}}\right] \mathrm{Tl}$ complexes, e.g. $\left\{\left[\mathrm{Tm}^{\mathrm{Bu}}\right] \mathrm{Tl}\right\}_{2}{ }^{31}$ and $\left\{\left[\mathrm{Tm}^{\mathrm{Ph}}\right] \mathrm{Tl}\right\}_{2},{ }^{26}$ exist as dimeric compounds in which two of the sulfur donors coordinate to different thallium centers (Figure 10). In this regard, it is worth noting that the $\operatorname{bis}\left(\right.$ mercaptoimidazolyl)borohydride counterparts $\left\{\left[\mathrm{Bm}^{\mathrm{Bu}}\right] \mathrm{Tl}\right\}_{2}{ }^{36}$ and $\left\{\left[\mathrm{Bm}^{\mathrm{Me}}\right] \mathrm{Tl}\right\}_{x}{ }^{37}$ also feature bridging $\left[\mathrm{Bm}^{\mathrm{R}}\right]$ ligands and that thallium(I) often forms polymeric arrays. ${ }^{38}$

With respect to the observation that the three sulfur donors of the [ $\left.\mathrm{Tm}^{\mathrm{RBenz}}\right]$ ligands of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ and $\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{B}} \mathrm{Benz}}\right] \mathrm{Tl}$ chelate to the thallium center, we have recently demonstrated that the $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right]$ ligand of $\left\{\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Na}\right\}_{2}(\mu-\mathrm{THF})_{3}$ also coordinates in a $\kappa^{3}$-manner, in contrast to the $\kappa^{2}-, \kappa^{1}$ - and $\kappa^{0}$-modes that are observed for various $\left[\mathrm{Tm}^{\mathrm{Me}}\right] \mathrm{Na}$ derivatives. ${ }^{8}$ Thus, while $\left[\mathrm{Tm}^{\mathrm{R}}\right]$ ligands can adopt a variety of coordination modes, which may depend critically on the nature of coligands, it is evident that benzannulation has the effect of promoting $\kappa^{3}-S_{3}$ coordination.

The significance of $\kappa^{3}-S_{3}$ coordination in this system is reinforced by consideration of the fact that other tripodal $\mathrm{L}_{2} \mathrm{X}\left[S_{3}\right]$ donor ligands do not bind to monovalent thallium in a $\kappa^{3}-S_{3}$ manner, but rather adopt other coordination modes. For example, $\left\{\left[\mathrm{PhB}\left(\mathrm{CH}_{2} \mathrm{SBu}^{\mathrm{t}}\right)_{3}\right] \mathrm{Tl}\right\}_{\infty}$ possesses a polymeric structure in which each thallium is coordinated by two sulfur atoms of one $\left[\mathrm{PhB}\left(\mathrm{CH}_{2} \mathrm{SBu}^{\mathrm{t}}\right)_{3}\right]$ moiety and is bridged to a second moiety by the remaining sulfur atom and an $\eta^{6}$-interaction involving the phenyl group. ${ }^{39}$ Likewise, the adamantyl counterpart, $\left\{\left[\mathrm{PhB}\left(\mathrm{CH}_{2} \mathrm{SAd}\right)_{3}\right] \mathrm{Tl}\right\}_{\infty},{ }^{40}$ possesses a polymeric structure similar to that of $\left\{\left[\mathrm{PhB}\left(\mathrm{CH}_{2} \mathrm{SBu}^{\mathrm{t}}\right)_{3}\right] \mathrm{Tl}\right\}_{\infty}$.

The average $\mathrm{S}-\mathrm{Tl}-\mathrm{S}$ bond angles in $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}\left(85.5^{\circ}\right)$ and $\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{t}} \mathrm{Benz}}\right] \mathrm{Tl}\left(88.8^{\circ}\right)$ are acute, such that the thallium centers are highly pyramidal. An indication of the degree of the pyramidality $(P)$ of a $\mathrm{MX}_{3}$ center is provided by the deviation of the sum of the $\mathrm{X}-\mathrm{M}-\mathrm{X}$ bond angles from $360^{\circ}$, i.e. $P=360^{\circ}-\Sigma(\mathrm{X}-\mathrm{M}-\mathrm{X}) .{ }^{41}$ As such, the $P$ values indicate that the thallium centers of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ and $\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{Benz}}\right] \mathrm{Tl}$ are more pyramidal than those in the trivalent compounds, but are significantly less pyramidal than those in the tris(pyrazolyl)hydroborato counterparts, $\left[\mathrm{Tp}^{\mathrm{R}}\right] \mathrm{Tl}^{42,43,44,45,46}$ (Table 8). The reduced pyramidality of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ and $\left[\mathrm{Tm}^{B u^{\mathrm{t}} \mathrm{Benz}}\right] \mathrm{Tl}$, compared to $\left[\mathrm{Tp}^{\mathrm{R}}\right] \mathrm{Tl}$, is presumably a consequence of the greater flexibility of the $\left[\mathrm{Tm}^{\mathrm{R}}\right]$ ligands, which allows for a larger $\mathrm{S}-\mathrm{Tl}-\mathrm{S}$ than $\mathrm{N}-\mathrm{Tl}-\mathrm{N}$ bond angle.

## CONCLUSIONS

In summary, benzannulated $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}$ is a rare example of a tris(mercaptoimidazolyl)borohydride complex that adopts an inverted $\kappa^{4}-S_{3} H$ coordination mode in which the potassium binds to all three sulfur donors and the hydrogen of the $\mathrm{B}-\mathrm{H}$ group. Furthermore, benzannulated ligands have also been used to synthesize $\left[\mathrm{Tm}{ }^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ and $\left[\mathrm{Tm}^{\mathrm{But}}{ }^{\mathrm{t}} \mathrm{Benz}\right] \mathrm{Tl}$, the first examples of $\left[\mathrm{Tm}^{\mathrm{R}}\right] \mathrm{Tl}$ complexes that feature chelation of all
three sulfur donors to thallium, rather than forming dinuclear molecules in which two of the sulfur donors coordinate to different thallium centers. This observation provides further evidence that benzannulation may promote $\kappa^{3}-S_{3}$ coordination and thereby provide a potential means to modulate the reactivity of a metal center.

## EXPERIMENTAL SECTION

## General Considerations

All manipulations were performed by using a combination of glovebox, high vacuum, and Schlenk techniques under a nitrogen or argon atmosphere. ${ }^{47}$ Solvents were purified and degassed by standard procedures. NMR spectra were measured on Bruker 300 DRX, Bruker 400 DRX, and Bruker Avance 500 DMX spectrometers. ${ }^{1} \mathrm{H}$ NMR spectra are reported in ppm relative to $\mathrm{SiMe}_{4}(\delta=0)$ and were referenced internally with respect to the protio solvent impurity ( $\delta 7.26$ for $\mathrm{CDCl}_{3}, 5.32$ for $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ and 2.50 for $d_{6}$-DMSO). ${ }^{48}{ }^{13} \mathrm{C}$ NMR spectra are reported in ppm relative to $\mathrm{SiMe}_{4}(\delta=0)$ and were referenced internally with respect to the solvent ( $\delta 77.23$ for $\mathrm{CDCl}_{3}$ and 39.52 for $d_{6}$-DMSO). ${ }^{48}$ Coupling constants are given in hertz. IR spectra were recorded on a PerkinElmer Spectrum Two spectrometer that was used in attenuated total reflectance (ATR) mode. IR data are reported in reciprocal centimeters $\left(\mathrm{cm}^{-1}\right)$. Mass spectra were obtained on Voyager DE pro (MALDI-TOF) mass spectrometer using matrix assisted laser desorption ionization. $\mathrm{NaBH}_{4}$ (Aldrich), $\mathrm{KBH}_{4}$ (Alfa Aesar), TlOAc (Aldrich) and 1-methyl-1,3-dihydro-2H-benzimidazol-2-thione (Aldrich) were obtained commercially and used as received, while 1-t-butylbenzimidazole-2-thione ${ }^{49}$ and $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Na}^{8}$ were synthesized according to literature methods.

## X-ray structure determinations

Single crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer and crystal data, data collection and refinement parameters are summarized in Table 9. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on $F^{2}$ with SHELXTL (Version 2008/4). ${ }^{50}$

## Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 7.7 (release 107) suite of ab initio quantum chemistry programs. ${ }^{51}$ Geometry optimizations were performed with the B3LYP density functional ${ }^{52}$ using the $6-31 G^{* *}(\mathrm{H}, \mathrm{B}, \mathrm{C}, \mathrm{N}, \mathrm{S})$ and LAV3P (Tl) basis sets. ${ }^{53}$

## Synthesis of [ $\left.\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{t}} \mathrm{Benz}}\right] \mathrm{Na}$

A mixture of 1-t-butyl-2-benzimidazole-2-thione ( $515 \mathrm{mg}, 2.50 \mathrm{mmol}$ ) and $\mathrm{NaBH}_{4}$ ( 32 mg , 0.85 mmol ) was placed in a pressure vessel and treated with THF ( $c a .6 \mathrm{~mL}$ ). The mixture was heated at $160^{\circ} \mathrm{C}$ for 4 days. After this period, the mixture was filtered and the precipitate was washed sequentially with toluene ( 2 mL ) and pentane ( $3 \times 4 \mathrm{~mL}$ ) and dried in vacuo to give $\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{B}} \mathrm{Benz}}\right] \mathrm{Na} \cdot \mathrm{THF}$ as a white powder $(200 \mathrm{mg}, 33 \%)$. Anal. calcd. for
 $\% .^{1} \mathrm{H}$ NMR $\left(d_{6}\right.$-DMSO): $1.76\left[\mathrm{~m}, 4 \mathrm{H}\right.$ of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{8} \mathrm{O}\right)\right], 2.03$ [ s , 27 H of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)\right], 3.61$ [m, 4 H of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{8} \mathrm{O}\right)\right], 6.63$ [broad, 3 H of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)\right], 6.76\left[\mathrm{t},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=8 \mathrm{~Hz}, 3 \mathrm{H}\right.$ of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)\right], 7.58\left[\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=8 \mathrm{~Hz}, 3 \mathrm{H}\right.$ of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)$ ], $6.5-7.2$ [broad, 3 H of
$\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)\right] .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(d_{6}\right.$-DMSO): 25.1 [2C of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\underline{\mathrm{C}}_{4} \mathrm{H}_{8} \mathrm{O}\right)\right], 30.0$ [ 9 C of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)\right], 60.8$ [ 3 C of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)\right], 67.0$ [2C of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\underline{\mathrm{C}}_{4} \mathrm{H}_{8} \mathrm{O}\right)\right], 111.6[3 \mathrm{C}$ of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)\right], 113.0$ [3C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)$ ], 119.3 [3C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)$ ], 119.9 [3C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)$ ], 133.8 [ 3 C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)$ ], 137.6 [3C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)$ ], 173.3 [3C of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \underline{\mathrm{CS}}\right\}_{3} \mathrm{Na}\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}\right)\right]$. Crystals of composition $\left\{\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{H}} \mathrm{Benz}}\right] \mathrm{Na}(\mathrm{THF})\right\}_{2}(\mu-\mathrm{THF})_{2}$, suitable for X-ray diffraction, were obtained by allowing a hot THF solution to cool to room temperature.

## Synthesis of [Tm $\left.{ }^{\text {MeBenz }}\right] K$

A mixture of 1-methyl-2-benzimidazole-2-thione ( $454 \mathrm{mg}, 2.8 \mathrm{mmol}$ ) and $\mathrm{KBH}_{4}(50 \mathrm{mg}$, $0.93 \mathrm{mmol})$ was treated with THF $(5 \mathrm{~mL})$ in a pressure vessel and heated to $150{ }^{\circ} \mathrm{C}$ for three days, resulting in a suspension consisting of a white solid in a yellow solution. The mixture was allowed to cool to room temperature, filtered in air and washed sequentially with THF $(30 \mathrm{~mL}), \mathrm{Et}_{2} \mathrm{O}(30 \mathrm{~mL})$, and hexanes ( 30 mL ), and then dried in vacuo to yield $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{K}$ as a white solid ( $446 \mathrm{mg}, 89 \%$ ). Colorless crystals of composition $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}$ suitable for X-ray diffraction were obtained by diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into a solution in acetone. Anal. calcd. for [Tm $\left.{ }^{\mathrm{MeBenz}}\right] \mathrm{K}: \mathrm{C}, 53.3 \%$; H, $4.1 \%$; N, $15.5 \%$. Found: C, $52.2 \% ; \mathrm{H}, 3.9 \%$; N, $15.3 \%$. ${ }^{1} \mathrm{H}$ NMR ( $d_{6}$-DMSO): $\delta 3.64[\mathrm{~s}, 9 \mathrm{H}$ of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}\right], 5.42\left[\mathrm{br} \mathrm{s}, 1 \mathrm{H}\right.$ of $\left.\underline{\mathrm{HB}}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}\right], 6.74$ [ $\mathrm{t},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=8,3 \mathrm{H}$ of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}\right], 6.87[\mathrm{br} \mathrm{s}, 3 \mathrm{H}$ of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}\right], 6.95\left[\mathrm{t},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=8,3 \mathrm{H}\right.$ of of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}\right]$, $7.18\left[\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=8,3 \mathrm{H}\right.$ of of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}\right] .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(d_{6}\right.$-DMSO $): \delta$ 30.3 [ 3 C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}$ ], 107.7 [3C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}$ ], 112.6 [ 3 C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}, 120.3$ [ 3 C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}$ ], 121.0 [ 3 C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}$ ], 133.8 [ 3 C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \underline{\mathrm{C}}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}$ ], 136.6 [3C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}$ ], 172.8 [ 3 C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{~K}$ ]. IR (ATR, $\mathrm{cm}^{-1}$ ): 2936 (vw), 2454 (vw), 1612 (vw), 1482 (m), 1428 (w), 1387 (m), 1337 (vs), 1299 (s), 1228 (m), 1195 (w), 1179 (w), 1156 (m), 1127 (m), 1107 (m), 1092 (m), 1022 (w), 989 (w), 922 (vw), 856 (vw), 809 (w), 743 (s), 676 (vw), 615 (w), 581 (w), 569 (w), 553 (m), 528 (w).

## Synthesis of [Tm $\left.{ }^{\text {MeBenz }}\right]$ TI

A solution of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Na} \bullet 1.5 \mathrm{THF}(135 \mathrm{mg}, 0.21 \mathrm{mmol})$ in diglyme $(2 \mathrm{~mL})$ was treated with a solution of TlOAc ( $68 \mathrm{mg}, 0.26 \mathrm{mmol}$ ) in distilled water ( 3 mL ), resulting in the formation of a white precipitate in a light yellow solution. The mixture was stirred at room temperature for 1 hour and then treated with distilled water $(10 \mathrm{~mL})$. The mixture was filtered and the precipitate was washed with water $(c a .15 \mathrm{~mL})$ to give $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ as a white solid that was dried in air overnight and then dried in vacuo ( $126 \mathrm{mg}, 84 \%$ ). Crystals of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$ suitable for X-ray diffraction were obtained by slow evaporation of a concentrated $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution in air. Anal. calcd. for [ $\left.\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}: \mathrm{C}, 40.8 \% ; \mathrm{H}, 3.1 \%$; N , $11.9 \%$. Found: C, $41.0 \% ; \mathrm{H}, 3.2 \% ; \mathrm{N}, 11.7 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): 3.74[\mathrm{~s}, 9 \mathrm{H}$ of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right], 7.13\left[\mathrm{t},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=8 \mathrm{~Hz}, 3 \mathrm{H}\right.$ of
$\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right], 7.23$ [m, 6 H of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right], 7.31$
[d, ${ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=8 \mathrm{~Hz}, 3 \mathrm{H}$ of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{CH}_{3}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right]$. IR (ATR, $\left.\mathrm{cm}^{-1}\right): 2932$ (vw), 2414 (vw), 2243 (vw), 1612 (vw), 1484 (m), 1430 (m), 1393 (m), 1370 (w), 1339 (vs), 1296 (m),

1232 (m), 1194 (m), 1142 (m), 1123 (m), 1090 (m), 1014 (m), 914 (w), 858 (m), 814 (w), 739 (vs), 619 (m), 570 (w), 557 (m), 532 (w). FAB-MS: $m / z=704.8[\mathrm{M}-1]^{+}, \mathrm{M}=$ [ $\left.\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$.

A solution of $\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{t}} \mathrm{Benz}}\right] \mathrm{Na} \bullet \mathrm{THF}(150 \mathrm{mg}, 0.21 \mathrm{mmol})$ in diglyme $(2 \mathrm{~mL})$ was treated with a solution of TlOAc ( $65 \mathrm{mg}, 0.25 \mathrm{mmol}$ ) in distilled water ( 3 mL ), resulting in the formation of a white precipitate in a light pink solution. The mixture was stirred at room temperature for 1 hour and then treated with distilled water $(10 \mathrm{~mL})$. The mixture was filtered and the precipitate was washed with water $(c a .15 \mathrm{~mL})$ to give $\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{Benz}}\right] \mathrm{Tl}$ as a white solid that was dried in air overnight and then dried in vacuo ( $159 \mathrm{mg}, 92 \%$ ). Crystals suitable for Xray diffraction were obtained by slow evaporation of a concentrated $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution containing one drop of benzene in air. Anal. calcd. for [ $\left.\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{t}} \mathrm{Benz}}\right] \mathrm{Tl}: \mathrm{C}, 47.6 \% ; \mathrm{H}, 4.8 \%$; $\mathrm{N}, 10.1 \%$. Found: C, $48.4 \%$; H, $4.7 \%$; N, $10.1 \% .^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): 2.02$ [s, 27 H of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right], 7.05\left[\mathrm{~m}, 6 \mathrm{H}\right.$ of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right], 7.24[\mathrm{~m}$, 3 H of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right], 7.78$ [m, 3 H of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \underline{\mathrm{H}}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right] .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 31.3$ [s, 9 C of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\underline{\mathrm{C}}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right], 62.9$ [s, 3C of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\underline{\mathrm{C}}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right]$, 113.3 [s, 3 C of $\left.\mathrm{HB}\left\{\left(\underline{\mathrm{C}}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right], 113.7$ [s, 3C of $\left.\mathrm{HB}\left\{\left(\underline{\mathrm{C}}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right]$, 121.9 [s, 3C of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right], 122.0$ [s,3C of
$\left.\mathrm{HB}\left\{\left(\underline{\mathrm{C}}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right], 134.2$ [s, 3C of $\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \underline{\mathrm{C}}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right], 136.9$ [s, 3 C of $\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \underline{\mathrm{C}}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}$ ], not observed [3C of
$\left.\mathrm{HB}\left\{\left(\mathrm{C}_{4} \mathrm{H}_{4}\right) \mathrm{C}_{2} \mathrm{~N}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right) \mathrm{CS}\right\}_{3} \mathrm{Tl}\right]$. IR (ATR, cm ${ }^{-1}$ ): 2968 (w), 2584 (w), 1595 (w), 1474 (m), 1367 (m), 1319 (vs), 1275 (m), 1226 (m), 1188 (m), 1117 (m), 1066 (w), 1031 (m), 975 (m), 929 (w), 823 (m), 786 (m), 742 ( s$), 633$ (m), 583 (m), $554(\mathrm{~m})$. FAB-MS: $m / z=830.9$
$[\mathrm{M}-1]^{+}, \mathrm{M}=\left[\mathrm{Tm}^{\mathrm{But}^{\mathrm{B}} \mathrm{Benz}}\right] \mathrm{Tl}$.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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$\left[\mathrm{Tm}^{\mathrm{R}}\right] \mathrm{M}$

$\left[\mathrm{Tm}^{\text {RBenz }}\right] \mathrm{M}$

Figure 1.
$\left[\mathrm{Tm}^{\mathrm{R}}\right]$ and $\left[\mathrm{Tm}^{\mathrm{RBenz}}\right]$ ligands, as illustrated in a $\kappa^{3}$-coordination mode.


Figure 2.
Molecular structure of $\left\{\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{B}} \mathrm{Benz}\right] \mathrm{Na}(\mathrm{THF})\right\}_{2}(\mu-\mathrm{THF})_{2}$.


Figure 3.
Structure of $\left\{\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Na}\right\}_{2}(\mathrm{THF})_{3}$.


Figure 4.
Molecular Structure of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}$.


Figure 5.
Molecular Structure of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$.


Figure 6.
Molecular Structure of $\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{t}} \mathrm{Benz}\right] \mathrm{Tl}$.


Figure 7.
Intermolecular $\mathrm{Tl} \bullet \bullet \bullet \mathrm{S}$ contacts in $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{Tl}$.


Figure 8.
Intermolecular contacts in $\left[\mathrm{Tm}^{\mathrm{Bu}}{ }^{\mathrm{t}} \mathrm{Benz}\right] \mathrm{Tl}$.


Figure 9.
DFT Geometry optimized structure of $\left[\mathrm{Tm}^{\mathrm{Bu}^{\mathrm{B}} \mathrm{Benz}}\right] \mathrm{Tl}$.


Figure 10.
Dinuclear structure of $\left\{\left[\mathrm{Tm}^{\mathrm{Bu}}\right] \mathrm{Tl}\right\}_{2}$ with a bridging $\left[\mathrm{Tm}^{\mathrm{Bu}}\right]$ ligand. Coordinates taken from reference 31.




Scheme 1.


## Scheme 2.

Table 1

|  | $d(\mathrm{Na}-\mathrm{S}) / \mathrm{I}$ | $d\left(\mathrm{Na}-\mathrm{O}_{\mathrm{br}}\right) / \mathrm{A}$ | $d\left(\mathbf{N a}-\mathrm{O}_{\text {term }}\right) / \AA$ | $d(\mathrm{Na}-\mathrm{H}) / \mathrm{A}$ | Reference |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\left\{\left[\mathrm{Tm}^{\text {Bu }}\right.\right.$ ' $\left.\left.{ }^{\text {Benz }}\right] \mathrm{Na}(\mathrm{THF})\right\} 2(\mu-\mathrm{THF})_{2}$ | $\begin{gathered} 2.945(3), \\ 3.078(3), \\ 3.552(3)^{(a)} \end{gathered}$ | $\begin{aligned} & 2.430(5) \\ & 2.508(5) \end{aligned}$ | $2.406(5)$ | 2.12(5) | this work |
| $\left\{\left[\mathrm{Tm}^{\text {MeBenz }}\right] \mathrm{Na}\right\} 2(\mu-\mathrm{THF})_{3}$ | $\begin{aligned} & 2.802(1), \\ & 2.816(1), \\ & 2.973(1) \end{aligned}$ | $\begin{aligned} & 2.443(2), \\ & 2.472(2), \\ & 2.520(2) \end{aligned}$ | - | - | 8 |
| $\left\{\mu-\left[\mathrm{Bm}^{\text {MeBenz }}\right] \mathrm{Na}(\mathrm{THF})_{2}\right\}_{2}$ | $\begin{aligned} & 2.8016(9), \\ & 2.8391(9) \end{aligned}$ | - | $\begin{aligned} & 2.312(2) \\ & 2.409(2) \end{aligned}$ | $\begin{aligned} & 2.48(2), \\ & 2.45(2) \end{aligned}$ | 8 |
| $\left\{\left[\mathrm{Tm}_{\mathrm{Me}}\right] \mathrm{Na}(\mu-\mathrm{DMF})\right\}_{2}$ | $\begin{aligned} & 2.7370(7), \\ & 2.8075(7) \end{aligned}$ | $\begin{aligned} & 2.321(1) \\ & 2.253(1) \end{aligned}$ | - | 2.36 | 13 |

[^1]Selected bond lengths for the two crystallographically independent molecules of $\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}$.

|  | Molecule \#1 | Molecule \#2 | Average |
| :--- | :---: | :---: | :---: |
| $d(\mathrm{~K}-\mathrm{S}) / \AA$ | $3.4103(5)$ | $3.3268(5)$ | 3.37 |
| $d(\mathrm{~K} \cdots \mathrm{H}) / \AA$ | $2.39(3)$ | $2.44(3)$ | 2.42 |
| $d(\mathrm{~K} \cdots \mathrm{~B}) / \AA$ | $3.518(3)$ | $3.553(3)$ | 3.54 |
| $d(\mathrm{~K}-\mathrm{O}) / \AA$ | $2.6839(14)$ | $2.7676(12)$ | 2.73 |
| $d(\mathrm{~B}-\mathrm{H}) / \AA$ | $1.12(3)$ | $1.12(3)$ | 1.12 |

Table 3

|  | $d\left(\mathrm{M}-\mathrm{S}_{\mathrm{av}}\right) / \AA$ | $d(\mathbf{M}-\mathrm{H}) /$ ® | $\mathrm{d}(\mathrm{M} \cdots \mathrm{\cdots}) / \AA{ }^{\text {a }}$ | M-H-M/ ${ }^{\circ}$ | Reference |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\left[\mathrm{Tm}^{\text {MeBenz }} \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}\right.$ | 3.37 | 2.42 | 3.54 | 180.0 | this work |
| $\mathrm{K}_{2}\left[\mathrm{HB}\left(\mathrm{Pn}^{\mathrm{Me}}\right)_{3}\right]_{2}\left(\mathrm{OH}_{2}\right)_{3}$ | 3.29 | 2.51 | 3.52 | 180.0 | 18 |
| $\left\{\mathrm{K}\left[\mathrm{HB}(\mathrm{mtda})_{3}\right](\mathrm{MeOH})\right\}_{\infty}$ | 3.30 | 2.548 | 3.593 | 175.2 | 19 |
| $\left\{\mathrm{K}\left[\mathrm{HB}(\mathrm{mtda})_{3}\right](\mathrm{MeCN})\right\}_{\infty}$ | 3.31 | 2.590 | 3.588(3) | 176.4 | 20 |
| $\left\{\mathrm{Na}\left[\mathrm{HB}(\mathrm{mtda})_{3}\right]_{\}_{\infty}}\right.$ | 2.93 | 2.34 | 3.34 | 180.0 | 20 |
| $\left[\mathrm{Tm}^{\mathrm{Ph}}\right]_{2} \mathrm{~Pb}$ | 3.17 | 2.39 (3) | 3.471 (5) | 180.0 | 17 |

Selected bond lengths for crown ether $\mathrm{KBH}_{4}$ derivatives that feature tridentate $\kappa^{3}-H_{3}$ interactions.

|  | $d\left(\mathrm{~K}-\mathrm{H}_{\mathrm{av}}\right) / \mathbf{\AA}$ | $d(\mathrm{~K} \cdots \mathrm{CB}) / \mathbf{\AA}$ | Reference |
| :---: | :---: | :---: | :---: |
| [K(18-crown-6)][ $\left.\mathrm{BH}_{4}\right]$ | 2.79 | 2.947(3) | 21 |
| [K(18-crown-6)][ $\left.\mathrm{BH}_{4}\right]$ | 2.74 | 2.964 (9) | 22 |
| $\begin{aligned} & {[\mathrm{K}(\mathrm{THF})(\text { dibenzo-18- }} \\ & \text { crown-6) }]\left[\mathrm{BH}_{4}\right] \end{aligned}$ | 2.83 | 2.993(4) | 21 |
| [K(1-aza-18-crown6) $]\left[\mathrm{BH}_{4}\right]$ | 2.79 | 2.980(2) | 23 |
| [ K (monobenzo-18-crown6) $\left[\right.$ [ $\left.\mathrm{BH}_{4}\right]$ | 2.80 | 3.005 | 24 |

Table 5
Selected bond lengths for for crown ether $\mathrm{K}\left[\mathrm{H}_{2} \mathrm{BR}_{2}\right]$ derivatives that feature bidentate $\mathrm{K}^{2}-\mathrm{H}_{2}$ interactions.

|  | $d\left(\mathbf{K}-\mathbf{H}_{\text {av }}\right) / \AA$ | $d(\mathbf{K} \cdots \mathbf{B}) / \AA$ | Reference |
| :--- | :---: | :---: | :---: |
| $[\mathrm{K}(18-$ crown-6 $)]\left[\mathrm{H}_{2} \mathrm{BC}_{5} \mathrm{H}_{10}\right]$ | 2.64 | 3.05 | 22 |
| $[\mathrm{~K}(18-$ crown-6 $)]\left[\mathrm{H}_{2} \mathrm{BC}_{4} \mathrm{H}_{8} \mathrm{NC}\left(\mathrm{CH}_{3}\right)_{3}\right]$ | 2.67 | $3.027(4)$ | 25 |


|  | $d$ (Tl-S1)/® | $d$ (Tl-S2)/® | $d$ (Tl-S3)/® |
| :---: | :---: | :---: | :---: |
| $\left[\mathrm{Tm}^{\text {MeBenz }}\right.$ Tl | 2.951(1) | 3.112(1) | 2.926(1) |
|  | 2.892(2) | 2.892(2) | 2.892(2) |


|  | $\boldsymbol{d}$ (Tl-S $\mathrm{S}_{\text {range }} /$ / ${ }^{\text {d }}$ | $d\left(\mathrm{Tl}-\mathrm{S}_{\text {av }} /\right.$ / ${ }^{\text {a }}$ | Reference |
| :---: | :---: | :---: | :---: |
| $\left[\mathrm{Tm}^{\text {MeBenz }}\right.$ Tl ${ }^{\text {l }}$ | 2.926-3.112 | 2.996 | this work |
| $\left[\mathrm{Tm}^{\text {But }}{ }^{\text {Penz }}\right] \mathrm{Tl}$ | 2.892 | 2.892 | this work |
| $\left\{\left[\mathrm{Tm}^{\mathrm{Pl}}\right] \mathrm{Tl}\right\}_{2}$ | $3.049-3.400$ | 3.189 | 26 |
| $\left\{\left[\mathrm{TmBu}{ }^{\text {t }} \text { Tl }\right\}_{2}\right.$ | 2.992-3.239 | 3.124 | 31 |
| $\left[\left\{\mathrm{k}^{3}-\left(\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{~S}\right)_{3}\right\} \mathrm{Tl}\right]\left[\mathrm{PF}_{6}\right]$ | $3.092-3.114$ | 3.105 | 30 |
| $\left\{\left[\mathrm{Tm}^{\mathrm{Me}}\right]_{2} \mathrm{Tl}\right\}\left[\mathrm{Tli}_{4}\right]$ | 2.668-2.679 | 2.675 | 32 |
| $\left\{\left[\mathrm{Tm}^{\mathrm{Me}}\right]_{2} \mathrm{Tl}\right\} \mathrm{I}$ | 2.682-2.689 | 2.686 | 32 |
| $\left\{\left[\mathrm{Tm}^{\mathrm{Ph}}\right]_{2} \mathrm{Tl}\right\}\left[\mathrm{ClO}_{4}\right]$ | $2.674-2.699$ | 2.686 | 26 |

Table 8


## Table 9

Crystal, intensity collection and refinement data.

|  | $\begin{gathered} \left\{\left[\mathrm{Tm}^{\left.\mathrm{Bu} \mathrm{t}_{\mathrm{Benz}}\right] \mathrm{Na}(\mathrm{THF})} \underset{\mathrm{THF})_{2}}{ } \mathrm{~T}(\mu-\right.\right. \\ \hline \end{gathered}$ | $\begin{gathered} {\left[\mathrm{Tm}^{\mathrm{MeBenz}}\right] \mathrm{K}\left(\mathrm{OCMe}_{2}\right)_{3}} \\ \cdot \mathrm{OCMe}_{2} \end{gathered}$ |
| :---: | :---: | :---: |
| lattice | Triclinic | Rhombohedral |
| formula | $\mathrm{C}_{82} \mathrm{H}_{112} \mathrm{~B}_{2} \mathrm{~N}_{12} \mathrm{Na}_{2} \mathrm{O}_{4} \mathrm{~S}_{6}$ | $\mathrm{C}_{36} \mathrm{H}_{46} \mathrm{BKN}_{6} \mathrm{O}_{4} \mathrm{~S}_{3}$ |
| formula weight | 1589.80 | 772.88 |
| space group | P-1 | R-3 |
| $a / \AA{ }^{\text {A }}$ | 11.523(5) | 15.7585(12) |
| b/Å | 11.542(5) | 15.7585(12) |
| $c / A ̊$ | 17.423(8) | 52.744(4) |
| $\mathrm{a} /{ }^{\circ}$ | 88.111(7) | 90 |
| $\beta /{ }^{\circ}$ | 83.839(7) | 90 |
| $\gamma{ }^{\circ}$ | 59.901(6) | 120 |
| $V / \AA^{3}$ | 1992.7(15) | 11343.1(15) |
| Z | 1 | 12 |
| temperature (K) | 130(2) | 130(2) |
| radiation ( $\lambda, \AA$ ) | 0.71073 | 0.71073 |
| $\rho$ (calcd.), $\mathrm{g} \mathrm{cm}^{-3}$ | 1.325 | 1.358 |
| $\mu$ (Mo Ka), mm ${ }^{-1}$ | 0.242 | 0.354 |
| $\theta$ max, deg. | 26.48 | 30.61 |
| no. of data collected | 34362 | 56765 |
| no. of data used | 8186 | 7721 |
| no. of parameters | 500 | 291 |
| $R_{l}[I>2 \sigma(I)]$ | 0.0802 | 0.0440 |
| $w R_{2}[I>2 \sigma(I)]$ | 0.1650 | 0.1149 |
| $R_{l}$ [all data] | 0.1378 | 0.0696 |
| $w R_{2}$ [all data] | 0.1901 | 0.1237 |
| GOF | 1.033 | 1.025 |
| $R_{\text {int }}$ | 0.1380 | 0.0605 |


|  | $\left[\mathrm{Tm}^{\mathrm{MeBen}}\right] \mathrm{Tl}$ |  |
| :---: | :---: | :---: |
| lattice | Monoclinic | Rhombohedral |
| formula | $\mathrm{C}_{24} \mathrm{H}_{22} \mathrm{BN}_{6} \mathrm{~S}_{3} \mathrm{Tl}$ | $\mathrm{C}_{72} \mathrm{H}_{86} \mathrm{~B}_{2} \mathrm{~N}_{12} \mathrm{~S}_{6} \mathrm{Tl}_{2}$ |
| formula weight | 705.84 | 1742.25 |
| space group | $P 2_{1 / n}$ | $R$-3 |
| $a / \AA{ }^{\text {a }}$ | 9.3299(7) | 17.793(4) |
| b/Å | $12.4112(10)$ | 17.793(4) |
| clÅ | 21.2348(17) | 20.084(5) |
| a/ ${ }^{\circ}$ | 90 | 90 |
| $\beta /{ }^{\circ}$ | 94.2250(10) | 90 |


|  | $\left[\mathrm{Tm}^{\text {MeBenz }}\right] \mathbf{T l}$ |  |
| :---: | :---: | :---: |
| $\gamma{ }^{\circ}$ | 90 | 120 |
| $V / \AA^{3}$ | 2452.2(3) | 5506(2) |
| Z | 4 | 3 |
| temperature (K) | 150(2) | 150(2) |
| radiation ( $\lambda, \AA$ ) | 0.71073 | 0.71073 |
| $\rho$ (calcd.), $\mathrm{g} \mathrm{cm}^{-3}$ | 1.912 | 1.576 |
| $\mu$ (Mo Ka), mm ${ }^{-1}$ | 6.869 | 4.605 |
| $\theta$ max, deg. | 30.65 | 25.02 |
| no. of data collected | 39361 | 17413 |
| no. of data used | 7560 | 2132 |
| no. of parameters | 322 | 146 |
| $R_{l}[I>2 \sigma(I)]$ | 0.0435 | 0.0444 |
| $w R_{2}[I>2 \sigma(I)]$ | 0.0727 | 0.0720 |
| $R_{l}$ [all data] | 0.0869 | 0.0833 |
| $w R_{2}$ [all data] | 0.0850 | 0.0790 |
| GOF | 1.019 | 0.974 |
| $R_{\text {int }}$ | 0.1004 | 0.1773 |


[^0]:    Supporting Information: CIF files and Cartesian coordinates for geometry optimized structures. See http://dx.doi.org/10.1039/ b000000x/.

[^1]:    ${ }^{(a)}$ Value for the uncoordinated thione.

