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Synthesis and Structural Characterization of Tris(2-mercapto-1-adamantylimidazolyl)hydroborato Complexes: A Sterically Demanding Tripodal [S_3] Donor Ligand

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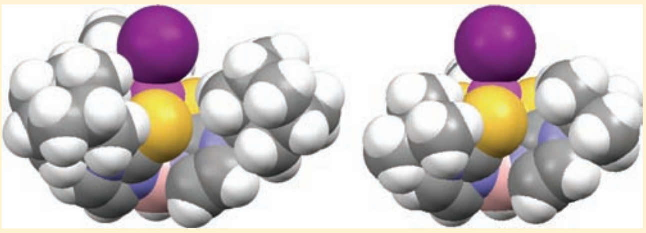
Supporting Information



ABSTRACT: The tris(2-mercapto-1-adamantylimidazolyl)hydroborato ligand, [$\mathrm{Tm^{Ad}}$], has been synthesized via the reaction of 1-adamantyl-2-mercaptoimidazole with MBH_4 (M = Li, K). [$\mathrm{Tm^{Ad}}$]M has been used to synthesize a variety of compounds of the main-group and transition elements, including [$\mathrm{Tm^{Ad}}$]ZnI, {[$\mathrm{Tm^{Ad}}$]GaI}[GaI_4], {[$\mathrm{Tm^{Ad}}$]GaCl}[$GaCl_4$], {[$\mathrm{Tm^{Ad}}$]GaGa[$\mathrm{Tm^{Ad}}$]}[$GaCl_4$]$_2$, {[$\mathrm{Tm^{Ad}}$]$_2$In}[InI_4], [$\mathrm{Tm^{Ad}}$]In(κ^2-$\mathrm{mim^{Ad}}$)Cl, [$\mathrm{Tm^{Ad}}$]Ga→B(C_6F_5)$_3$, [$\mathrm{Tm^{Ad}}$]In→B(C_6F_5)$_3$, and [$\mathrm{Tm^{Ad}}$]Re(CO)$_3$. Structural characterization of [$\mathrm{Tm^{Ad}}$]Re(CO)$_3$ demonstrates that the [$\mathrm{Tm^{Ad}}$] ligand is more encapsulating than other [$\mathrm{Tm^{R}}$] ligands, including [$\mathrm{Tm^{Bu^t}}$], while IR spectroscopic studies indicate that the [$\mathrm{Tm^{Ad}}$] and [$\mathrm{Tm^{Bu^t}}$] ligands have very similar electron-donating properties.

INTRODUCTION

Tris(2-oxoimidazolyl)hydroborato, [$\mathrm{To^R}$],[1] tris(2-mercaptoimidazolyl)hydroborato, [$\mathrm{Tm^R}$],[2,3] and tris(2-selenoimidazolyl)hydroborato ligands, [$\mathrm{Tse^R}$],[3−5] comprise a class of tripodal ligands that respectively provide [O_3], [S_3], and [Se_3] donor arrays (Figure 1). Of these, the [$\mathrm{Tm^R}$] ligands were the first to be synthesized[2] and have found extensive use, with applications as diverse as bioinorganic chemistry, surface chemistry, and sensing.[3]

For example, we have used the [$\mathrm{Tm^R}$] ligand to provide an [S_3] donor array that is of use for mimicking aspects of zinc enzymes and proteins that have sulfur-rich active sites.[3b,6] As an illustration, the catalytic site of 5-aminolevulinate dehydratase (ALAD) has the composition [(Cys)$_3$Zn$^{\mathrm{II}}$(OH$_2$)], such that [$\mathrm{Tm^{Ph}}$]ZnOH provides a good structural analogue in which the three sulfur donors of the [$\mathrm{Tm^R}$] ligand emulate the three cysteine residues in ALAD (Figure 2).[7] The Ada DNA repair protein also has a sulfur-rich active site, [Cys_4Zn], and simple synthetic analogues are provided by the thiolate complexes [$\mathrm{Tm^R}$]ZnSPh (e.g., R = Ph, Bu^t)[8,9] and [$\mathrm{Tm^R}$]ZnSCH$_2$C(O)N(H)Ph,[8b,10] of which the latter feature intramolecular N−H···S hydrogen-bonding interactions involving the thiolate ligand (Figure 2). In addition to zinc thiolate derivatives, cationic mercaptoimidazole adducts {[$\mathrm{Tm^{Ar}}$]Zn(Hmim$^{\mathrm{Ar}}$)}$^+$ with a tetrahedral [ZnS_4] motif also serve as structural analogues of the Ada DNA repair protein.[11]

[$\mathrm{Tm^R}$] ligands have also provided insight into mercury detoxification. For example, the mercury alkyl compounds [κ^1-$\mathrm{Tm^{Bu^t}}$]HgR (R = Me, Et) react with PhSH to yield [$\mathrm{Tm^{Bu^t}}$]HgSPh and RH, a reaction that emulates mercury detoxification by the organomercurial lyase, *MerB* (Scheme 1).[12] The facility with which the Hg−C bond is cleaved is particularly noteworthy in view of the fact that two-coordinate monoalkylmercury compounds of the type X−Hg−R are notoriously inert towards protolytic cleavage, and the ability of the [κ^1-$\mathrm{Tm^{Bu^t}}$]HgR compounds to undergo cleavage is attributed to the ability to access activated κ^2 or κ^3 isomers in which the mercury is no longer two-coordinate and linear.

One mechanism of mercury toxicity has been attributed to its impact on the biochemical roles of selenium,[13] and some insight into this suggestion has been obtained by an investigation of a series of chalcogenolate compounds [$\mathrm{Tm^{Bu^t}}$]MEPh (M = Zn, Cd, Hg; E = S, Se, Te), as illustrated in Figure 3.[14] X-ray diffraction studies indicate that the Zn−EPh, Cd−EPh, and Hg−EPh bond lengths do not scale equally with the covalent radii of the chalcogens, with all M−SePh and M−TePh bond lengths being shorter than would be predicted on the basis of the value for the M−SPh bond length and the change in the covalent radius of the chalcogen (Figure 3). However, the deviation is particularly significant for mercury, suggesting that mercury is exceptional with respect to its interactions with selenium and tellurium. In this regard, treatment of the mercury thiolate [$\mathrm{Tm^{Bu^t}}$]HgSCH$_2$C(O)N(H)Ph with the zinc selenolate [$\mathrm{Tm^{Bu^t}}$]ZnSePh results in the formation of the mercury selenolate complex [$\mathrm{Tm^{Bu^t}}$]HgSePh and the zinc thiolate derivative [$\mathrm{Tm^{Bu^t}}$]ZnSCH$_2$C(O)N(H)Ph (Scheme 2); the latter observation indicates a greater preference of mercury, relative to zinc, to bind to selenolate rather than thiolate in this system. This observation

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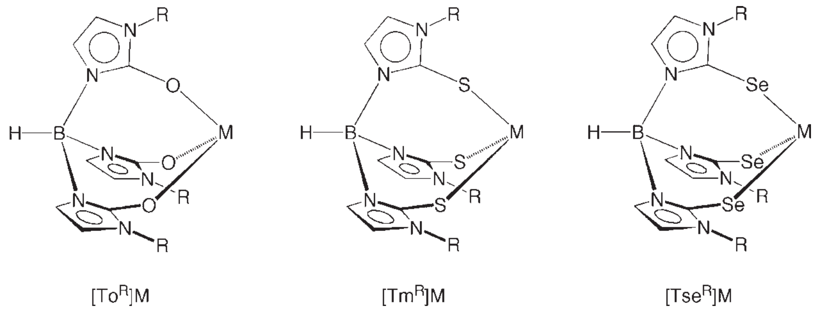


Figure 1. Tris(2-oxoimidazolyl)hydroborato, [To^R], tris(2-mercaptoimidazolyl)hydroborato, [Tm^R], and tris(2-selenoimidazolyl)hydroborato ligands, [Tse^R].

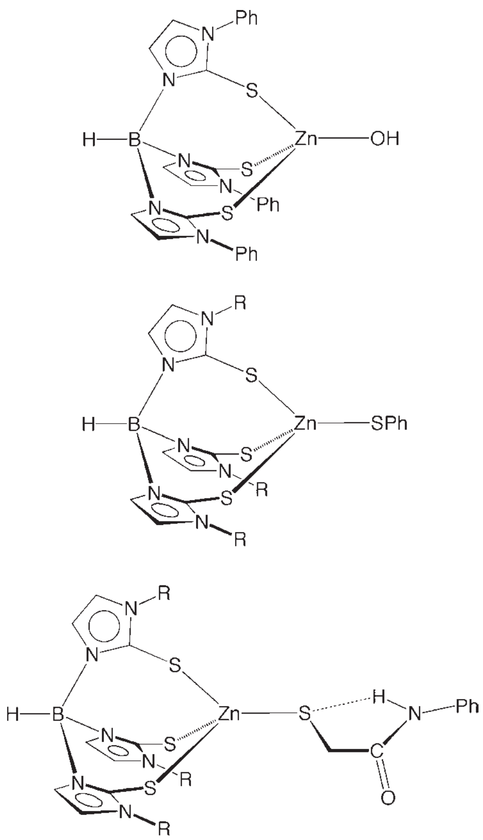
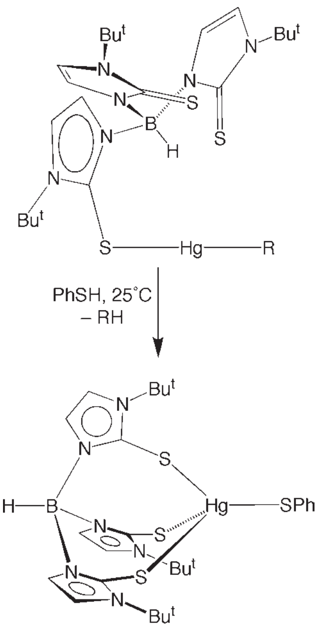


Figure 2. Synthetic analogues of ALAD and the Ada DNA repair protein.

Scheme 1



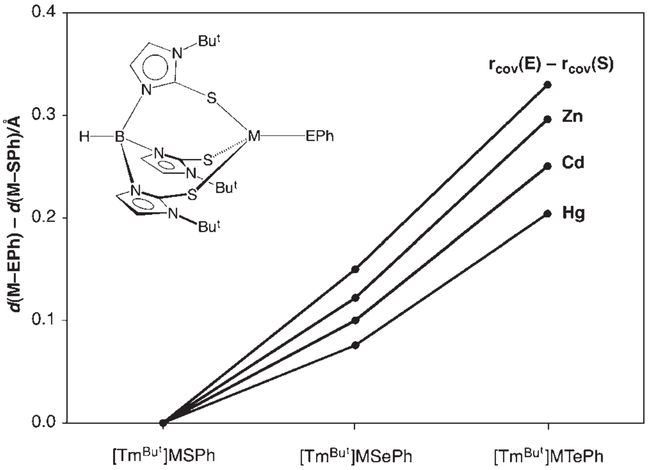


Figure 3. Relative M–EPh bond lengths and the values predicted on the basis of the covalent radii of sulfur, selenium, and tellurium. Note that the Hg–Se and Hg–Te bonds are exceptionally short.

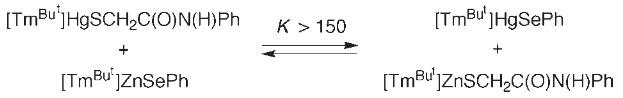
thereby reinforces the suggestion that mercury can exert an impact on the biological roles of selenium.

With respect to group 13 element chemistry, we have demonstrated that the [Tm$^{Bu^t}$] ligand is capable of supporting a monovalent indium center[15] and forming gallium compounds that feature Ga–Ga bonds,[16] as illustrated in Figure 4.

Another interesting application of [Tm^R] ligands is that cleavage of the B–H bond affords a means to synthesize a novel class of metallaboratrane compounds {[κ^4-B(mim^R)$_3$]M} (Figure 5).[17–19] Significantly, these compounds feature the first well-defined examples of transition metal-to-ligand M → B dative bonds.[17a]

An important aspect of [Tm^R] ligands is that a large variety of alkyl and aryl substituents may be incorporated into the 1-position (i.e., the nitrogen atom adjacent to the thione group), thereby providing a means to influence the chemistry of the system. Thus, examples of 1-alkyl and 1-aryl substituents that have been incorporated into [Tm^R] ligands include Me, Et, Bu^t, Bz, Cy, Ph, *p*-Tol, *o*-Tol, *p*-$C_6H_4Pr^i$, 2,6-$C_6H_3Me_2$,

Scheme 2



$$[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{HgSCH_2C(O)N(H)Ph} + [\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnSePh} \xrightleftharpoons{K > 150} [\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{HgSePh} + [\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnSCH_2C(O)N(H)Ph}$$

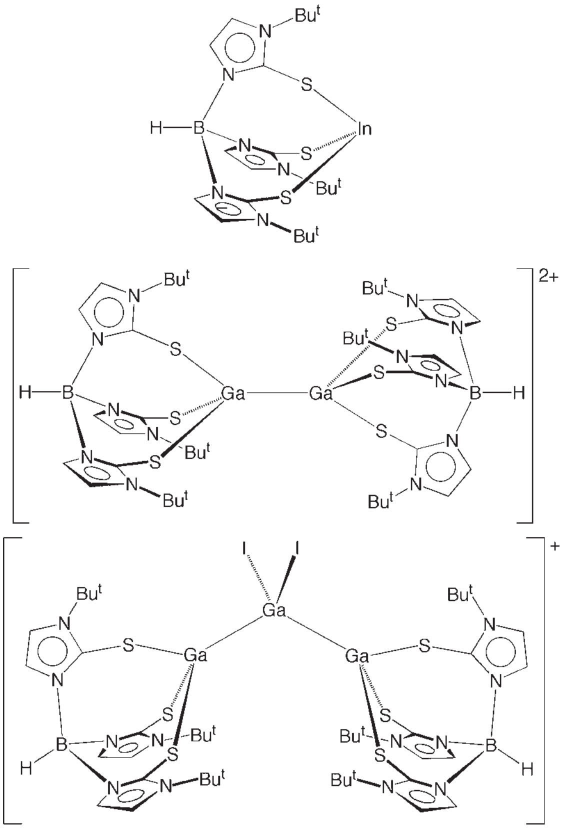


Figure 4. A monovalent indium compound and gallium compounds that feature Ga−Ga bonds.

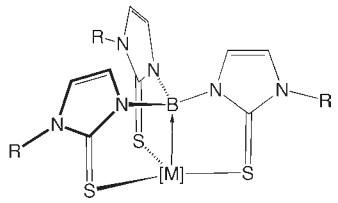
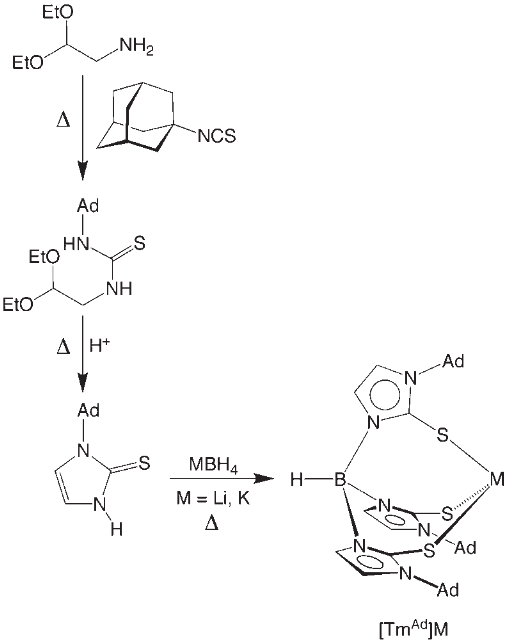


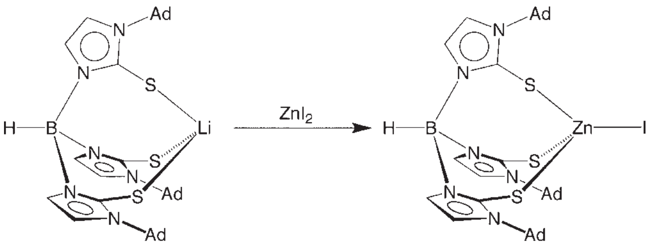
Figure 5. Metallaboratrane compounds derived from $[\mathrm{Tm}^{\mathrm{R}}]$ ligands.

$2,6\text{-}\mathrm{C_6H_3Pr^i_2}$, Mes, and 2-biphenyl.[2] Absent from this list, however, is the 1-adamantyl (Ad) group. Therefore, we sought to synthesize the tris(2-mercapto-1-adamantylimidazolyl)hydroborato ligand, $[\mathrm{Tm}^{\mathrm{Ad}}]$, especially because incorporation of the 1-adamantyl group into the structurally related phenyltris(alkylthiomethyl)borate ligand system has been shown to have a profound effect on the reactivity.[20] Hence, we report here the synthesis of $[\mathrm{Tm}^{\mathrm{Ad}}]\mathrm{M}$ (M = Li, K) and describe some applications of the $[\mathrm{Tm}^{\mathrm{Ad}}]$ ligand to main-group and transition-metal chemistry.

Scheme 3



Scheme 4

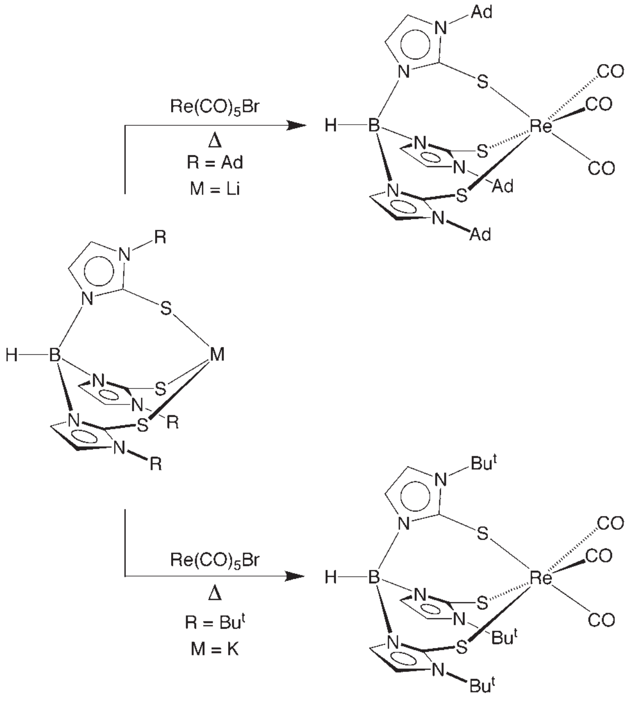


■ RESULTS AND DISCUSSION

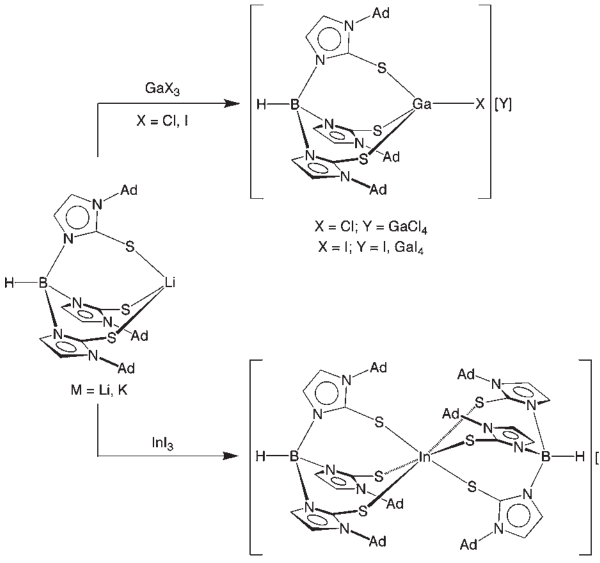
1. Synthesis of $[\mathrm{Tm}^{\mathrm{Ad}}]\mathrm{M}$ (M = Li, K) and Evaluation of the Steric and Electronic Properties of the $[\mathrm{Tm}^{\mathrm{Ad}}]$ Ligand. Access to the lithium and potassium reagents $[\mathrm{Tm}^{\mathrm{Ad}}]\mathrm{M}$ (M = Li, K) is provided by the reaction of $\mathrm{MBH_4}$ with 1-adamantyl-2-mercaptoimidazole ($\mathrm{Hmim}^{\mathrm{Ad}}$), which is obtained via treatment of aminoacetaldehyde diethyl acetal $[\mathrm{H_2NCH_2CH(OEt)_2}]$ with 1-adamantyl isothiocyanate [AdNCS], as illustrated in Scheme 3. $[\mathrm{Tm}^{\mathrm{Ad}}]\mathrm{M}$ may be used to obtain a variety of metal complexes, as illustrated in Schemes 4−8. For example, $[\mathrm{Tm}^{\mathrm{Ad}}]\mathrm{Li}$ reacts with $\mathrm{ZnI_2}$ to give $[\mathrm{Tm}^{\mathrm{Ad}}]\mathrm{ZnI}$ (Scheme 4). The molecular structure of $[\mathrm{Tm}^{\mathrm{Ad}}]\mathrm{ZnI}$ has been determined by X-ray diffraction (Figure 6), thereby illustrating how the adamantyl groups provide a protective pocket about the metal center. For comparison, the space-filling views of $[\mathrm{Tm}^{\mathrm{Ad}}]\mathrm{ZnI}$ and $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnI}$[21] are presented in Figure 7, which demonstrate that the three adamantyl groups provide a more encapsulating environment than that provided by three *tert*-butyl groups.

A more quantitative evaluation of the steric protection afforded by the adamantyl groups is provided by measurement of the cone angle.[22−25] In this regard, the crystallographic cone angle[25] of 251° for the $[\mathrm{Tm}^{\mathrm{Ad}}]$ ligand in $[\mathrm{Tm}^{\mathrm{Ad}}]\mathrm{ZnI}$ is substantially larger than the value of 223° for $[\mathrm{Tm}^{\mathrm{Bu}^t}]$ in $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnI}$.

Scheme 5



Scheme 6



For purposes of comparison, however, it is important to note that the cone angle of a ligand is a function of the covalent radius of the metal to which it is attached. In this regard, the cone angles of PR_3 ligands correspond to a fixed M−P bond length of 2.28 Å (corresponding to a Ni−P bond length) because Tolman's early studies to assess the steric and electronic properties of PR_3 ligands focused on nickel complexes of the types $Ni(PR_3)_4$ and $Ni(PR_3)_3(CO)$.[22] Nickel, however, is not an ideal choice for evaluating steric and electronic data for face-capping L_2X ligands[26] because a suitable series of nickel compounds is not available.[27] Fortunately, however, a variety of rhenium and manganese complexes of the type $[L_2X]M(CO)_3$ are known and provide a good basis for evaluating the steric and electronic properties of such ligands.[4,5,28−31] Therefore, we sought the rhenium carbonyl compounds $[Tm^{Ad}]Re(CO)_3$ and $[Tm^{Bu^t}]Re(CO)_3$ to provide a more pertinent comparison of ligand cone angles with data in the literature.

$[Tm^{Ad}]Re(CO)_3$ and $[Tm^{Bu^t}]Re(CO)_3$ may be synthesized via treatment of $Re(CO)_5Br$ with $[Tm^{Ad}]Li$ and $[Tm^{Bu^t}]K$, respectively (Scheme 5), and have been structurally characterized by X-ray diffraction (Figures 8 and 9). Comparison of the cone angles in $[Tm^{Ad}]Re(CO)_3$ (232°) and $[Tm^{Bu^t}]Re(CO)_3$ (208°) also demonstrates that $[Tm^{Ad}]$ is sterically more demanding than the $[Tm^{Bu^t}]$ ligand, thereby reinforcing the analogous observation made for the zinc system. Furthermore, comparison with the data compiled in Table 1 illustrates that the cone angle for $[Tm^{Ad}]$ is also larger than that for other $[Tm^R]$ ligands.

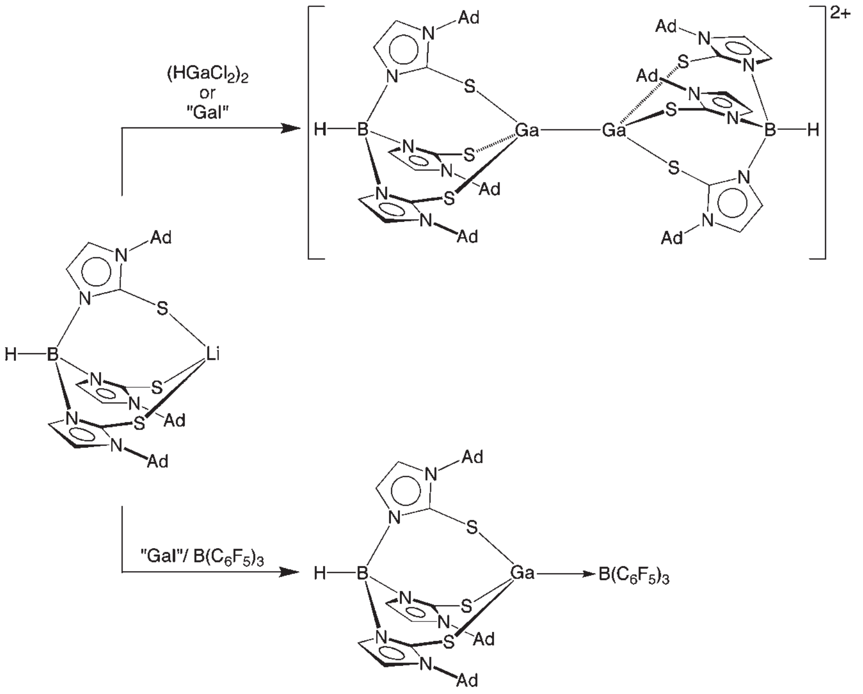
In addition to the steric properties, the carbonyl compounds $[Tm^{Ad}]Re(CO)_3$ and $[Tm^{Bu^t}]Re(CO)_3$ also provide a means to assess the relative electronic properties of $[Tm^{Ad}]$ and $[Tm^{Bu^t}]$ ligands. In this regard, the ν_{CO} stretching frequencies of $[Tm^{Ad}]Re(CO)_3$ (2005 and 1887 cm^{-1} in CH_2Cl_2; average = 1946 cm^{-1}) are very similar to those for $[Tm^{Bu^t}]Re(CO)_3$ (2007 and 1887 cm^{-1} in CH_2Cl_2; average = 1947 cm^{-1}), thereby indicating that the $[Tm^{Ad}]$ and $[Tm^{Bu^t}]$ ligands have very similar electron-donating properties. The similar electronic properties of these ligands is a consequence of the comparable inductive effects of the 1-adamantyl and *tert*-butyl groups, coupled with the fact that they are well separated from the metal by four bonds. As such, the principal differences between $[Tm^{Ad}]$ and $[Tm^{Bu^t}]$ complexes are expected to be a consequence of the larger degree of steric protection provided by the adamantyl substituents.

2. Synthesis of $[Tm^{Ad}]$ Gallium and Indium Derivatives: Complexes with Ga−Ga Bonds and Lewis Acid Adducts.

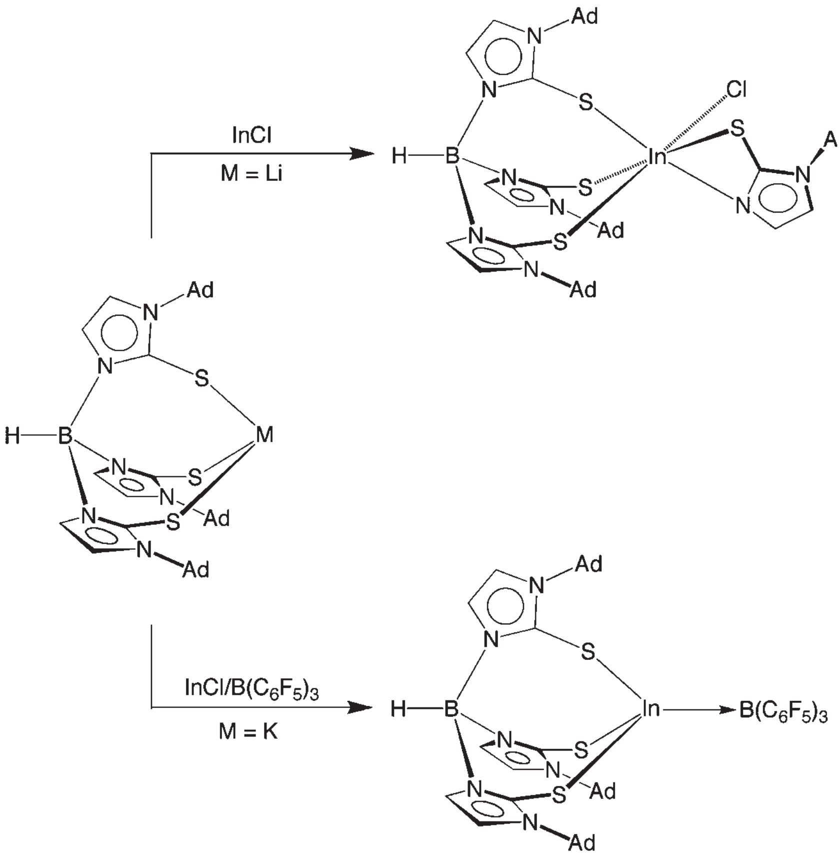
In addition to zinc, simple tetrahedral complexes have also been isolated for gallium, the adjacent element in the Periodic Table.[32] Thus, $[Tm^{Ad}]M$ (M = Li, K) reacts with trivalent GaI_3 and $GaCl_3$ to give tetrahedral $\{[Tm^{Ad}]GaX\}^+$ complexes, namely, $\{[Tm^{Ad}]GaI\}I$, $\{[Tm^{Ad}]GaI\}[GaI_4]$, and $\{[Tm^{Ad}]GaCl\}[GaCl_4]$ (Scheme 6), of which the iodide derivatives have been structurally characterized by X-ray diffraction, as illustrated for $\{[Tm^{Ad}]GaI\}I$ in Figure 10. In contrast to the formation of tetrahedral compounds, the corresponding reaction between $[Tm^{Ad}]K$ and InI_3 yields $\{[Tm^{Ad}]_2In\}[InI_4]$, which possesses octahedrally coordinated indium.[32] The molecular structure of $\{[Tm^{Ad}]_2In\}[InI_4]$ has been determined by X-ray diffraction (Figure 11), which thereby demonstrates that, despite the large cone angle of the $[Tm^{Ad}]$ ligand, the flanking adamantyl groups do not prevent two $[Tm^{Ad}]$ ligands from coordinating in a κ^3 manner. The approximately 0.2 Å larger covalent radius of indium, compared to that of gallium,[33] is undoubtedly one factor that facilitates the ability to isolate an octahedral complex of this type.

Whereas the reaction of $[Tm^{Ad}]Li$ with $GaCl_3$ yields a simple mononuclear species, $\{[Tm^{Ad}]GaCl\}^+$, the corresponding reaction with the hydride complex $(HGaCl_2)_2$[34] yields the Ga−Ga-bonded dimer $\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}[GaCl_4]_2$ (Scheme 7). The formation of $\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}^{2+}$ is in accord with the observation that Lewis bases promote reductive dehydrogenation of $(HGaCl_2)_2$.[34,35] The dinuclear complex $\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}^{2+}$ is also formed upon treatment of $[Tm^{Ad}]Li$ with monovalent "GaI",[36] a reaction that is accompanied by

Scheme 7



Scheme 8



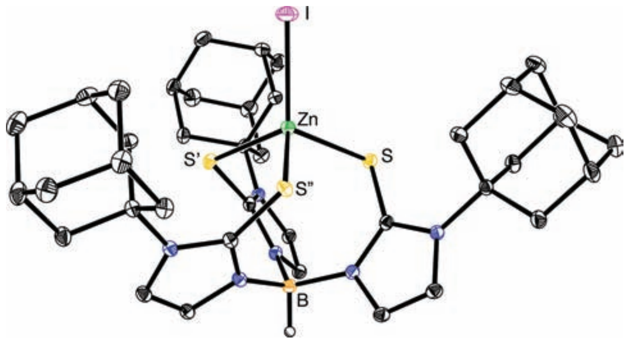


Figure 6. Molecular structure of [Tm^{Ad}]ZnI.

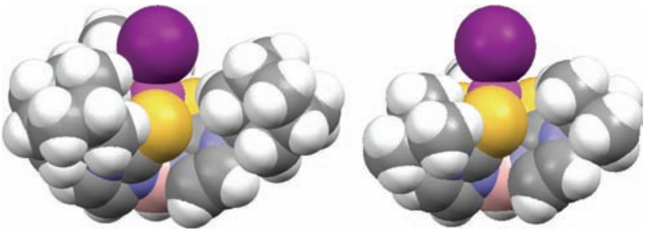


Figure 7. Comparison of the space-filling models of [Tm^{Ad}]ZnI (left) and [Tm$^{Bu^t}$]ZnI (right).

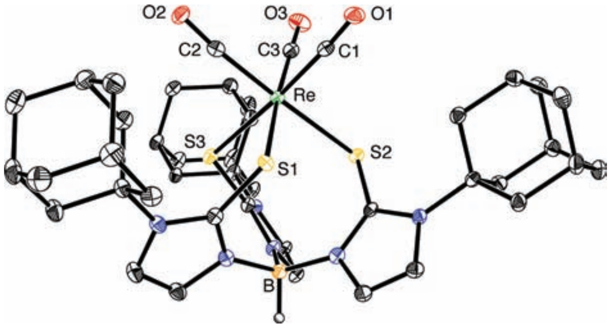


Figure 8. Molecular structure of [Tm^{Ad}]Re(CO)$_3$.

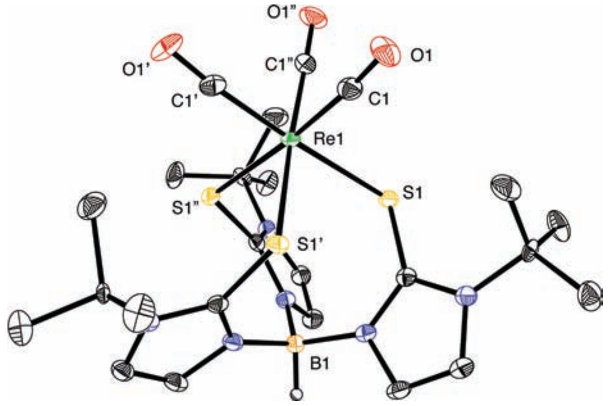


Figure 9. Molecular structure of [Tm$^{Bu^t}$]Re(CO)$_3$.

Table 1. Cone Angles (Θ) for [Tm^R] and Other Face-Capping L$_2$X Ligands in [L$_2$X]Re(CO)$_3$ Complexes

[L$_2$X]Re(CO)$_3$	Θ (deg)	ref
[Tm^{Me}]	191	*b*
[Tm$^{Bu^t}$]	213^a	*c*
[Tm^{Mes}]	219	*b*
[Tm^{Ad}]	232	*c*
[Tse^{Me}]	180	*d*
[Tse^{Mes}]	211	*b*
[Tp]	211	*b*
[Tp^{Me_2}]	255	*b*
Cp	141	*b*
Cp*	170	*b*

[a] Average values of two components (211° and 215°). [b] Data compiled in ref 4. [c] This work. [d] Reference 5.

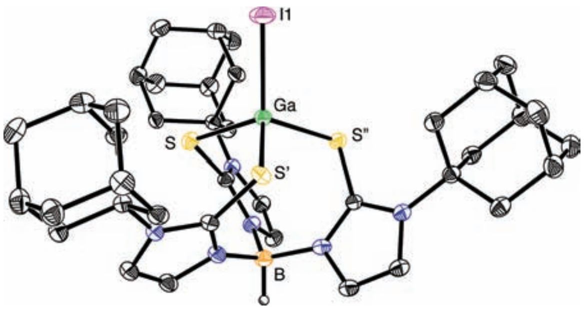


Figure 10. Molecular structure of {[Tm^{Ad}]GaI}I (only the cation is shown).

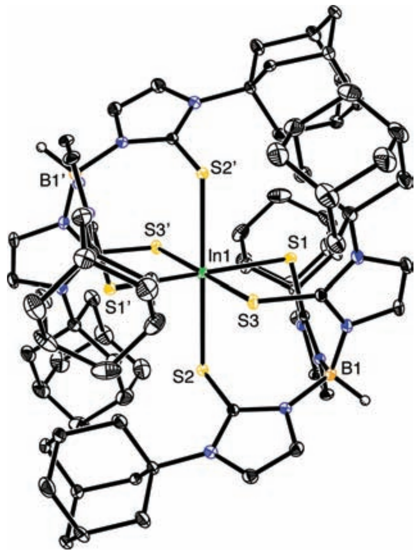


Figure 11. Molecular structure of {[Tm^{Ad}]$_2$In}[InI$_4$] (only the cation is shown).

disproportionation.[36−39] The molecular structure of {[Tm^{Ad}]GaGa[Tm^{Ad}]}[Ga$_2$I$_{4.9}$Cl$_{1.1}$] has been determined by X-ray diffraction, as illustrated in Figure 12. The Ga−Ga bond length of {[Tm^{Ad}]GaGa[Tm^{Ad}]}$^+$ [2.427(2) Å] is comparable to those for {[Tm$^{Bu^t}$]GaGa[Tm$^{Bu^t}$]}[GaCl$_4$]$_2$ [2.410(2) Å] and {[Tm$^{Bu^t}$]GaGa[Tm$^{Bu^t}$]}I$_2$ [2.412(2) Å].[40]

Analogous to the reaction of "GaI", the reaction of [Tm^{Ad}]Li with InCl is also accompanied by disproportionation,[41,42] al-

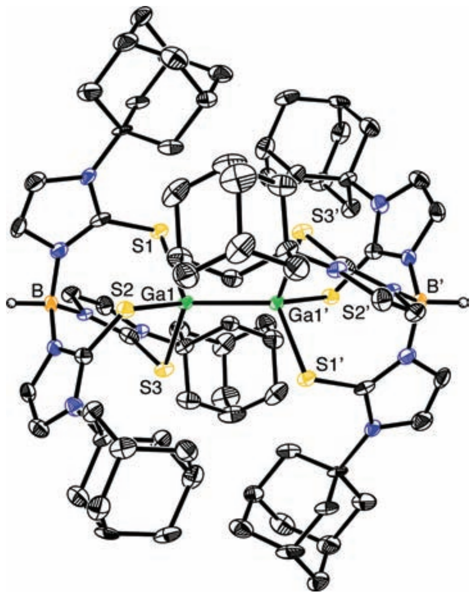


Figure 12. Molecular structure of $\{[\mathrm{Tm^{Ad}}]\mathrm{GaGa}[\mathrm{Tm^{Ad}}]\}[\mathrm{Ga_2I_{4.9}Cl_{1.1}}]$ (only the cation is shown).

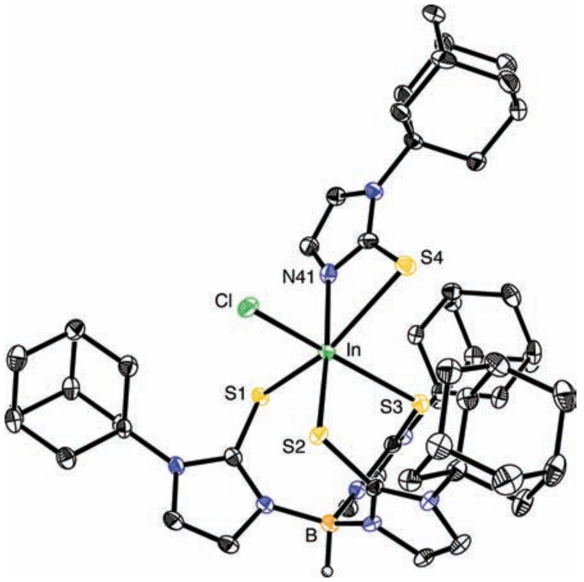


Figure 13. Molecular structure of $[\mathrm{Tm^{Ad}}]\mathrm{In}(\kappa^2\text{-}\mathrm{mim^{Ad}})\mathrm{Cl}$.

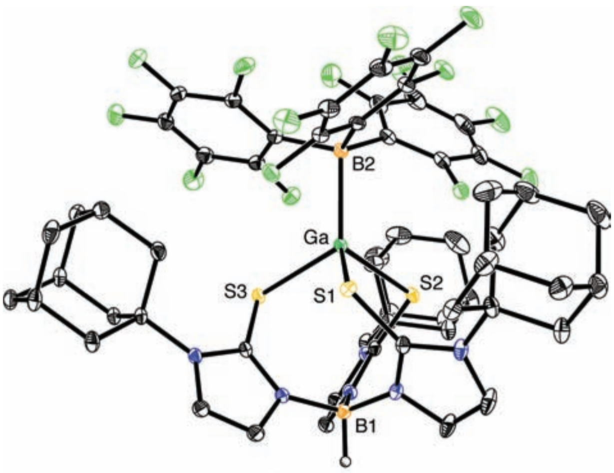


Figure 14. Molecular structure of $[\mathrm{Tm^{Ad}}]\mathrm{Ga}{\rightarrow}\mathrm{B(C_6F_5)_3}$.

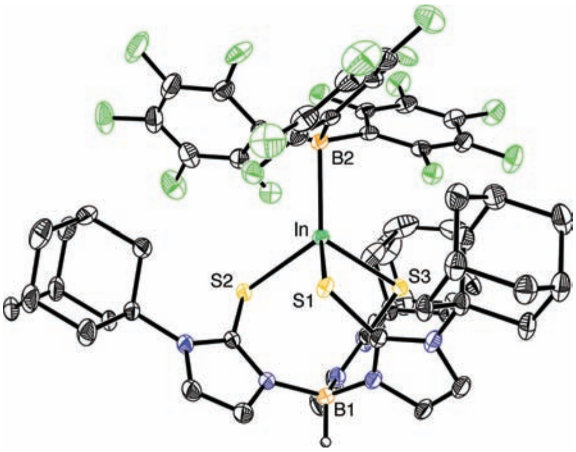


Figure 15. Molecular structure of $[\mathrm{Tm^{Ad}}]\mathrm{In}{\rightarrow}\mathrm{B(C_6F_5)_3}$.

though the product isolated is a mononuclear complex, namely, $[\mathrm{Tm^{Ad}}]\mathrm{In}(\kappa^2\text{-}\mathrm{mim^{Ad}})\mathrm{Cl}$ (Scheme 8), which has been structurally characterized by X-ray diffraction (Figure 13). The latter complex is a six-coordinate counterpart to $[\mathrm{Bm^{Bu^t}}]\mathrm{In}(\kappa^2\text{-}\mathrm{mim^{Bu^t}})\mathrm{Cl}$.[16] Interestingly, while the In−S bond lengths of $[\mathrm{Tm^{Ad}}]\mathrm{In}(\kappa^2\text{-}\mathrm{mim^{Ad}})\mathrm{Cl}$ are longer than the respective values for $[\mathrm{Bm^{Bu^t}}]\mathrm{In}(\kappa^2\text{-}\mathrm{mim^{Bu^t}})\mathrm{Cl}$, the In−N bond length of the κ^2-mim$^{\mathrm{Ad}}$ ligand [2.279(3) Å] is actually shorter than that of the κ^2-mim$^{\mathrm{Bu^t}}$ ligand [2.341(12) and 2.359(12) Å]. This observation may reflect the fact that nitrogen is trans to chlorine in $[\mathrm{Bm^{Bu^t}}]\mathrm{InCl}(\kappa^2\text{-}\mathrm{mim^{Bu^t}})$, but trans to sulfur in $[\mathrm{Tm^{Ad}}]\mathrm{In}(\kappa^2\text{-}\mathrm{mim^{Ad}})\mathrm{Cl}$.[43]

While disproportionation products are isolated from the reactions of $[\mathrm{Tm^{Ad}}]\mathrm{M}$ with "GaI" and InCl, the Lewis acid adducts $[\mathrm{Tm^{Ad}}]\mathrm{Ga}{\rightarrow}\mathrm{B(C_6F_5)_3}$ and $[\mathrm{Tm^{Ad}}]\mathrm{In}{\rightarrow}\mathrm{B(C_6F_5)_3}$ may be obtained if the reactions are performed in the presence of $\mathrm{B(C_6F_5)_3}$ (Schemes 7 and 8). The molecular structures of $[\mathrm{Tm^{Ad}}]\mathrm{Ga}{\rightarrow}\mathrm{B(C_6F_5)_3}$ and $[\mathrm{Tm^{Ad}}]\mathrm{In}{\rightarrow}\mathrm{B(C_6F_5)_3}$ have been determined by X-ray diffraction, as illustrated in Figures 14 and 15.

A simple indication of the strength of the interaction of the metal center with an $\mathrm{XY_3}$ trigonal-planar Lewis acid is provided by the deviation from planarity, as measured by the sum of the Y−X−Y bond angles, Σ(Y−X−Y).[44−46] In this regard, a comparison of Σ(C−B−C) for $[\mathrm{Tm^{Ad}}]\mathrm{Ga}{\rightarrow}\mathrm{B(C_6F_5)_3}$ (340.7°) and $[\mathrm{Tm^{Ad}}]\mathrm{In}{\rightarrow}\mathrm{B(C_6F_5)_3}$ (345.5°) indicates that the M → B interaction is greater for the gallium compound, thereby indicating that monovalent $[\mathrm{Tm^{Ad}}]\mathrm{Ga}$ is a better donor than is $[\mathrm{Tm^{Ad}}]\mathrm{In}$. In accord with this observation, density functional theory (DFT) calculations indicate that coordination of $\mathrm{B(C_6F_5)_3}$ to $[\mathrm{Tm^{Ad}}]\mathrm{Ga}$ (-28.8 kcal mol^{-1}) is more exothermic than is coordination to $[\mathrm{Tm^{Ad}}]\mathrm{In}$ (-22.0 kcal mol^{-1}). Also of note, the Σ(C−B−C) values for $[\mathrm{Tm^{Ad}}]\mathrm{Ga}{\rightarrow}\mathrm{B(C_6F_5)_3}$ and $[\mathrm{Tm^{Ad}}]\mathrm{In}{\rightarrow}\mathrm{B(C_6F_5)_3}$ are similar to the respective values for $[\mathrm{Tm^{Bu^t}}]\mathrm{Ga}{\rightarrow}\mathrm{B(C_6F_5)_3}$ (342.2°) and $[\mathrm{Tm^{Bu^t}}]\mathrm{In}{\rightarrow}\mathrm{B(C_6F_5)_3}$ (347.9°), suggesting that the $[\mathrm{Tm^{Ad}}]$ and $[\mathrm{Tm^{Bu^t}}]$ ligands have comparable electron-donating properties, in agreement with the IR spectroscopic studies on $[\mathrm{Tm^{Ad}}]\mathrm{Re(CO)_3}$ and $[\mathrm{Tm^{Bu^t}}]\mathrm{Re(CO)_3}$.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques under a nitrogen or argon atmosphere unless otherwise specified.[47] Solvents were purified and degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker 400 DRX, and Bruker 400 AVIII spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C_6D_5H, 7.26 for $CHCl_3$, and 2.50 for DMSO-d_6, where DMSO = dimethyl sulfoxide).[48] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 77.16 for $CDCl_3$, 128.06 for C_6D_6,[48] and 39.52 for DMSO-d_6). Coupling constants are given in hertz. IR spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer and are reported in cm^{-1}. Mass spectra were obtained on a Jeol JMS-HX110H tandem double-focusing mass spectrometer with a 10 kV accelerated voltage equipped with a fast atom bombardment (FAB) ion source. $[Tm^{Bu^t}]K$,[49] $HGaCl_2$,[50] and "GaI"[51] were prepared by literature methods. $GaCl_3$ (Strem & VWR), GaI_3 (Aldrich), InI_3 (Aldrich), ZnI_2 (Aldrich), InCl (Strem), $Re(CO_5)Br$ (Strem), 1-adamantyl isothiocyanate (Aldrich), and aminoacetaldehyde diethyl acetal (Aldrich) were obtained commercially and used as received.

Synthesis of Hmim^{Ad}. Hmim^{Ad} was prepared by a method analogous to other derivatives.[52] A solution of $H_2NCH_2CH(OEt)_2$ (3.44 g, 25.9 mmol) in ethanol (100 mL) was treated with 1-adamantyl isothiocyanate (5.00 g, 25.8 mmol). The resulting white slurry was refluxed at 95 °C for 20 h under a nitrogen atmosphere. The volatile components were removed from the mixture under reduced pressure, and the resulting pale-yellow oil was treated with an aqueous solution of H_2SO_4 (60 mL, 10% by weight) and refluxed at 110 °C for 13 h. The mixture was cooled to room temperature over a period of 2 h and then cooled to 10 °C for 0.5 h. The mixture was filtered, and the precipitate was washed sequentially with water (4 × 100 mL) and diethyl ether (2 × 50 mL) and dried in vacuo to give Hmim^{Ad} as a white solid (3.11 g, 52% yield). Anal. Calcd for Hmim^{Ad}: C, 66.6; H, 7.7; N, 12.0. Found: C, 66.4; H, 7.8; N, 11.9. ^{1}H NMR (DMSO-d_6): δ 1.67 [br, 6 H of $(C_3N_2H_2\{C_{10}\underline{H}_{15}\}S)$], 2.14 [br, 3 H of $H(C_3N_2H_2\{C_{10}\underline{H}_{15}\}S)$], 2.50 [br s, 6 H of $H(C_3N_2H_2\{C_{10}\underline{H}_{15}\}S)$], 6.83 [d, $^3J_{H-H}$ = 2 Hz, 1 H of $H(C_3N_2\underline{H}_2\{C_{10}H_{15}\}S)$], 7.02 [d, $^3J_{H-H}$ = 2 Hz, 1 H of $H(C_3N_2\underline{H}_2\{C_{10}H_{15}\}S)$], 11.90 [br, 1 H of $\underline{H}(C_3N_2H_2\{C_{10}H_{15}\}S)$]. $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 29.2 [3 C of $(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)$], 35.5 [3 C of $H(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)$], 38.9 [3 C of $H(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)$], 58.2 [3 C of $H(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)$], 113.8 [1 C of $H(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)$], 115.8 [1 C of $H(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)$], 159.3 [1 C of $H(C_2N_2H_2\{C_{10}H_{15}\}\underline{C}S)$]. IR data (KBr, cm^{-1}): 3148 (m), 3128 (s), 3084 (s), 3020 (s), 2911 (vs), 2848 (s), 2795 (m), 2735 (m), 1574 (m), 1527 (br), 1485 (s), 1461 (m), 1407 (m), 1373 (m), 1362 (m), 1345 (m), 1324 (m), 1316 (vs), 1289 (m), 1255 (vs), 1224 (vs), 1191 (w), 1182 (w), 1143 (m), 1120 (m), 1107 (m), 1073 (w), 1042 (w), 1011 (m), 982 (w), 969 (w), 938 (w), 913 (m), 828 (m), 820 (m), 786 (m), 711 (s), 686 (m), 666 (vs). FAB-MS: *m/z* 235.4 ($[M]^+$); M = mim^{Ad}).

Synthesis of [Tm^{Ad}]Li. A mixture of lithium borohydride (0.120 g, 5.51 mmol) and Hmim^{Ad} (2.96 g, 12.6 mmol) was treated with xylene (50 mL). The mixture was heated at 175 °C for 4 days in a thick-walled ampule (*Caution!*). The resulting white slurry was cooled to room temperature, and the precipitate was isolated by filtration and dried in vacuo to give $[Tm^{Ad}]Li$ as a white powder (2.52 g, 83% yield). ^{1}H NMR ($CDCl_3$): δ 1.59 [d, $^2J_{H-H}$ = 12 Hz, 9 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 1.65 [d, $^2J_{H-H}$ = 12 Hz, 9 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 2.07 [br, 9 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 2.50 [br, 18 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 4.4 [br, 1 H of $\underline{H}B(C_2N_2H_2\{C_{10}H_{15}\}CS)_3$], 6.01 [d, $^3J_{H-H}$ = 2 Hz, 3 H of $HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3$], 6.69 [d, $^3J_{H-H}$ = 2 Hz, 3 H of $HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3$]. ^{13}C NMR ($CDCl_3$): δ 30.1 [d, $^1J_{C-H}$ = 133 Hz, 9 C of $HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3$], 36.2 [t, $^1J_{C-H}$ = 125 Hz, 9 C of $HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3$], 39.8 [t, $^1J_{C-H}$ = 130 Hz, 9 C of $HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3$], 59.2 [s, 3 C of $HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3$], 114.8 [d, $^1J_{C-H}$ = 197 Hz, 3 C of $HB(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)_3$], 118.6 [d, $^1J_{C-H}$ = 192 Hz, 3 C of $HB(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)_3$], 161.1 [s, 3 C of $HB(C_2N_2H_2\{C_{10}H_{15}\}\underline{C}S)_3$]. IR data (KBr, cm^{-1}): 3383 (br), 2905 (vs), 2850 (vs), 2675 (w), 2523 (m), 2292 (w), 2225 (w), 1625 (br), 1566 (w), 1456 (m), 1437 (w), 1410 (s), 1382 (vs), 1358 (vs), 1340 (vs), 1318 (m), 1308 (m), 1281 (s), 1246 (s), 1190 (s), 1177 (s), 1158 (s), 1101 (s), 1077 (s), 1025 (m), 980 (m), 963 (w), 939 (w), 829 (m), 817 (m), 772 (m), 738 (m), 713 (s), 679 (s). FAB-MS: *m/z* 718.7 ($[M]^+$), 711.7 ($[M - Li]^+$); M = $[Tm^{Ad}]Li$.

Synthesis of [Tm^{Ad}]K. A mixture of potassium borohydride (0.133 g, 2.47 mmol) and Hmim^{Ad} (1.734 g, 7.40 mmol) was treated with toluene (50 mL). The mixture was refluxed for 5 days at 135 °C and then heated for 2 days at 165 °C and 2 days at 180 °C in a thick-walled ampule (*Caution!*). The resulting white slurry was cooled to room temperature, and the precipitate was isolated by filtration and dried in vacuo to give $[Tm^{Ad}]K$ as a white powder (0.930 g, 50% yield). ^{1}H NMR (DMSO-d_6): δ 1.67 [m, 18 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 2.11 [br, 9 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 2.57 [br, 18 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 4.4 [br, 1 H of $\underline{H}B(C_2N_2H_2\{C_{10}H_{15}\}CS)_3$], 5.83 [br s, 3 H of $HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3$], 6.79 [d, $^3J_{H-H}$ = 2 Hz, 3 H of $HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3$]. FAB-MS: *m/z* 750.4 ($[M]^+$), 711.4 ($[M - K]^+$); M = $[Tm^{Ad}]K$.

Synthesis of [Tm^{Ad}]Re(CO)$_3$. A mixture of $[Tm^{Ad}]Li$ (25 mg, 0.035 mmol) and $Re(CO)_5Br$ (14 mg, 0.034 mmol) was treated with C_6D_6 (0.7 mL) and transferred to an NMR tube equipped with a J. Young valve. The mixture was heated at 60 °C, thereby depositing colorless crystals of $[Tm^{Ad}]Re(CO)_3$ (ca. 10 mg, 29%) over a period of 18 h. Anal. Calcd for $[Tm^{Ad}]Re(CO)_3 \cdot 0.75C_6H_6$: C, 53.7; H, 5.5; N, 8.1. Found: C, 53.7; H, 5.8; N, 7.6. ^{1}H NMR (C_6D_6): δ 1.38 [d, $^2J_{H-H}$ = 12 Hz, 9 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 1.50 [d, $^2J_{H-H}$ = 12 Hz, 9 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 1.96 [br, 9 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 2.43 [d, $^2J_{H-H}$ = 11 Hz, 9 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 2.56 [d, $^2J_{H-H}$ = 10 Hz, 9 H of $HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3$], 6.46 [d, $^3J_{H-H}$ = 2 Hz, 3 H of $HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3$], 6.68 [d, $^3J_{H-H}$ = 2 Hz, 3 H of $HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3$]. IR data ($CH_2Cl_2$, cm^{-1}): 2005, 1887 ($\nu_{CO}$). IR data (KBr, cm^{-1}): 2911 (s), 2853 (m), 2366 (w), 1999 (vs, ν_{CO}), 1886 (vs, ν_{CO}), 1567 (w), 1456 (w), 1420 (w), 1379 (s), 1358 (m), 1343 (m), 1306 (m), 1253 (m), 1196 (vs), 1178 (m), 1044 (w), 832 (m), 776 (w), 727 (m), 686 (m), 638 (w), 540 (w), 515 (w), 499 (m). FAB-MS: *m/z* 982.5 ($[M]^+$); M = $[Tm^{Ad}]Re(CO)_3$.

Synthesis of [Tm$^{Bu^t}$]Re(CO)$_3$. A mixture of $[Tm^{Bu^t}]K$ (50 mg, 0.10 mmol) and $Re(CO)_5Br$ (39 mg, 0.10 mmol) was treated with CD_3CN (0.7 mL) and transferred to an NMR tube equipped with a J. Young valve. The mixture was heated at 60 °C, thereby depositing colorless crystals of $[Tm^{Bu^t}]Re(CO)_3$ (16 mg, 22%) over a period of 12 h. ^{1}H NMR ($CDCl_3$): δ 1.82 [s, 27 H of $HB\{C_3N_2H_2[C(C\underline{H}_3)_3]S\}_3$], 4.5 [br, 1 H of $\underline{H}B\{C_3N_2H_2[C(CH_3)_3]S\}_3$], 6. 78 [d, $^3J_{H-H}$ = 2 Hz, 3 H of $HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3$], 6.96 [d, $^3J_{H-H}$ = 2 Hz, 3 H of $HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.7 [9 C of $HB\{C_2N_2H_2[C(\underline{C}H_3)_3]CS\}_3$], 59.9 [3 C of $HB\{C_2N_2H_2[\underline{C}(CH_3)_3]CS\}_3$], 116.7 [3 C of $HB\{C_2N_2H_2[\underline{C}(CH_3)_3]CS\}_3$], 122.9 [3 C of $HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CS\}_3$], 3 C of $HB\{C_2N_2H_2[C(CH_3)_3]\underline{C}S\}_3$ not observed. IR data (CH_2Cl_2, cm^{-1}): 2007, 1887 (ν_{CO}). IR data (KBr, cm^{-1}): 3145 (w), 2968 (m), 2364 (w), 2008 (vs, ν_{CO}), 1880 (vs, ν_{CO}), 1564 (m), 1480 (m), 1421 (s), 1397 (m), 1359 (vs), 1306 (s), 1262 (s), 1231 (m), 1197 (s), 1071 (w), 822 (m), 764 (s), 733 (vs), 691 (s), 637 (m), 588 (m), 546 (w), 520 (s), 490 (m).

Synthesis of [Tm^{Ad}]ZnI. A mixture of $[Tm^{Ad}]Li$ (9 mg, 0.01 mmol) and ZnI_2 (13 mg, 0.04 mmol) was treated with $CDCl_3$ (0.7 mL), mixed via a pipet, and transferred to an NMR tube equipped with a

J. Young valve. The reaction was monitored by ^{1}H NMR spectroscopy and filtered after 14 h. The solution was allowed to stand at room temperature, thereby resulting in the deposition of colorless crystals of $\mathrm{[Tm^{Ad}]ZnI \cdot 2.3CHCl_3}$ (6 mg, 41%) over a period of 3 days. Colorless crystals of composition $\mathrm{[Tm^{Ad}]ZnI \cdot 2CH_2Cl_2}$ suitable for X-ray diffraction were isolated from a concentrated $\mathrm{CH_2Cl_2}$ solution at room temperature. Anal. Calcd for $\mathrm{[Tm^{Ad}]ZnI \cdot 2.3CHCl_3}$: C, 42.1; H, 4.6; N, 7.1. Found: C, 42.1; H, 4.6; N, 7.0. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.68 [d, $^2J_{\mathrm{H-H}} = 13$ Hz, 9 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 1.74 [d, $^2J_{\mathrm{H-H}} = 12$ Hz, 9 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 2.20 [br, 9 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 2.46 [d, $^2J_{\mathrm{H-H}} = 11$ Hz, 9 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 2.59 [d, $^2J_{\mathrm{H-H}} = 12$ Hz, 9 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 4.2 [br, 1 H of $\mathrm{\underline{H}B(C_2N_2H_2\{C_{10}H_{15}\}CS)_3}$], 6.85 [d, $^3J_{\mathrm{H-H}} = 2$ Hz, 3 H of $\mathrm{HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3}$], 6.98 [d, $^3J_{\mathrm{H-H}} = 2$ Hz, 3H of $\mathrm{HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3}$]. FAB-MS: *m*/*z* 775.2 ($\mathrm{[M - I]^+}$); M = $\mathrm{[Tm^{Ad}]ZnI}$.

Synthesis of $\mathrm{\{[Tm^{Ad}]GaCl\}[GaCl_4]}$. A mixture of $\mathrm{GaCl_3}$ (49 mg, 0.28 mmol) and $\mathrm{[Tm^{Ad}]Li}$ (100 mg, 0.14 mmol) was treated with $\mathrm{CH_2Cl_2}$ (2 mL), and the suspension was stirred for 4 h, thereby resulting in the formation of a white precipitate. The mixture was filtered, and the volatile components of the filtrate were removed in vacuo to give $\mathrm{\{[Tm^{Ad}]GaCl\}[GaCl_4] \cdot 2.33CH_2Cl_2}$ as a white solid (114 mg, 67%). Anal. Calcd for $\mathrm{\{[Tm^{Ad}]GaCl\}[GaCl_4] \cdot 2.33CH_2Cl_2}$: C, 40.5; H, 4.7; N, 6.9. Found: C, 40.4; H, 4.7; N, 7.0. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.75 [s, 18 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 2.27 [br, 9 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 2.34 [d, $^2J_{\mathrm{H-H}} = 11$ Hz, 9 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 2.53 [d, $^2J_{\mathrm{H-H}} = 11$ Hz, 9 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 4.7 [br, 1 H of $\mathrm{\underline{H}B(C_2N_2H_2\{C_{10}H_{15}\}CS)_3}$], 7.27 [d, $^3J_{\mathrm{H-H}} = 2$ Hz, 3 H of $\mathrm{HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3}$], 7.33 [d, $^3J_{\mathrm{H-H}} = 2$ Hz, 3 H of $\mathrm{HB(C_2N2\underline{H}2\{C_{10}H_{15}\}CS)_3}$]. ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 30.0 [9 C of $\mathrm{HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3}$], 35.6 [9 C of $\mathrm{HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3}$], 40.9 [9 C of $\mathrm{HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3}$], 62.8 [3 C of $\mathrm{HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3}$], 120.3 [3 C of $\mathrm{HB(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)_3}$], 126.8 [3 C of $\mathrm{HB(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)_3}$], 144.5 [3 C of $\mathrm{HB(C_2N_2H_2\{C_{10}H_{15}\}CS)_3}$]. IR data (KBr, cm^{-1}): 3182 (m), 3150 (m), 3100 (w), 2911 (vs), 2853 (vs), 2669 (w), 2462 (m), 1698 (w), 1617 (m), 1562 (s), 1478 (w), 1456 (s), 1438 (m), 1427 (s), 1381 (s), 1359 (s), 1344 (s), 1327 (m), 1306 (s), 1290 (w), 1250 (s), 1197 (vs), 1178 (vs), 1132 (m), 1106 (m), 1083 (m), 1043 (s), 982 (m), 965 (w), 940 (w), 828 (s), 775 (m), 740 (vs), 689 (w), 681 (m). FAB-MS: *m*/*z* 817.4 ($\mathrm{[M - GaCl_4]^+}$); M = $\mathrm{\{[Tm^{Bu^t}]GaCl\}[GaCl_4]}$.

Synthesis of $\mathrm{\{[Tm^{Ad}]GaI\}X}$ (X = I, $\mathrm{GaI_4}$). (i) A mixture of $\mathrm{GaI_3}$ (69 mg, 0.15 mmol) and $\mathrm{[Tm^{Ad}]Li}$ (100 mg, 0.14 mmol) was treated with $\mathrm{CH_2Cl_2}$ (2 mL), and the suspension was stirred for 4 h, thereby resulting in the formation of a white precipitate. The mixture was filtered, and the volatile components were removed from the filtrate in vacuo to give $\mathrm{\{[Tm^{Ad}]GaI\}I \cdot 3CH_2Cl_2}$ as a white solid (75 mg, 42%). Colorless crystals of composition $\mathrm{\{[Tm^{Ad}]GaI\}I \cdot 3CH_2Cl_2}$ suitable for X-ray diffraction were isolated from a concentrated $\mathrm{CH_2Cl_2}$ solution at room temperature over a period of 2 weeks. Anal. Calcd for $\mathrm{\{[Tm^{Ad}]GaI\}I \cdot 1.5CH_2Cl_2}$: C, 41.8; H, 4.8; N, 7.2. Found: C, 42.0; H, 4.4; N, 7.2. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.75 [s, 18 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 2.28 [br, 9 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 2.35 [d, $^2J_{\mathrm{H-H}} = 11$ Hz, 9 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 2.53 [d, $^2J_{\mathrm{H-H}} = 11$ Hz, 9 H of $\mathrm{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3}$], 4.8 [br, 1 H of $\mathrm{\underline{H}B(C_2N_2H_2\{C_{10}H_{15}\}CS)_3}$], 7.41 [s, 6 H of $\mathrm{HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3}$]. ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 30.0 [9 C of $\mathrm{HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3}$], 35.7 [9 C of $\mathrm{HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3}$], 41.2 [9 C of $\mathrm{HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3}$], 62.8 [3 C of $\mathrm{HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3}$], 120.5 [3 C of $\mathrm{HB(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)_3}$], 127.1 [3 C of $\mathrm{HB(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)_3}$], 3 C of $\mathrm{HB(C_2N_2H_2\{C_{10}H_{15}\}\underline{C}S)_3}$ not observed. IR data (KBr, cm^{-1}): 3163 (m), 3125 (m), 3086 (m), 2909 (vs), 2853 (vs), 2661 (w), 2435 (m), 1733 (w), 1615 (m), 1557 (s), 1455 (m), 1421 (s), 1377 (s), 1357 (s), 1343 (s), 1325 (m), 1317 (w), 1305 (vs), 1270 (m), 1249 (s), 1194 (vs), 1177 (vs), 1128 (m), 1106 (m), 1080 (m), 1041 (s), 981 (m), 965 (w), 940 (w), 914 (w), 868 (w), 828 (s), 775 (m), 764 (m), 742 (s), 689 (w), 680 (m). FAB-MS: *m*/*z* 1035.5 ($\mathrm{[M]^+}$, M = $\mathrm{[(Tm^{Bu^t})GaI]I}$), 907.5 ($\mathrm{[M - I]^+}$, M = $\mathrm{[Tm^{Bu^t}]GaI}$).

(ii) A mixture of $\mathrm{GaI_3}$ (56 mg, 0.13 mmol) and $\mathrm{[Tm^{Ad}]K}$ (75 mg, 0.10 mmol) was treated with $\mathrm{CH_2Cl_2}$ (2 mL), and the suspension was stirred for 2 h, thereby resulting in the formation of a white precipitate. The mixture was filtered, and crystals of composition $\mathrm{\{[Tm^{Adam}]GaI\}[GaI_4] \cdot CH_2Cl_2}$ were obtained by direct crystallization of the filtrate over a period of 3 weeks at room temperature and analyzed by X-ray diffraction.

Synthesis of $\mathrm{\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}[GaCl_4]_2}$. A mixture of $\mathrm{[Tm^{Ad}]Li}$ (100 mg, 0.14 mmol) and $\mathrm{HGaCl_2}$ (43 mg, 0.31 mmol) was treated with $\mathrm{CH_2Cl_2}$ (2 mL), and the suspension was stirred for 3 h, thereby resulting in the formation of a pale-yellow precipitate. The mixture was filtered, and pentane (1 mL) was added to the filtrate. The volatile components were removed in vacuo to give $\mathrm{\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}[GaCl_4]_2}$ as a pale-yellow solid (69 mg, 50%). Anal. Calcd for $\mathrm{\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}[GaCl_4]_2 \cdot CH_2Cl_2}$: C, 45.8; H, 5.2; N, 8.1. Found: C, 45.8; H, 4.9; N, 7.8. ^{1}H NMR (DMSO-d_6): δ 1.69 [br, 36 H of $\mathrm{[HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3]_2}$], 2.10 [br, 18 H of $\mathrm{[HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3]_2}$], 2.22 [d, $^2J_{\mathrm{H-H}} = 14$ Hz, 18 H of $\mathrm{\{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3\}_2}$], 2.46 [d, $^2J_{\mathrm{H-H}} = 14$ Hz, 18 H of $\mathrm{\{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3\}_2}$], 7.53 [d, $^3J_{\mathrm{H-H}} = 2$ Hz, 6 H of $\mathrm{[HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3]_2}$], 7.65 [d, $^3J_{\mathrm{H-H}} = 2$ Hz, 5 H of $\mathrm{[HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3]_2}$], 7.69 [d, $^3J_{\mathrm{H-H}} = 2$ Hz, 1 H of $\mathrm{[HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3]_2}$], 2 H of $\mathrm{[\underline{H}B(C_2N_2H_2\{C_{10}H_{15}\}CS)_3]_2}$ not observed. ^{13}C{^{1}H} NMR (DMSO-d_6): δ 29.4 [18 C of $\mathrm{[HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3]_2}$], 34.7 [18 C of $\mathrm{[HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3]_2}$], 18 C of $\mathrm{[HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3]_2}$ not observed, 61.1 [6 C of $\mathrm{[HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3]_2}$], 120.6 [6 C of $\mathrm{[HB(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)_3]_2}$], 126.0 [6 C of $\mathrm{[HB(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)_3]_2}$], 145.6 [6 C of $\mathrm{[HB(C_2N_2H_2\{C_{10}H_{15}\}\underline{C}S)_3]_2}$]. IR data (KBr, cm^{-1}): 3432 (br), 3181 (m), 3145 (m), 3099 (w), 2907 (vs), 2854 (m), 2660 (w), 2436 (m), 1562 (m), 1478 (w), 1456 (m), 1425 (s), 1380 (s), 1359 (s), 1344 (s), 1324 (m), 1306 (s), 1290 (w), 1251 (m), 1197 (vs), 1178 (vs), 1132 (m), 1106 (m), 1083 (m), 1043 (s), 982 (m), 965 (w), 940 (w), 829 (s), 775 (m), 737 (s), 688 (m), 681 (m). FAB-MS: *m*/*z* 1774.9 ($\mathrm{[M - GaCl_4]^+}$); M = $\mathrm{\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}[GaCl_4]_2}$.

Synthesis of $\mathrm{\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}X}$ (X = $\mathrm{[Ga_2I_6]_{0.5}I}$, $\mathrm{[Ga_2I_{4.9}Cl_{1.1}]}$). (i) A mixture of $\mathrm{[Tm^{Ad}]Li}$ (100 mg, 0.14 mmol) and “GaI” (60 mg, 0.31 mmol) was treated with $\mathrm{CH_2Cl_2}$ (2 mL), and the suspension was stirred for 3 h, thereby resulting in the formation of a pale-yellow precipitate. The mixture was filtered, and pentane (1 mL) was added to the filtrate. The volatile components were removed from the filtrate in vacuo to give $\mathrm{\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}[Ga_2I_6]_{0.5}I \cdot 0.5CH_2Cl_2}$ as a pale-yellow solid (70 mg, 46%). Anal. Calcd for $\mathrm{\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}[Ga_2I_6]_{0.5}I \cdot 0.5CH_2Cl_2}$: C, 43.2; H, 4.9; N, 7.7. Found: C, 43.3; H, 4.9; N, 7.4. ^{1}H NMR (DMSO-d_6): δ 1.69 [br, 36 H of $\mathrm{[HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3]_2}$], 2.26 [d, $^2J_{\mathrm{H-H}} = 11$ Hz, 18 H of $\mathrm{\{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3\}_2}$], 2.47 [d, $^2J_{\mathrm{H-H}} = 11$ Hz, 18 H of $\mathrm{\{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3\}_2}$], 7.54 [s, 6 H of $\mathrm{[HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3]_2}$], 7.65 [s, 4 H of $\mathrm{[HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3]_2}$], 7.70 [s, 2 H of $\mathrm{[HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3]_2}$], 2 H of $\mathrm{[\underline{H}B(C_2N_2H_2\{C_{10}H_{15}\}CS)_3]_2}$ not observed. ^{13}C{^{1}H} NMR (DMSO-d_6): δ 29.4 [18 C of $\mathrm{[HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3]_2}$], 34.7 [18 C of $\mathrm{[HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3]_2}$], 18 C of $\mathrm{[HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3]_2}$ not observed, 61.1 [6 C of $\mathrm{[HB(C_2N_2H_2\{\underline{C}_{10}H_{15}\}CS)_3]_2}$], 120.6 [6 C of $\mathrm{[HB(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)_3]_2}$], 126.0 [6 C of $\mathrm{[HB(\underline{C}_2N_2H_2\{C_{10}H_{15}\}CS)_3]_2}$], 145.6 [6 C of $\mathrm{[HB(C_2N_2H_2\{C_{10}H_{15}\}\underline{C}S)_3]_2}$]. IR data (KBr, cm^{-1}): 3408 (br), 3181 (m), 2907 (vs), 2852 (s), 2659 (w), 2435 (m), 1618 (br), 1561 (m), 1478 (w), 1455 (m), 1423 (s), 1379 (s), 1358 (s), 1343 (s), 1323 (m), 1305 (s), 1289 (w), 1251 (s), 1196 (vs), 1178 (vs), 1133 (w), 1105 (m), 1082 (m), 1043 (s), 982 (m), 965 (w), 940 (w), 829 (s), 775 (m), 735 (s), 681 (m). FAB-MS: *m*/*z* 1691.1 ($[M - [GaI_3]]^+$); M = $\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}[Ga_2I_6]_{0.5}I$.

(ii) A mixture of $[Tm^{Ad}]K$ (75 mg, 0.10 mmol) and "GaI" (56 mg, 0.31 mmol) was treated with CH_3CN (2 mL), and the suspension was stirred for 3 h, thereby resulting in the formation of a pale-yellow precipitate. The mixture was treated with CH_2Cl_2 (1 mL) to facilitate filtration, and the filtrate was allowed to stand at room temperature. Colorless crystals of composition $\{[Tm^{Ad}]GaGa[Tm^{Ad}]\}[Ga_2I_{4.9}Cl_{1.1}] \cdot 2MeCN \cdot 4CH_2Cl_2$ were obtained over a period of 4 weeks.

Synthesis of $[Tm^{Ad}]Ga{\rightarrow}B(C_6F_5)_3$. A mixture of $[Tm^{Ad}]Li$ (100 mg, 0.14 mmol), "GaI" (60 mg, 0.31 mmol), and $B(C_6F_5)_3$ (157 mg, 0.31 mmol) was treated with CH_2Cl_2 (2 mL). The resulting slurry was stirred for 3 h and filtered, and crystals of composition $[Tm^{Ad}]Ga{\rightarrow}B(C_6F_5)_3 \cdot (CH_2Cl_2)_2$ were isolated after allowing the filtrate stand for several days.

Synthesis of $\{[Tm^{Ad}]_2In\}[InI_4]$. A mixture of $[Tm^{Ad}]Li$ (10 mg, 0.01 mmol) and InI_3 (4 mg, 0.01 mmol) was treated with $CDCl_3$ (0.7 mL), mixed via a pipet, and transferred to an NMR tube equipped with a J. Young valve. The reaction was monitored by ^1H NMR spectroscopy, and colorless crystals of composition $\{[Tm^{Ad}]_2In\}[InI_4] \cdot 2CHCl_3$ (6 mg, 62%) were deposited over a period of 1 day and isolated. Crystals of $\{[Tm^{Ad}]_2In\}[InI_4]$ suitable for X-ray diffraction were obtained from a concentrated CH_2Cl_2 solution over a period of 2 days at room temperature. Anal. Calcd for $\{[Tm^{Ad}]_2In\}[InI_4] \cdot 1.5CHCl_3$: C, 40.8; H, 4.5; N, 7.2. Found: C, 40.8; H, 4.5; N, 7.0. ^1H NMR ($CDCl_3$): δ 1.66 [d, $^2J_{H-H}$ = 11 Hz, 18 H of $\{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3\}_2$], 1.70 [d, $^2J_{H-H}$ = 12 Hz, 18 H of $\{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3\}_2$], 2.18 [br s, 18 H of $\{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3\}_2$], 2.45 [d, $^2J_{H-H}$ = 12 Hz, 18 H of $\{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3\}_2$], 2.56 [d, $^2J_{H-H}$ = 12 Hz, 18 H of $\{HB(C_2N_2H_2\{C_{10}\underline{H}_{15}\}CS)_3\}_2$], 6.81 [d, $^3J_{H-H}$ = 2 Hz, 6 H of $\{HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3\}_2$], 7.03 [d, $^3J_{H-H}$ = 2 Hz, 6 H of $\{HB(C_2N_2\underline{H}_2\{C_{10}H_{15}\}CS)_3\}_2$], 2 H of $\{\underline{H}B(C_2N_2H_2\{C_{10}H_{15}\}CS)_3\}_2$ not observed. FAB-MS: *m*/*z* 1537.8 ($[M - InI_4]^+$); M = $\{[Tm^{Ad}]_2In\}[InI_4]$.

Synthesis of $[Tm^{Ad}]In(\kappa^2\text{-}mim^{Ad})Cl$. A mixture of $[Tm^{Ad}]Li$ (200 mg, 0.278 mmol) and InCl (100 mg, 0.665 mmol) was treated with cold (−78 °C) MeOH (25 mL). The resulting slurry was allowed to warm to ambient temperature, stirred for 3 h, and filtered. The volatile components were removed from the filtrate in vacuo, and the resulting solid was extracted into benzene (25 mL). The volatile components were removed from the extract via lyophilization to give a white solid. Colorless crystals of composition $[Tm^{Ad}]In(\kappa^2\text{-}mim^{Ad})Cl$ were isolated from a concentrated acetonitrile solution after a period of 1 week at room temperature and were identified by single-crystal X-ray diffraction.

Synthesis of $[Tm^{Ad}]In{\rightarrow}B(C_6F_5)_3$. A mixture of $[Tm^{Ad}]K$ (75 mg, 0.10 mmol), InCl (15 mg, 0.10 mmol), and $B(C_6F_5)_3$ (64 mg, 0.13 mmol) was treated with CH_3CN (2 mL). The resulting mixture was stirred for 3 h and filtered. The colorless filtrate was permitted to stand for 2 weeks at room temperature, leading to the formation of colorless crystals of composition $\{[Tm^{Ad}]In{\rightarrow}B(C_6F_5)_3$, which were identified by single-crystal X-ray diffraction.

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection, and refinement parameters are summarized in the Supporting Information. 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 6.10).[53]

Computational Details. All calculations were carried out using DFT, as implemented in the *Jaguar* 7.5 (release 207) suite of ab initio quantum chemistry programs.[54] Geometry optimizations were performed with the B3LYP density functional[55] and LACVP** basis sets, i.e., the 6-31G** (C, H, B, N, F, and S) and LAV3P (Ga and In) basis sets.[56] Cartesian coordinates for geometry-optimized structures are listed in the Supporting Information. The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using cc-pVTZ(-f) correlation consistent triple-ζ (C, H, B, N, F, and S) and LAV3P (Ga and In) basis sets.

■ SUMMARY

In conclusion, a new tris(2-mercaptoimidazolyl)hydroborato ligand that features adamantyl substituents, $[Tm^{Ad}]$, has been synthesized via the reaction of 1-adamantyl-2-mercaptoimidazole with MBH_4. Structural characterization of $[Tm^{Ad}]Re(CO)_3$ demonstrates that the $[Tm^{Ad}]$ ligand is more encapsulating than other $[Tm^R]$ ligands, but is electronically similar to $[Tm^{Bu^t}]$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. CIF files and tables of crystallographic data 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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