Synthesis and Structural Characterization of Thallium and Cadmium Carbatrane Compounds, [Tism$^{Pr^iBenz}$]Tl and [Tism$^{Pr^iBenz}$]CdMe[‡]

Matthew Hammond, David A. Vaccaro and Gerard Parkin,*

Department of Chemistry,

Columbia University,

New York, New York 10027, USA.

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Abstract: The *tris*[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl ligand, [Tism$^{Pr^iBenz}$], has been used to afford a carbatrane complex of an element of the sixth period, namely [Tism$^{Pr^iBenz}$]Tl, *via* the reaction of [Tism$^{Pr^iBenz}$]Li with TlOAc. [Tism$^{Pr^iBenz}$]Tl may be employed as a reagent for the synthesis of other [Tism$^{Pr^iBenz}$]MX complexes, including the cadmium methyl compound, [Tism$^{Pr^iBenz}$]CdMe. The molecular structure of [Tism$^{Pr^iBenz}$]CdMe has been determined by X-ray diffraction, which indicates that it possesses an atrane motif, in contrast to the κ^3-coordination observed for the zinc congener, [κ^3-Tism$^{Pr^iBenz}$]ZnMe. Furthermore, the structure of [Tism$^{Pr^iBenz}$]CdMe is also different to other [Tism$^{Pr^iBenz}$]CdX compounds because the Cd–C$_{atrane}$ bond of [Tism$^{Pr^iBenz}$]CdMe is distinctly shorter than in other derivatives, while the Cd–N bond lengths are considerably longer.

[‡] Dedicated to the memory of Professor Malcolm L. H. Green, a true inspiration whose enthusiasm and creative ideas have had the most significant impact not only on developing inorganic chemistry, but also on its teaching. GP is most fortunate to have been his mentee and experience both of these issues first hand, thereby having a profound impression that continues to this day.

INTRODUCTION

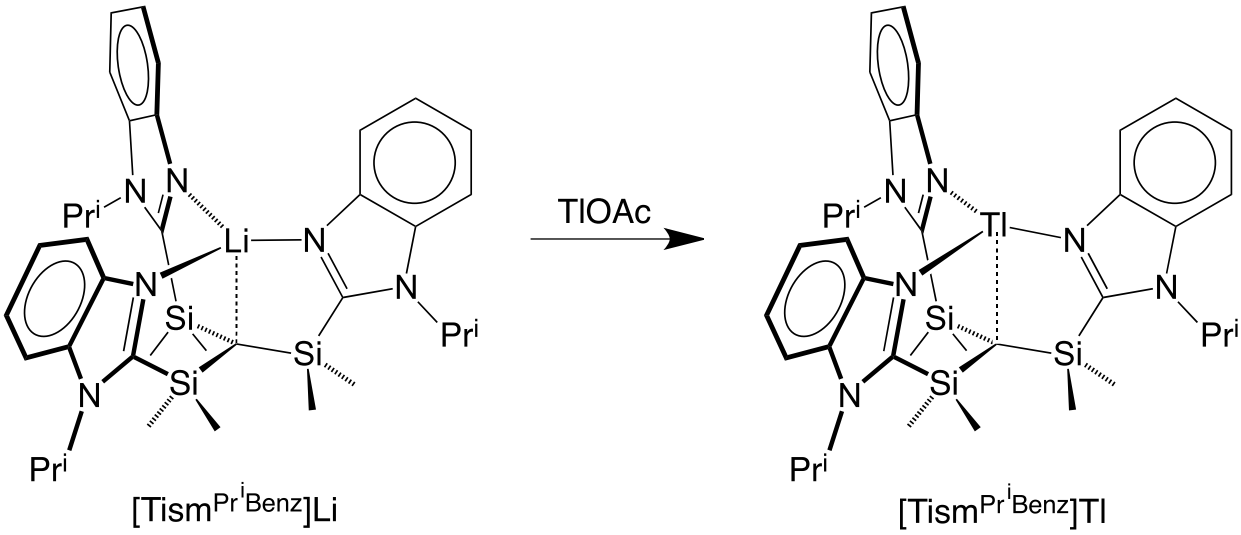
Atranes are a class of molecules that possess a tricyclic motif by virtue of a bond between two bridgehead atoms.[1] A variety of different types of atranes, which are differentiated according to the identity of the bridgehead atom, are known, as illustrated by metallacarbatranes that feature transannular M–C interactions.[2,3,4,5] In this regard, we have recently described the use of the L_2X^6 *tris*[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl ligand, [Tism$^{Pr^iBenz}$], to afford metallacarbatrane compounds of both main group and transition metals.[5] However, to date, only [Tism$^{Pr^iBenz}$] carbatranes of metals belonging to the second (Li), third (Mg), fourth (Ni, Cu and Zn) and fifth (Cd) periods have been reported.[5] Here, we extend this class of molecules to a metal of the sixth period with the synthesis of the thallium carbatrane, [Tism$^{Pr^iBenz}$]Tl. In addition, we describe the use of [Tism$^{Pr^iBenz}$]Tl as a reagent for the synthesis of other [Tism$^{Pr^iBenz}$]MX complexes, including the cadmium methyl compound, [Tism$^{Pr^iBenz}$]CdMe.

RESULTS AND DISCUSSION

1. Synthesis and Structural Characterization of [Tism$^{Pr^iBenz}$]Tl

The thallium carbatrane, [Tism$^{Pr^iBenz}$]Tl, may be obtained *via* the reaction of the lithium complex, [Tism$^{Pr^iBenz}$]Li, with TlOAc, as illustrated in Scheme 1. The molecular structure of [Tism$^{Pr^iBenz}$]Tl has been determined by X-ray diffraction (Figure 1), thereby demonstrating that the compound adopts an atrane motif in which the [Tism$^{Pr^iBenz}$] ligand exhibits κ^4-coordination with a Tl–C bond length of 2.626(4) Å and three Tl–N bond lengths of 2.763(2) Å . While this structure bears a resemblance to the two other [Tism$^{Pr^iBenz}$]M complexes that are devoid of an additional substituent on the metal, namely the lithium and copper complexes, [Tism$^{Pr^iBenz}$]Li and [Tism$^{Pr^iBenz}$]Cu,[5a] a significant difference pertains to the placement of the thallium atom relative to the plane of the three nitrogen atoms. Specifically, whereas the lithium and copper are displaced from the plane of the three nitrogen atoms towards the carbon atom, with C–

Li–N and C–Cu–N angles of 96.8° and 95.8° respectively, the thallium is displaced away from the carbon atom with C–Tl–N angles of 73.9°. Although this difference may be associated with the larger size of Tl compared to Li and Cu,[7] it is evident that the thallium lone pair is stereochemically active, such that the molecule possesses a so-called hemidirected geometry in which all coordinating atoms reside in one half of the coordination sphere.[8,9]



Scheme 1.

The atrane structure of $[Tism^{Pr^iBenz}]Tl$ is noteworthy because the related tris(pyrazolyl)methyl compound, $[pz_3C]Tl$,[10] does not adopt this motif. Rather, the $[pz_3C]$ ligand binds only with a κ^3-coordination mode with a Tl–C bond length of 2.541 Å and with Tl–N bond lengths of 2.736 Å and 2.931 Å; the coordination about thallium is, nevertheless, supplemented by an additional intermolecular Tl–N interaction (3.187 Å).[10]

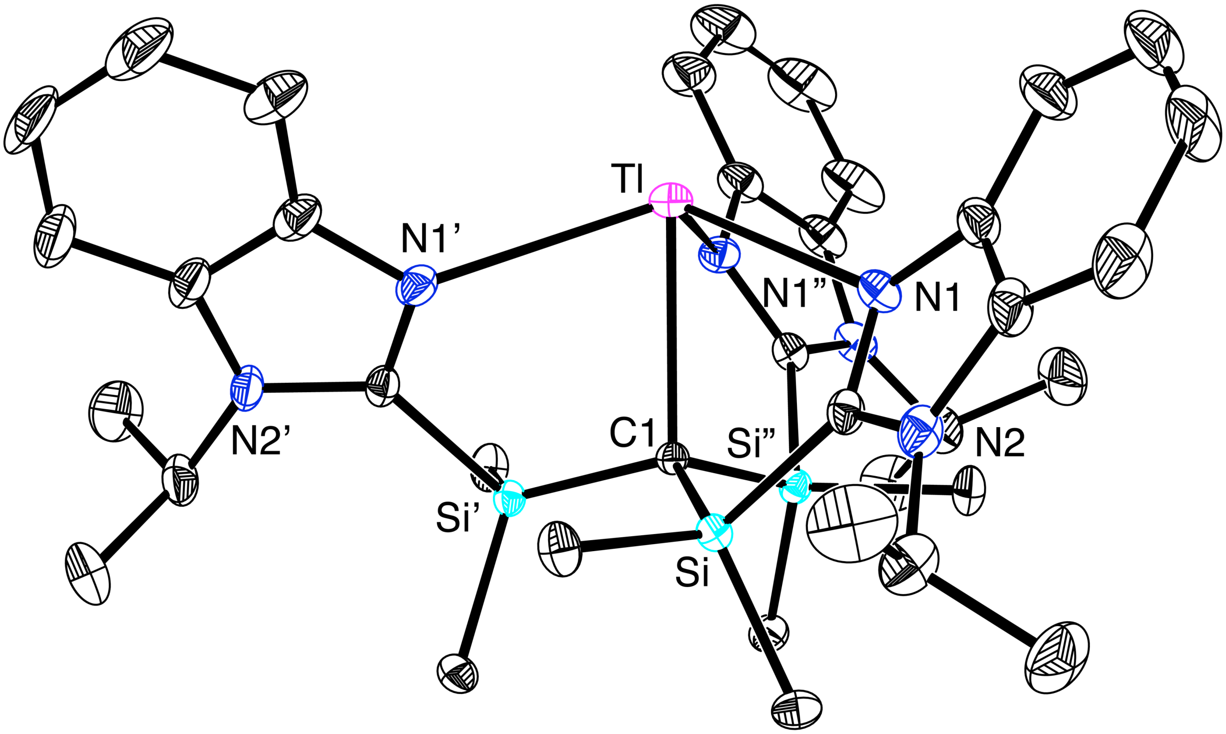


Figure 1. Molecular structure of [Tism$^{\mathrm{Pr^iBenz}}$]Tl.

While the symmetric coordination of the three nitrogen donors of [Tism$^{\mathrm{Pr^iBenz}}$]Tl does not resemble the coordination motif of [pz$_3$C]Tl, it is, nevertheless, similar to that in tris(pyrazolyl)borato thallium compounds, [Tp$^{\mathrm{R,R'}}$]Tl. The Tl–N bond lengths of [Tism$^{\mathrm{Pr^iBenz}}$]Tl [2.763(2) Å] are, however, longer than the average value for [Tp$^{\mathrm{R,R'}}$]Tl compounds (2.608 Å) listed in the Cambridge Structural Database (CSD),[11] with some representative examples being listed in Table 1.

Table 1. Comparison of Tl–N bond lengths in $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Tl}$ with those in $[\mathrm{Tp}^{\mathrm{R,R'}}]\mathrm{Tl}$ and compounds.

	***d*(Tl–N)/Å**			***d*(Tl-N$_{\mathrm{av}}$)/Å**	**Ref.**
$[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Tl}$	2.763(2)	2.763(2)	2.763(2)	2.763	this work
[Tp]Tl	2.665(6)	2.575(7)	2.730(7)	2.657	12
	2.651(7)	2.547(7)	2.590(8)	2.596	
	2.603(7)	2.621(7)	2.605(7)	2.609	13
	2.667(7)	2.549(7)	2.668(7)	2.628	
$[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{Tl}$	2.582(6)	2.582(6)	2.587(9)	2.584	14
$[\mathrm{Tp}^{\mathrm{Bu^t{}_2}}]\mathrm{Tl}$	2.584(7)	2.592(7)	2.543(7)	2.573	15
$[\mathrm{Tp}^{\mathrm{Trip}}]\mathrm{Tl}$	2.70(2)	2.72(2)	2.786(7)	2.735	16
	2.67(2)	2.80(2)	2.786(7)	2.752	
$[\mathrm{Tp}^{\mathrm{CF_3,Tn}}]\mathrm{Tl}$	2.603(2)	2.635(4)	2.623(6)	2.620	17
$[\mathrm{Tp}^{\mathrm{(CF_3)_2}}]\mathrm{Tl}$	2.663(4)	2.739(3)	2.739(3)	2.714	18
	2.675(10)	2.724(7)	2.724(7)	2.708	19
$[\mathrm{MeTp}^{\mathrm{(CF_3)}}]\mathrm{Tl}$	2.601(2)	2.6228(15)	2.6228(15)	2.616	20
$[\mathrm{HB(pz)_2(pz^{Bu^t{}_2})}]\mathrm{Tl}$	2.526(4)	2.588(4)	2.741(4)	2.618	21

Another noteworthy feature of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Tl}$ is that structurally characterized monovalent organothallium compounds are not common. For example, other than $[\mathrm{pz_3C}]\mathrm{Tl}$, the only monomeric monovalent organothallium complexes with a single Tl–C bond listed in the CSD are the *tris*(2-pyridonyl)methyl compound $[\mathrm{Tpom}^{\mathrm{Bu^t}}]\mathrm{Tl}$,[22] the *N*-heterocyclic carbene complexes $[(\mathrm{ITr})\mathrm{Tl}][\mathrm{BAr^F{}_4}]$[23] and [(ITr)Tl][OTf] (ITr = $[(\mathrm{HCNCPh_3})_2\mathrm{C}:]$),[23] and the aryl complex Ar′′′Tl (Ar′′′ = $\mathrm{C_6H_3}$-2,6-$\{\mathrm{C_6H_2}$-2,4,6-$\mathrm{Pr^i{}_2}\}_2$).[24] Other monovalent organothallium compounds are oligomeric, as illustrated by dinuclear $[Ar'Tl]_2$ ($Ar' = C_6H_3$-2,6-$\{C_6H_3$-2,6-$Pr^i_2\}_2$),[25] trinuclear $[Ar''Tl]_3$ ($Ar'' = C_6H_3$-2,6-$\{C_6H_3$-2,6-$Me_2\}_2$)[25] and tetranuclear $\{Tl[C(SiMe_3)_3]\}_4$.[26]

The Tl–C bond length of $[Tism^{Pr^iBenz}]Tl$ is compared with those of other monovalent compounds in Table 2, from which it is evident that it is longer than that in either $[pz_3C]Li$[10] or $[Tpom^{Bu^t}]Tl$;[22] indeed, the only other mononuclear monovalent thallium compound listed in the CSD with a longer Tl–C bond is the aforementioned *N*-heterocyclic carbene complex, [(ITr)Tl][OTf].[23,27] The Tl–C bond length in $[Tism^{Pr^iBenz}]Tl$ is also considerably longer than the values in simple monovalent thallium alkyl and aryl compounds that are devoid of additional donor groups, and which are in the range 2.31 Å – 2.37 Å (Table 2).[28,29] On the basis of these observations, it is evident that the Tl–C interaction in $[Tism^{Pr^iBenz}]Tl$ is not representative of a normal covalent bond, and that the bonding within $[Tism^{Pr^iBenz}]Tl$ possesses a zwitterionic component.

Table 2. Tl–C bond lengths in monovalent thallium compounds.

	***d*(Tl–C)/Å**	**reference**
$[Tism^{Pr^iBenz}]Tl$	2.626(4)	this work
$[pz_3C]Tl$	2.541	10
$[Tpom^{Bu^t}]Tl$	2.490(7)	22
[(ITr)Tl][OTf]	2.679(7)	23
$[(ITr)Tl][BAr^F_4]$	2.559(3)	23
Ar'''Tl	2.34(1)	24
$[Ar'Tl]_2$	2.313(5)	25
$[Ar''Tl]_3$	2.331(4)	25
$\{Tl[C(SiMe_3)_3]\}_4$	2.37	26

To address this aspect of the bonding within $[Tism^{Pr^iBenz}]Tl$, the molecular structure was evaluated computationally by using density functional theory (DFT) and the geometry optimized structure, as illustrated in Figure 2, possesses Tl–C (2.677 Å) and Tl–N (2.755 Å) bond lengths that are in close agreement with the experimental structure. In accord with the proposed zwitterionic formulation, analysis of the molecular orbitals indicates that there is no significant overlap between atomic orbitals on thallium and carbon. Thus, HOMO–1 is an orbital that is localized on carbon and which has predominantly 2p character, as illustrated in Figure 3. While HOMO–1 is localized on carbon, the HOMO is localized on thallium (Figure 3) and corresponds to the aforementioned stereochemically active thallium lone pair, which is largely composed of the 6s orbital.[30]

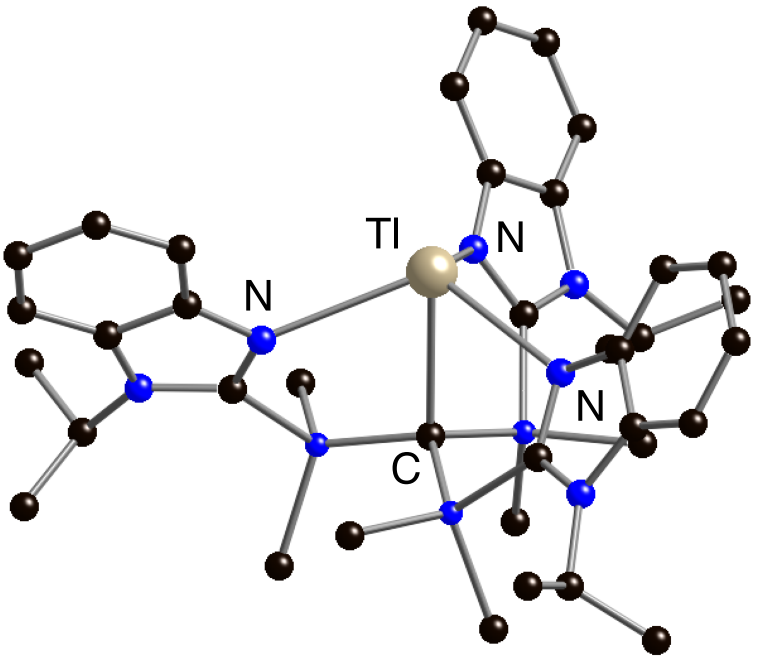


Figure 2. DFT geometry optimized structure of [Tism$^{\mathrm{Pr^iBenz}}$]Tl.

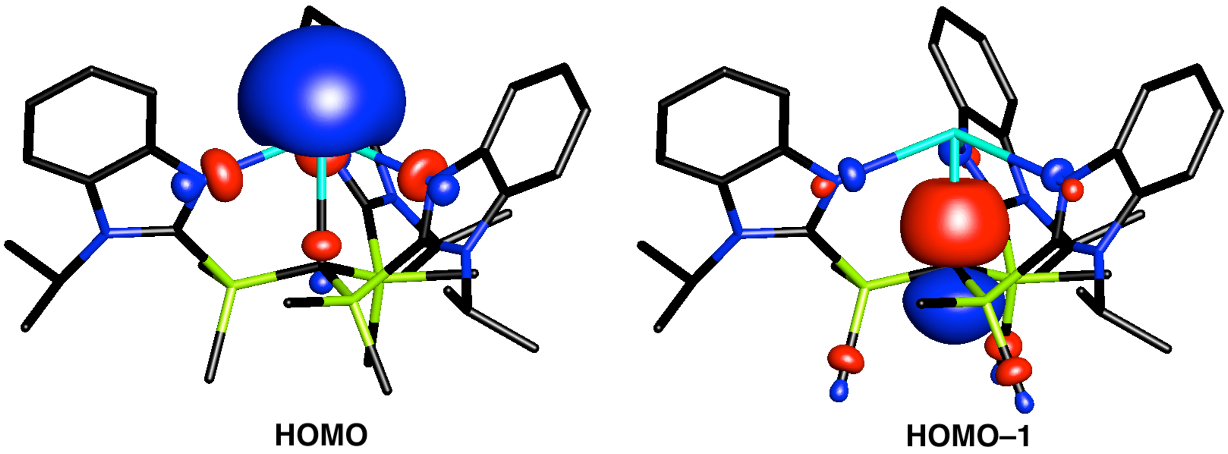
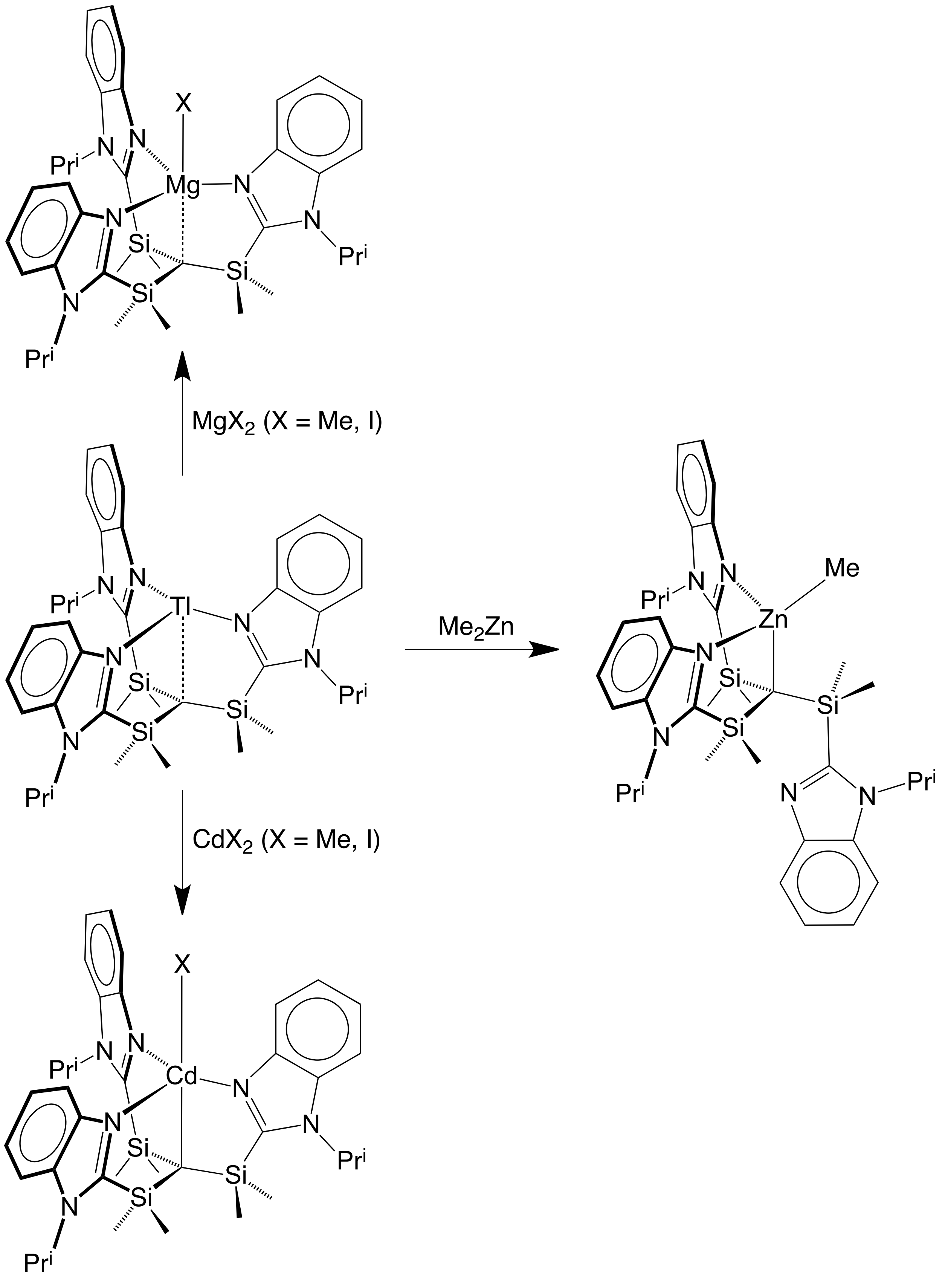


Figure 3. HOMO and HOMO–1 molecular orbitals of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Tl}$.

2. *Use of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Tl}$ as a $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]$ Transfer Reagent: Synthesis and Structural Characterization of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{CdMe}$*

The thallium compound $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Tl}$ may be employed as a reagent for the synthesis of other $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]$ derivatives. For example, $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Tl}$ reacts with $\mathrm{Me_2Zn}$ and $\mathrm{Me_2Mg}$ to afford $[\kappa^3\text{-}\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{ZnMe}$ and $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{MgMe}$, respectively (Scheme 2). The use of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Tl}$ as a transfer reagent with these alkyl metal reagents is associated with decomposition of incipient RTl that provides an effective driving force for the reactions.[31]



Scheme 2.

[Tism$^{\mathrm{Pr^iBenz}}$]Tl may also be used in an analogous manner to afford the cadmium counterpart [Tism$^{\mathrm{Pr^iBenz}}$]CdMe, a transformation that is of note because whereas the magnesium and zinc complexes, [Tism$^{\mathrm{Pr^iBenz}}$]MgMe and [κ^3-Tism$^{\mathrm{Pr^iBenz}}$]ZnMe, may be obtained by the reactions of [Tism$^{\mathrm{Pr^iBenz}}$]H with Me_2Mg and Me_2Zn, respectively, [Tism$^{\mathrm{Pr^iBenz}}$]H does not react readily with Me_2Cd to afford [Tism$^{\mathrm{Pr^iBenz}}$]CdMe.[32] For example, while [Tism$^{\mathrm{Pr^iBenz}}$]H reacts with Me_2Zn at 60°C to afford [κ^3-Tism$^{\mathrm{Pr^iBenz}}$]ZnMe over a period of one day,[5a] the corresponding reaction of Me_2Cd results in only *ca* 10% conversion to [Tism$^{\mathrm{Pr^iBenz}}$]CdMe. The lower reactivity of Me_2Cd relative to Me_2Zn towards [Tism$^{\mathrm{Pr^iBenz}}$]H is in accord with that observed for the reactions of R_2Cd and R_2Zn towards alcohols.[33]

The molecular structure of [Tism$^{\mathrm{Pr^iBenz}}$]CdMe has been determined by X-ray diffraction (Figure 4) and an important feature is that the [Tism$^{\mathrm{Pr^iBenz}}$] ligand coordinates in a κ^4-manner to afford an atrane motif, which is marked contrast to the zinc counterpart, [κ^3-Tism$^{\mathrm{Pr^iBenz}}$]ZnMe, in which the [Tism$^{\mathrm{Pr^iBenz}}$] ligand coordinates in a hypodentate manner.[5a] Interestingly, the magnesium methyl complex, [Tism$^{\mathrm{Pr^iBenz}}$]MgMe, does possess an atrane motif and so it is notable that the structure of [Tism$^{\mathrm{Pr^iBenz}}$]CdMe resembles more that of a Group 2 metal analogue than that of its Group 12 congener. Spectroscopically, the methyl group of [Tism$^{\mathrm{Pr^iBenz}}$]CdMe is characterized by a signal at δ 0.53 in the ^{1}H NMR spectrum that exhibits ^{111}Cd and ^{113}Cd satellites with $^2J_{^{111}Cd}$ and $^2J_{^{113}Cd}$ coupling constants of 64 Hz and 67 Hz, respectively.[34] These values are comparable to those for other cadmium methyl compounds. For example, [Tp$^{\mathrm{Bu^t,Me}}$]CdMe exhibits a signal at δ 0.56 with $^2J_{^{111}Cd}$ and $^2J_{^{113}Cd}$ coupling constants of 71 Hz and 74Hz, respectively,[35] while [Tm$^{\mathrm{Bu^t}}$]CdMe is characterized by a signal at δ 0.37 with $^2J_{^{111}Cd}$ and $^2J_{^{113}Cd}$ coupling constants of 67 Hz and 70 Hz).[32a,36]

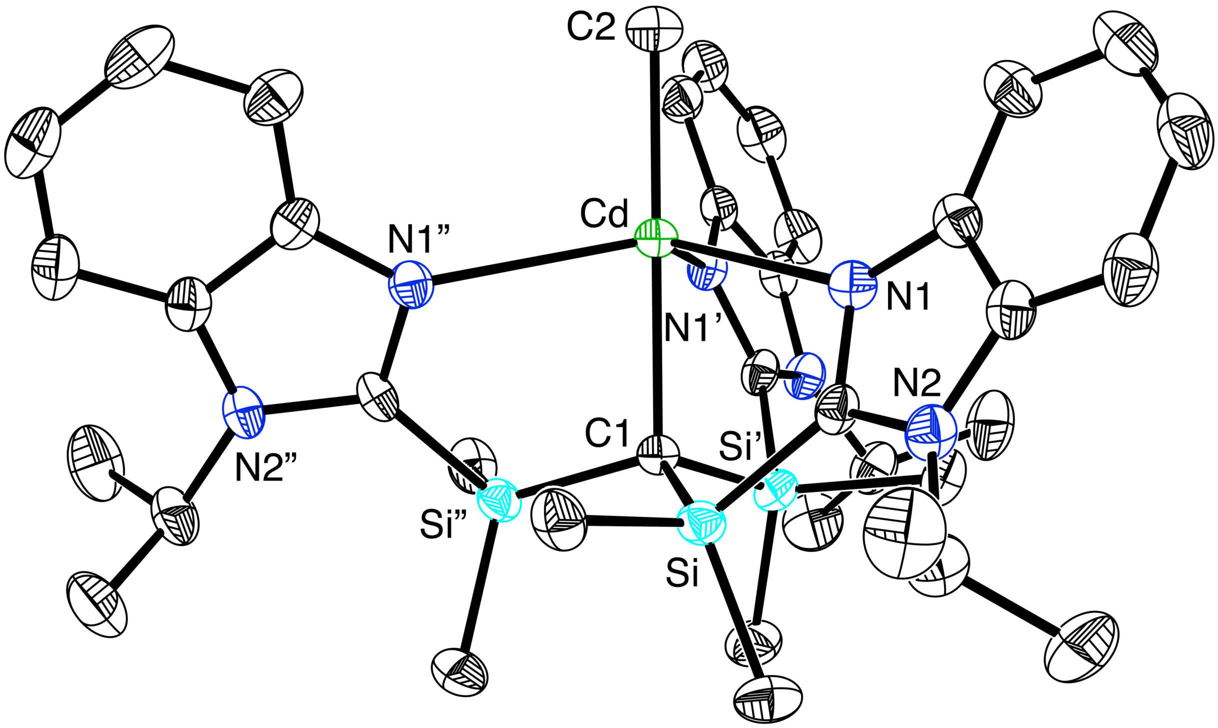
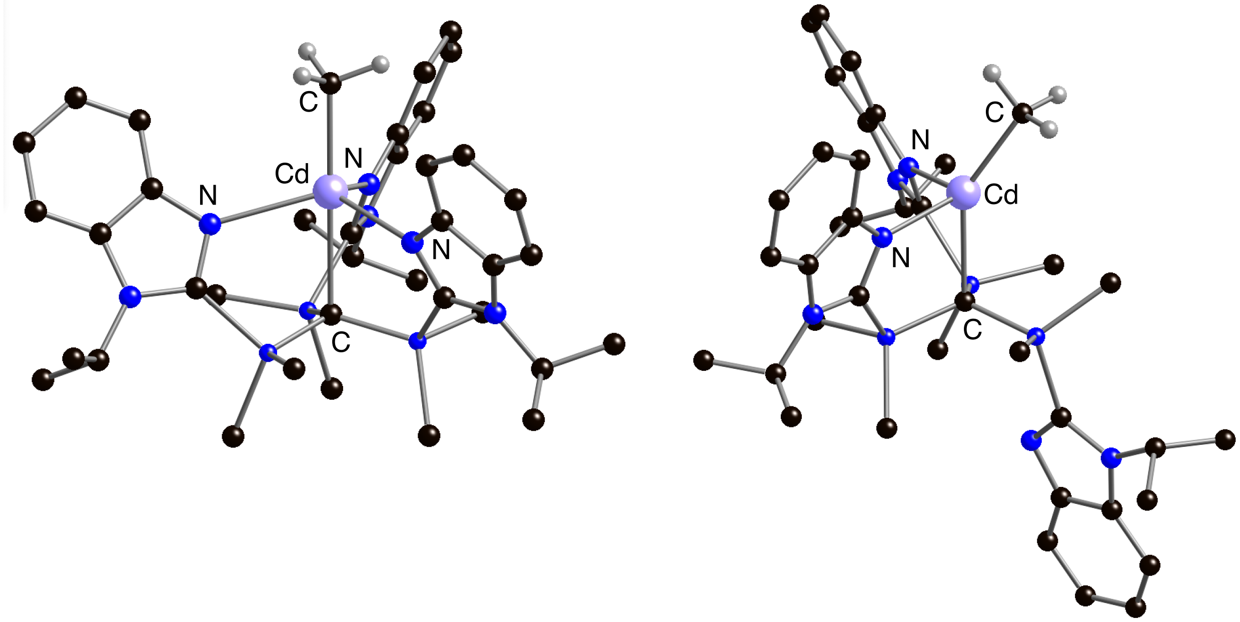


Figure 4. Molecular structure of [Tism$^{Pr^{i}Benz}$]CdMe.

In addition to the thallium reagent [Tism$^{Pr^{i}Benz}$]Tl undergoing metathesis with metal-carbon bonds, it also capable of reacting with other derivatives, as illustrated by the formation of the magnesium and cadmium iodide complexes, [Tism$^{Pr^{i}Benz}$]MgI[5b] [Tism$^{Pr^{i}Benz}$]CdI,[5g] upon treatment with MI_2 (Scheme 2).

With respect to the κ^3 *versus* κ^4 coordination modes of the [Tism$^{Pr^{i}Benz}$] ligand, it is pertinent to note that both motifs have been observed in cadmium chemistry. Specifically, the κ^3-coordination mode is observed for the cadmium hydride and bis(trimethylsily)amide derivatives, [κ^3-Tism$^{Pr^{i}Benz}$]CdH and [κ^3-Tism$^{Pr^{i}Benz}$]CdN($SiMe_3$)$_2$, while the κ^4-atrane motif is adopted by other [Tism$^{Pr^{i}Benz}$]CdX derivatives (X = Cl, Br, I, $OSiPh_3$, NCO, O_2CH, S_2CH), and also ionic {[Tism$^{Pr^{i}Benz}$]Cd}[HB(C_6F_5)$_3$].[5g] In accord with the experimental observation of an atrane motif, DFT geometry optimization of [Tism$^{Pr^{i}Benz}$]CdMe with the κ^4- and κ^3-coordination modes indicates that the structure with κ^4 atrane motif is more stable (Figure 5).



E_{rel} = 0.00 kcal mol^{-1} E_{rel} = 2.03 kcal mol^{-1}

Figure 5. DFT Geometry optimized structures of κ^4- and κ^3-[Tism$^{\mathrm{Pr^iBenz}}$]CdMe.

The coordination geometry of [Tism$^{\mathrm{Pr^iBenz}}$]CdMe corresponds closely to trigonal bipyramidal on the basis of both the τ_5 five-coordinate geometry index of 1.04[37] and the continuous shape measure (CShM) of 1.420 for a trigonal bipyramid.[38] It is, however, worth noting that the τ_5 value is slightly greater than unity, which indicates that the structure is not distorted towards a square pyramidal geometry, which is characterized by a τ_5 value of 0.00.[37] Rather, the distortion corresponds to an umbrella displacement of the three equatorial groups, in such a manner that the structure can be described as a face capped tetrahedron[39] in which the atrane carbon serves as the capping atom.

In addition to these geometrical features, an interesting aspect of the structure pertains to the Cd–C and Cd–N bond lengths. Specifically, the Cd–C_{atrane} bond of [Tism$^{\mathrm{Pr^iBenz}}$]CdMe [2.272(5) Å] is distinctly shorter than those of other [Tism$^{\mathrm{Pr^iBenz}}$]CdX derivatives [2.3556(19) – 2.451(3) Å], while the Cd–N bond length [2.672(2) Å] is considerably longer than the values in other derivatives (2.331 Å – 2.434 Å), as summarized in Table 3. Furthermore, the Cd–C_{atrane} bond of [Tism$^{Pr^iBenz}$]CdMe is also shorter than the value in cationic {[Tism$^{Pr^iBenz}$]Cd}$^+$. Indeed, the Cd–C_{atrane} bond length [2.272(5) Å] of [Tism$^{Pr^iBenz}$]CdMe is comparable to the Cd–CH_3 bond length [2.176(6) Å], which is similar to the Cd–CH_3 bond in other compounds. For example, the average Cd–CH_3 bond length for structurally characterized cadmium methyl compounds listed in the CSD is 2.152 Å, as illustrated by the values of 2.130(3) Å and 2.134(3) Å for Me_2Cd.[40,41] In view of the short Cd–C bond lengths [2.176(6) Å and 2.272(5) Å] and long Cd–N bond lengths [2.672(2) Å], the distorted five-coordinate trigonal bipyramidal structure of [Tism$^{Pr^iBenz}$]CdMe is better described in terms of a linear two-coordinate dialkyl cadmium species with secondary bonding *via* the three nitrogen donors. As such, there is a distinct difference with the structure of the magnesium counterpart, [Tism$^{Pr^iBenz}$]MgMe, in which the Mg–C_{atrane} bond [2.4925(12) Å] is significantly longer than both the Mg–CH_3 bond [2.1781(13) Å] and the Mg–N bonds [2.1890(11) Å – 2.2238(11) Å].

Table 3. Cd–C and Cd–N bond lengths in [Tism$^{Pr^iBenz}$]CdX derivatives.

	***d*(Cd–C)/Å**	***d*(Cd–N)$_{av}$/Å**
[Tism$^{Pr^iBenz}$]CdMe	2.272(5)	2.672
[Tism$^{Pr^iBenz}$]CdCl	2.4008(18)	2.351
[Tism$^{Pr^iBenz}$]CdBr	2.3556(19)	2.418
[Tism$^{Pr^iBenz}$]CdI	2.3804(17)	2.348
[Tism$^{Pr^iBenz}$]CdOSiPh$_3$^{a}	2.451(3), 2.418(3)	2.346, 2.346
[Tism$^{Pr^iBenz}$]CdNCO^a	2.405(3), 2.370(3)	2.331, 2.350
[Tism$^{Pr^iBenz}$]Cd(κ^1-O$_2$CH)	2.4087(16)	2.351
[Tism$^{Pr^iBenz}$]Cd(κ^1-S$_2$CH)	2.367(2)	2.434
{[Tism$^{Pr^iBenz}$]Cd}[HB(C$_6$F$_5$)$_3$]	2.308(3)	2.196
[κ^3-Tism$^{Pr^iBenz}$]CdH	2.353(5)	2.304
[κ^3-Tism$^{Pr^iBenz}$]CdN(SiMe$_3$)$_2$	2.3058(13)	2.347

(a) Values for two crystallographically independent molecules.

SUMMARY

In summary, atrane compounds derived from *tris*[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl ligand, [Tism$^{Pr^iBenz}$], have been extended to the sixth period of the Periodic Table with the synthesis of the thallium carbatrane, [Tism$^{Pr^iBenz}$]Tl. The structural characterization of [Tism$^{Pr^iBenz}$]Tl thereby demonstrates that that the [Tism$^{Pr^iBenz}$] ligand can coordinate with a similar motif to metals as diverse as lithium and thallium. In addition to the structural similarity between [Tism$^{Pr^iBenz}$]Li and [Tism$^{Pr^iBenz}$]Tl, the thallium complex may also serve as a reagent for the synthesis of other [Tism$^{Pr^iBenz}$]MX complexes, including the cadmium methyl compound, [Tism$^{Pr^iBenz}$]CdMe. Significantly, the atrane structure of [Tism$^{Pr^iBenz}$]CdMe is not only very different to that of the zinc counterpart which exhibits only κ^3-coordination, but is also different to other [Tism$^{Pr^iBenz}$]CdX compound because the Cd–C$_{atrane}$ bond of

[Tism$^{\mathrm{Pr^iBenz}}$]CdMe is distinctly shorter than those of other [Tism$^{\mathrm{Pr^iBenz}}$]CdX derivatives, while the Cd–N bond lengths are considerably longer. It is, therefore, evident that not only can the [Tism$^{\mathrm{Pr^iBenz}}$] ligand support different coordination modes, but there is also considerable flexibility with respect to M–C and M–N bond lengths.

EXPERIMENTAL SECTION

General considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under an argon atmosphere.[42] Solvents were purified and degassed by standard procedures. NMR spectra were recorded on Bruker AVIII 300, Bruker AVIII 400SL and Bruker AVIII 500 spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$), and were referenced with respect to the protio solvent impurity ($\delta = 7.16$ for C_6D_5H) or added Me_4Si.[43] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the solvent ($\delta = 128.06$ for C_6D_5H). Coupling constants are given in hertz. Infrared spectra were recorded on a Perkin Elmer Spectrum Two spectrometer in attenuated total reflectance (ATR) mode and are reported in reciprocal centimeters. [Tism$^{\mathrm{Pr^iBenz}}$]Li was obtained by the literature method.[44] Mass spectrometric measurements were performed on a Waters XEVO G2-XS QTOF MS with an electrospray ionization source in positive ion mode.

X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. The structures were solved by using SHELXS or SHELXT and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2014/7).[45] The unit cell of [Tism$^{\mathrm{Pr^iBenz}}$]Tl contains disordered benzene that was treated as diffuse contributions to the overall scattering without specific atom positions by use of

SQUEEZE/PLATON.[46,47] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC #2116280 – 2116281).

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 8.9 (release 15) suite of *ab initio* quantum chemistry programs.[48] Geometry optimizations were performed with the B3LYP density functional using the LACVP** basis sets (LAV3P: Tl & Cd; 6-31G**: H, C, N & Si) and Cartesian coordinates are provided in the Supporting Information. Molecular orbital analyses were performed with the aid of JIMP2,[49] which employs Fenske-Hall calculations and visualization using MOPLOT.[50]

Synthesis of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Tl}$

A mixture of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Li}$ (50 mg, 0.075 mmol) and TlOAc (62 mg, 0.235 mmol) in benzene (*ca* 2 mL) in an ampoule was stirred at 60°C for 20 hours. After this period, the mixture was filtered and the filtrate was lyophilized to give $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Tl}$ (40 mg, 60 % yield). Colorless crystals suitable for X-ray diffraction were obtained *via* vapor diffusion of pentane into a concentrated benzene solution. ^{1}H NMR (C_6D_6): 0.74 [s, 18H, $(C_6H_4N_2CH(CH_3)_2CSi(C\underline{H}_3)_2)_3CTl$], 1.20 [d, J = 7 Hz, 18H, $(C_6H_4N_2CH(C\underline{H}_3)_2CSi(CH_3)_2)_3CTl$], 4.81 [sep, J = 7 Hz, 3H, $(C_6H_4N_2C\underline{H}(CH_3)_2CSi(CH_3)_2)_3CTl$], 7.08 [m, 6H, $(C_6\underline{H}_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CTl$], 7.29 [m, J = 7 Hz, 3H, $(C_6\underline{H}_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CTl$], 7.85 [m, 3H, $(C_6\underline{H}_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CTl$]. $^{13}C\{^{1}H\}$ NMR (C_6D_6): 7.13 [s, 6C, $(C_6H_4N_2CH(CH_3)_2CSi(\underline{C}H_3)_2)_3CTl$], 21.09 [s, 6C, $(C_6H_4N_2CH(\underline{C}H_3)_2CSi(CH_3)_2)_3CCdTl$], 49.21 [s, 3C, $(C_6H_4N_2\underline{C}H(CH_3)_2CSi(CH_3)_2)_3CTl$], 112.58 [s, 3C, $(\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CTl$], 120.55 [s, 3C, $(\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CTl$], 121.72 [s, 3C, $(\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CTl$], 122.21 [s, 3C, $(\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CTl$], 134.33 [s, 3C, $(\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CTl$], 145.74 [b, 3C, ($\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CTl$], 167.91 [br, 3C, ($C_6H_4N_2CH(CH_3)_2\underline{C}Si(CH_3)_2)_3CTl$], not observed [($C_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3\underline{C}Tl$]. IR Data (ATR, cm^{-1}): 3849 (vw), 3644 (vw), 3051 (vw), 2973 (w), 2898 (w), 1485 (w), 1460 (w), 1391 (w), 1370 (w), 1337 (m), 1254 (m), 1229 (w), 1205 (w), 1158 (w), 1132 (w), 1103 (w), 1059 (m), 1010 (w), 900 (m), 841 (m), 821 (s), 793 (m), 739 (s), 689 (w), 672 (w), 588 (w), 548 (w), 536 (w), 501 (w), 430 (w).

Synthesis of [Tism$^{Pr^iBenz}$]CdMe

A solution of [Tism$^{Pr^iBenz}$]Tl (26 mg, 0.030 mmol) in benzene (*ca.* 2 mL) was treated with a solution of Me_2Cd in benzene (0.77 mmol), thereby resulting in the deposition of a grey powder. The mixture was filtered and the solution was lyophilized to afford [Tism$^{Pr^iBenz}$]CdMe (18 mg, 76 % yield). Colorless crystals of [Tism$^{Pr^iBenz}$]CdMe suitable for X-ray diffraction were obtained *via* vapor diffusion of pentane into a concentrated benzene solution. ^{1}H NMR (C_6D_6): 0.53 [s, 3H, ($C_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CCdC\underline{H}_3$], 0.69 [s, 18H, ($C_6H_4N_2CH(CH_3)_2CSi(C\underline{H}_3)_2)_3CCdCH_3$], 1.15 [d, J = 7 Hz, 18H, ($C_6H_4N_2CH(C\underline{H}_3)_2CSi(CH_3)_2)_3CCdCH_3$], 4.72 [sep, J = 7 Hz, 3H, ($C_6H_4N_2C\underline{H}(CH_3)_2CSi(CH_3)_2)_3CCdCH_3$], 7.09 [m, 6H, ($C_6\underline{H}_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CCH_3$], 7.24 [m, 3H, ($C_6\underline{H}_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CCdCH_3$], 8.14 [m, 3H, ($C_6\underline{H}_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CCdCH_3$]. Mass spectrum: m/z = 777.2642 (M–Me). IR Data (ATR, cm^{-1}): 2973 (w), 2947 (w), 2898 (w), 1483 (w), 1461 (w), 1390 (w), 1370 (w), 1344 (w), 1283 (w), 1254 (w), 1203 (vw), 1160 (w), 1133 (w), 1105 (w), 1062 (w), 1012 (w), 891 (s), 846 (m), 826 (m), 814 (m), 793 (m), 765 (w), 740 (s), 693 (w), 647 (w), 554 (w), 528 (w), 500 (w), 460 (w), 431 (w).

Reaction of [Tism$^{Pr^iBenz}$]Tl with Me_2Mg: Formation of [Tism$^{Pr^iBenz}$]MgMe

A solution of [Tism$^{\mathrm{Pr^iBenz}}$]Tl (5 mg, 0.006 mmol) in C_6D_6 (*ca* 0.7 mL) was treated with excess Me_2Mg (2 mg, 0.037 mmol) and stirred for 30 minutes. After this period, the reaction was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the quantitative formation of [Tism$^{\mathrm{Pr^iBenz}}$]MgMe.

Reaction of [Tism$^{\mathrm{Pr^iBenz}}$]Tl with Me_2Zn: Formation of [κ^3-Tism$^{\mathrm{Pr^iBenz}}$]ZnMe

A solution of [Tism$^{\mathrm{Pr^iBenz}}$]Tl (5 mg, 0.006 mmol) in C_6D_6 (*ca* 0.7 mL) was treated with excess Me_2Zn (0.16 mmol). The reaction was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of [Tism$^{\mathrm{Pr^iBenz}}$]ZnMe (53 %) after a period of 18 hours at room temperature.

Reaction of [Tism$^{\mathrm{Pr^iBenz}}$]Tl with CdI_2: Formation of [Tism$^{\mathrm{Pr^iBenz}}$]CdI

A solution of [Tism$^{\mathrm{Pr^iBenz}}$]Tl (8 mg, 0.009 mmol) in C_6D_6 (*ca* 0.7 mL) was treated with CdI_2 (5 mg, 0.013 mmol). The reaction was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the rapid quantitative formation of [Tism$^{\mathrm{Pr^iBenz}}$]CdI at room temperature.

Reaction of [Tism$^{\mathrm{Pr^iBenz}}$]Tl with MgI_2: Formation of [Tism$^{\mathrm{Pr^iBenz}}$]MgI

A solution of [Tism$^{\mathrm{Pr^iBenz}}$]Tl (2 mg, 0.002 mmol) in C_6D_6 (*ca* 0.7 mL) was treated with MgI_2 (3 mg, 0.011 mmol). The reaction was monitored by ^{1}H NMR spectroscopy, thereby demonstrating conversion to [Tism$^{\mathrm{Pr^iBenz}}$]MgI (64 %) over a period of 24 hours at room temperature.

APPENDIX A. Supplementary Data

Tables of computational data for the geometry optimized structures, NMR spectra, and crystallographic data in CIF format (CCDC #2116280 – 2116281). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK;

fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.xxxxxx.

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