Tris[(1-isopropylbenzimidazol-2-yl)dimethyl[silyl]methyl metal complexes, [Tism\textsubscript{Pr}Benz]M: a new class of metallacarbatranes, isomerization to a tris(N-heterocyclic carbene) derivative, and evidence for an inverted ligand field†

Serge Ruccolo, Michael Rauch and Gerard Parkin

The tris[(1-isopropylbenzimidazol-2-yl)dimethylsilylmethyl]ligand, [Tism\textsubscript{Pr}Benz], has been employed to form carbatrane compounds of both the main group metals and transition metals, namely [Tism\textsubscript{Pr}Benz]Li, [Tism\textsubscript{Pr}Benz]MgMe, [Tism\textsubscript{Pr}Benz]Cu and [Tism\textsubscript{Pr}Benz]NiBr. In addition to the formation of atranes, a zinc compound that exhibits $\kappa^3$-coordination, namely $\kappa^3$-[Tism\textsubscript{Pr}Benz]ZnMe, has also been obtained. Furthermore, the [Tism\textsubscript{Pr}Benz] ligand may undergo a thermally induced rearrangement to afford a novel tripodial tris(N-heterocyclic carbene) variant, as shown by the conversion of [Tism\textsubscript{Pr}Benz]Cu to $\kappa^3$-[4,4-C\textsubscript{4}Tism\textsubscript{Pr}Benz]-Cu. The transannular M–C bond lengths in the atrane compounds are 0.19–0.32 Å longer than the sum of the respective covalent radii, which is consistent with a bonding description that features a formally zwitterionic component. Interestingly, computational studies demonstrate that the Cu–C\textsubscript{atrace} interactions in [Tism\textsubscript{Pr}Benz]Cu and [4,4-C\textsubscript{4}Tism\textsubscript{Pr}Benz]-Cu are characterized by an ’inverted ligand field’, in which the occupied antibonding orbitals are localized more on carbon than on copper.

Introduction

Atranes comprise an interesting class of molecules in which two bridgehead atoms are joined by three three-atom linkers, thereby resulting in a tricyclic motif.\textsuperscript{1–3} A relatively recent development in this area is concerned with the synthesis of metallacarbatranes that feature transannular M–C interactions.\textsuperscript{4} Such compounds are of interest because the M–C bond corresponds to an M–X interaction, in contrast to the transannular M—L\textsuperscript{4,5} or M—Z\textsuperscript{6,7} dative bonds that are more commonly encountered in atranes (Fig. 1).\textsuperscript{7,8} For example, we have recently employed tris(2-pyridylthio)methyl ([Tptm])\textsuperscript{14,15} and tris(1-methylimidazol-2-ylthio)methyl ([TitmMe])\textsuperscript{16} as ligands for the construction of metallacarbatranes,\textsuperscript{11} and have demonstrated that the nature of the heterocyclic nitrogen donor has an impact on the structure of the carbatrane.\textsuperscript{16} Since a common feature of these ligands is the attachment of the heterocycles to the carbon bridgehead via a sulfur atom, we considered it worthwhile to investigate a different type of linker. Therefore, we report here a new class of tetradeutate tripodial ligands in which three imidazole donors are attached to a carbon bridgehead via C–Si linkages. In addition, we also describe isomerization of the tris(imidazole) ligand to afford a novel tripodial tris(N-heterocyclic carbene) derivative.

Results and discussion

We considered the [Me\textsubscript{2}Si] moiety to be an appealing linker for the construction of analogues of the above tetradeutate tripodal ligands because (i) C–Si bonds are typically robust,\textsuperscript{12} (ii) methyl substituents on silicon can provide a protective environment for the bridgehead carbon, and (iii) silyl groups lower the pK\textsubscript{a} of adjacent C–H groups,\textsuperscript{13} thereby facilitating protolytic cleavage. Furthermore, tripodal molecules of the type HC(SiMe\textsubscript{2}X)\textsubscript{3} are known, e.g. X = NR\textsubscript{3},\textsuperscript{14} PR\textsubscript{2},\textsuperscript{15} CH\textsubscript{2}PR\textsubscript{2},\textsuperscript{16} S,\textsuperscript{17} Se,\textsuperscript{17} and...
OC$_2$H$_4$OMe$^{18}$ and thus provide a precedent for the synthesis of variants that include heterocyclic nitrogen donors.

Indeed, tris[1-isopropylbenzimidazol-2-yl]dimethylsilylmethane, [Tism$^{\text{PrBenz}}$]H, and the lithium derivative, [Tism$^{\text{PrBenz}}$]Li, may be obtained from 1-isopropylbenzimidazole and HCSiMe$_2$Cl$_3$ via the sequence illustrated in Scheme 1.$^{19}$

Specifically, treatment of 1-isopropylbenzimidazole with MeLi, followed by addition of HCSiMe$_2$Cl$_3$, affords [Tism$^{\text{PrBenz}}$]Li, which is converted to [Tism$^{\text{PrBenz}}$]H upon reaction with H$_2$O.$^{28}$ [Tism$^{\text{PrBenz}}$]Li may also be regenerated by treatment of [Tism$^{\text{PrBenz}}$]H with Bu$_3$Li.

The molecular structure of [Tism$^{\text{PrBenz}}$]Li has been determined by X-ray diffraction (Fig. 2), thereby revealing that the compound possesses an atrane motif$^{23}$ in which the lithium adopts an approximately trigonal monopyramidal$^{22}$ coordination environment with N–Li–N and C–Li–N bond angles of 118.61(9)$^{21}$ and 96.8(2)$^{23,24}$ Trigonal monopyramidal coordination is not common for lithium, but a similar coordination environment is observed for tris(2-pyridylthio)methyl lithium, [Tptm]Li.$^{5,25}$ An interesting difference between [Tism$^{\text{PrBenz}}$]Li and [Tptm]Li, however, pertains to the geometry at the bridgehead carbon atom. Specifically, the [CSi$_3$] moiety of [Tism$^{\text{PrBenz}}$]Li adopts a much greater degree of planarity (Table 1) than does the [CSi$_3$] moiety of [Tptm]Li, as indicated by the fact that the sum of the Si–C–Si angles of [Tism$^{\text{PrBenz}}$]Li (345.8)$^{26}$ is much closer to 360° than is the sum of the S–C–S angles of [Tptm]Li (345.2)$^2$. Furthermore, the Li–C–Si angles of [Tism$^{\text{PrBenz}}$]Li [96.87(13)$^{21}$] are closer to 90° than are the Li–C–S angles of [Tptm]Li [103.05(7)$^{21}$].$^{27,28}$ Since silyl-substituted carbanions are close to planar$^{29}$ as illustrated by [Li(tmen)$_2$][C(SiMe$_2$-PPh$_3$)$_3$],$^{30,31,32}$ the planarity of the [CSi$_3$] moiety of [Tism$^{\text{PrBenz}}$]Li suggests that the molecule possesses a significant degree of formally zwitterionic character in which carbon bears a negative charge.$^{4,33-35}$ In support of this suggestion, while the Li–N bond lengths [2.017(2) Å] are comparable to the sum of the covalent radii (1.99 Å)$^{36}$ the Li–C bond length [2.273(9) Å] is distinctly longer (by 0.23 Å) than the sum of covalent radii (2.04 Å)$^{36,37}$ Moreover, the HOMO of [Tism$^{\text{PrBenz}}$]Li is largely composed of a p-orbital on carbon, similar to that of the planar [Tism$^{\text{PrBenz}}$]– anion with a comparable conformation (Fig. 3).

[Tism$^{\text{PrBenz}}$]H and [Tism$^{\text{PrBenz}}$]Li may be employed to form carbatrane compounds of the main group and transition metals. For example, [Tism$^{\text{PrBenz}}$]H reacts with Me$_2$Mg via elimination of methane to afford [Tism$^{\text{PrBenz}}$]MgMe (Scheme 2).

The molecular structure of [Tism$^{\text{PrBenz}}$]Cu has been determined by X-ray diffraction (Fig. 4), thereby demonstrating that the [Tism$^{\text{PrBenz}}$] ligand coordinates in a k$^4$-manner such that the molecule possesses a carbatrane motif,$^{24}$ but with a Mg–C$_{\text{caratane}}$ distance [2.4925(12) Å] that is significantly longer (by 0.32 Å) than both (i) the Mg–CH$_3$ bond length [2.1781(13) Å] and (ii) the sum of covalent radii (2.17 Å)$^{38,39,39}$ The long Mg–C$_{\text{caratane}}$ distance is, nevertheless, consistent with a zwitterionic description in which the carbon atom bears a formal negative charge. This qualitative view of the bonding is supported by computational studies which demonstrate that the HOMO-1 is

### Table 1 Metrical data for [Tism$^{\text{PrBenz}}$]M derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>d(M–C)/Å</th>
<th>d(M–C) – $\sum$(cov. radii)$^a$</th>
<th>$\sum$(Si–C–Si)$^a$</th>
<th>d(C–[Si$_3$])$^b$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Tism$^{\text{PrBenz}}$]Li</td>
<td>2.273(9)</td>
<td>0.23</td>
<td>355.8</td>
<td>0.22</td>
</tr>
<tr>
<td>[Tism$^{\text{PrBenz}}$]MgMe</td>
<td>2.4925(12)</td>
<td>0.32</td>
<td>347.8</td>
<td>0.37</td>
</tr>
<tr>
<td>[k$^4$Tism$^{\text{PrBenz}}$]ZnMe</td>
<td>2.171(3)</td>
<td>0.19</td>
<td>346.3</td>
<td>0.40</td>
</tr>
<tr>
<td>[Tism$^{\text{PrBenz}}$]Cu</td>
<td>2.281(7)</td>
<td>0.20</td>
<td>355.2</td>
<td>0.23</td>
</tr>
<tr>
<td>[k$^4$C$_4$Tism$^{\text{PrBenz}}$]Cu</td>
<td>2.4283(18)</td>
<td>0.35</td>
<td>357.8</td>
<td>0.15</td>
</tr>
<tr>
<td>[Tism$^{\text{PrBenz}}$]NiBr</td>
<td>2.2197(16)</td>
<td>0.22</td>
<td>347.7</td>
<td>0.38</td>
</tr>
<tr>
<td>[Tism$^{\text{PrBenz}}$]H</td>
<td>—</td>
<td>—</td>
<td>342.3</td>
<td>0.47</td>
</tr>
</tbody>
</table>

$^a$ Ref. 36. $^b$ Distance of bridgehead carbon from the [Si$_3$] plane.
effectively a lone pair orbital on carbon, with very little contribution from magnesium (Fig. 5). As such, the HOMO-1 of [TismPrBenz]MgMe is similar in nature to the HOMO of [TismPrBenz]Li. Despite the comparable atrane motifs of [TismPrBenz]MgMe and [TismPrBenz]Li, however, a notable difference is that the [CSi3] moiety of [TismPrBenz]MgMe is more pyramidal than that of [TismPrBenz]Li, as indicated by the fact that the sum of the Si–C–Si angles of [TismPrBenz]MgMe (347.8°) is smaller than that for [TismPrBenz]Li (355.8°).

[TismPrBenz]H can also be used as a reagent in zinc chemistry. Thus, [TismPrBenz]H reacts with Me2Zn to afford [κ4-TismPrBenz]-ZnMe (Scheme 2). Although the reaction is analogous to that between [TismPrBenz]H and Me2Mg, X-ray diffraction demonstrates that the zinc product, [κ4-TismPrBenz]ZnMe, has a notably different structure to that of the magnesium counterpart. Specifically, rather than coordinating to zinc in a κ4-manner to afford a carbatrane motif, the ligand binds to zinc in a hypodentateκ3-manner, such that one of the imidazolyl groups remains uncoordinated (Fig. 6). Also in contrast to the magnesium derivative, [TismPrBenz]MgMe, for which the Mg–CH3 and Mg–Cartrane bond lengths are very different, the corresponding bonds for [κ4-TismPrBenz]ZnMe are more similar: d(Zn–CH3) = 1.989(3) Å and d(Zn–Cartrane) = 2.171(3)Å, and the former is comparable to the sum of covalent radii (1.98 Å).

Density functional theory (DFT) calculations on the isomeric forms of [TismPrBenz]MgMe and [TismPrBenz]ZnMe support the experimental observations. Specifically, the DFT calculations demonstrate that the κ4-isomer is 1.94 kcal mol⁻¹ more stable than the κ3-isomer for [TismPrBenz]MgMe, whereas the
The lithium compound, $[\text{Tism}^{\text{PriBenz}}]\text{Li}$, has also been used to synthesize metal complexes via metathesis reactions involving metal halides. For example, $[\text{Tism}^{\text{PriBenz}}]\text{Li}$ reacts with $[(\text{Me}_3\text{P})\text{CuCl}]_4$ to give $[\text{Tism}^{\text{PriBenz}}]\text{Cu}$ (Scheme 3), which has been shown by X-ray diffraction (Fig. 8) to possess a trigonal monopyramidal structure similar to that of $[\text{Tism}^{\text{PriBenz}}]\text{Li}$, with Cu–C and Cu–N distances of 2.281(7) Å and 2.014(3) Å, respectively.\textsuperscript{47,48} As with the lithium and magnesium carbatranes, the Cu–Atrance bond of $[\text{Tism}^{\text{PriBenz}}]\text{Cu}$ is also longer (by 0.20 Å) than the sum of covalent radii (2.08 Å).\textsuperscript{36,49,50}

A distinct difference between $[\text{Tism}^{\text{PriBenz}}]\text{Cu}$ and the lithium and magnesium complexes, $[\text{Tism}^{\text{PriBenz}}]\text{Li}$ and $[\text{Tism}^{\text{PriBenz}}]\text{MgMe}$, however, is the degree of covalent interaction between copper and the atrance carbon atom. Specifically, overlap between the carbon 2p\textsubscript{z} orbital and the copper 3d\textsubscript{z2} orbital gives rise to Cu–C bonding and antibonding combinations, the latter of which is the HOMO (Fig. 9), as illustrated in the qualitative molecular orbital diagram shown in Fig. 10. Interestingly, the bonding combination possesses a significant copper component, while the antibonding combination possesses a significant carbon component; indeed, a natural bond orbital analysis of $[\text{Tism}^{\text{PriBenz}}]\text{Cu}$ classifies the HOMO as a carbon lone pair orbital. This arrangement is counter to that observed for most transition metal compounds with \(s\)-donor ligands, for which the bonding combination usually possesses more ligand character because the ligand orbitals are typically lower in energy than the metal orbitals.\textsuperscript{51,52}

Fig. 7 Relative energies of geometry optimized structures of \(\kappa^3\)- and \(\kappa^4\)-\([\text{Tism}^{\text{PriBenz}}]\text{MMe}\) (\(\text{M} = \text{Mg, Zn}\)). Hydrogen atoms on \([\text{Tism}^{\text{PriBenz}}]\) are omitted for clarity.

Fig. 8 Molecular structure of $[\text{Tism}^{\text{PriBenz}}]\text{Cu}$.

Fig. 9 Frontier orbitals of $[\text{Tism}^{\text{PriBenz}}]\text{Cu}$. Note that the in-phase interaction between the carbon 2p\textsubscript{z} orbital and the copper 3d\textsubscript{z2} orbital is a component of two molecular orbitals with similar energies (HOMO-6, --0.2169 eV; HOMO-9, --0.2192 eV).
Although several tripod tris(N-heterocyclic carbene) ligands have been reported, the formation of [\( \kappa^4\)-C\(_4\)-Tism\( ^{PrBenz}\)]Cu is notable because [\( \kappa^4\)-C\(_4\)-Tism\( ^{PrBenz}\)] is an example of such a ligand that also features an additional potential X-type binding site.\(^{36}\) The isomerization of [Tism\( ^{PrBenz}\)]Cu to [\( \kappa^4\)-C\(_4\)-Tism\( ^{PrBenz}\)]Cu is, however, accompanied by an increase in the axial Cu–C\(_{\text{ax}}\) distance from 2.281(7) Å to 2.4283(18) Å, a value that is 0.35 Å longer than the sum of the covalent radii.\(^{36,61}\) Despite this lengthening, the copper 3d\(_x^2\) and carbon 2p\(_x\) orbitals interact, and the derived bonding and antibonding orbitals are illustrated in Fig. 12. As observed for [Tism\( ^{PrBenz}\)]Cu, the antibonding orbital possesses mainly carbon character such that the bonding situation also corresponds to an “inverted ligand field”.

DFT calculations indicate that [\( \kappa^4\)-C\(_4\)-Tism\( ^{PrBenz}\)]Cu is more stable than [Tism\( ^{PrBenz}\)]Cu by 4.18 kcal mol\(^{-1}\), which is in accord with the experimental observations. In contrast, isomerization of the structurally analogous lithium derivative, [Tism\( ^{PrBenz}\)]Li, to [\( \kappa^4\)-C\(_4\)-Tism\( ^{PrBenz}\)]Li is predicted to be thermodynamically unfavorable by 35.3 kcal mol\(^{-1}\).\(^{62}\) The different thermodynamic trends reflect, \textit{inter alia}, (i) the intrinsic stability of [Tism\( ^{PrBenz}\)] versus [Tism\( ^{PrBenz}\)] and (ii) the relative preferences of copper and lithium to coordinate to a N-heterocyclic carbene versus an imidazolate donor.\(^{63}\) With respect to the former, the tris(N-heterocyclic carbene), [Tism\( ^{PrBenz}\)]H, is calculated to be 41.1 kcal mol\(^{-1}\) higher in energy than the tris-imidazolate, [Tism\( ^{PrBenz}\)]H, with the 3 : 0 conformation\(^{64}\) that is used for \( \kappa^4\)-coordination.\(^{36,65}\) As such, it is evident that coordination of the copper to the carbon donors provides a driving force for the isomerization.\(^{67}\) While the tautomerization of imidazolates to C-coordinated ligand at a metal center has been previously observed,\(^{68-70}\) we are unaware of the corresponding transformations involving migration of a silyl group rather than a hydrogen atom.\(^{71}\) Furthermore, the formation of [\( \kappa^4\)-C\(_4\)-Tism\( ^{PrBenz}\)]Cu is also noteworthy because C-coordination has been predicted to be less favorable than N-coordination of imidazolate to CuCl.\(^{66,69}\)

The nickel compound, [Tism\( ^{PrBenz}\)]NiBr, may be obtained via metathesis of [Tism\( ^{PrBenz}\)]Li with (Ph\(_3\))\(_2\)NiBr\(_2\) (Scheme 3).
Conclusions

In summary, [Tism\textsuperscript{Pr}Benz] is a flexible ligand that can coordinate to a metal center in both $\kappa^3$ and $\kappa^4$-manners, with the latter affording a carbatrane motif. Furthermore, when coordinating in a $\kappa^4$-manner, the [Tism\textsuperscript{Pr}Benz] ligand can adopt either a trigonal monopyramidal geometry or a seesaw geometry. Interestingly, we have also demonstrated that the [Tism\textsuperscript{Pr}Benz] ligand may undergo a thermally induced rearrangement to afford a novel tripodal tris(N-heterocyclic carbene) ligand, as demonstrated by the conversion of [Tism\textsuperscript{Pr}Benz]Cu to [k$^4$C$_1$Tism\textsuperscript{Pr}Benz]Cu. A notable feature of the atrane compounds is that the transannular M–C bond lengths are 0.19–0.32 Å longer than the sum of the respective covalent radii, which is consistent with a zwitterionic component for the description of the molecules. Finally, a particularly noteworthy feature of both [Tism\textsuperscript{Pr}Benz]Cu and [k$^4$C$_1$Tism\textsuperscript{Pr}Benz]Cu is that Cu–C$_\text{atrane}$ interaction is characterized by an “inverted ligand field”, in which the occupied antibonding orbital is more localized on carbon than on copper.

Acknowledgements

We thank the National Science Foundation (CHE-1058987 and CHE-1465095) for support of this research. M. R. acknowledges the National Science Foundation for a Graduate Research Fellowship under Grant No. DGE-16-44869.

Notes and references

3 Although the term “atran” was originally introduced to describe compounds in which the transannular interaction involved a nitrogen atom, the classification has been expanded to include other atoms. See, for example: N. Chakrabarti, W. Sattler and G. Parkin, Polyhedron, 2013, 58, 235–246 and references therein.
For example, the C–Si bond in CH3SiH3 (89.6 kcal mol−1) is stronger than the C–S bond in CH3SH (75.0 kcal mol−1). See: Y.-R. Luo, in Comprehensive Handbook of Chemical Bond Energies, CRC Press, 2007, ch. 8 and 9.

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14 See, for example, ref. 8a.


19 Unless otherwise specified, the abbreviation [Tism]4− refers to coordination to a metal via a nominal κ^4-N,C manner.


21 To the extent that M–Catrane distances are larger than the sum of the covalent radii, the compounds may be better described as quasi-atranes (see ref. 1).

23 Correspondingly, the four-coordinate \( t_4 \) (0.87) and \( t_4 \) (0.87) geometry indices are close to the idealized value for a trigonal monopyramid (0.85). \( t_4 = \frac{\sqrt{360 - (\alpha + \beta)}}{141} \), where \( \alpha \) and \( \beta \) are the two largest angles, and \( t_4 = \frac{\alpha}{\beta} \). See: (a) L. Yang, D. R. Powell and R. P. Houser, *Dalton Trans.*, 2007, 955–964; (b) M. H. Reineke, M. D. Sampson, A. L. Rheingold and C. P. Kubiak, *Inorg. Chem.*, 2015, 54, 3211–3217.

24 Note that the lithium is displaced by 0.24 Å from the trigonal plane of the three nitrogen atoms towards the carbon.

25 [Tptm]Li is characterized respectively by (i) N–Li–N and C–Li–N bond angles of 119.86(2)° and 92.21(1)° and (ii) Li–C and Li–N bond lengths of 2.210(5) Å and 2.002(1) Å.

26 For reference, the average value of the sum of the Si–C–Si angles in molecules with the C(SiMe3)4 moiety listed in the Cambridge Structural Database is 333.9°. Searches of the Cambridge Structural Database were performed with version 5.37. See: C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr.*, 2016, B72, 171–179.

27 It is also worth noting that [C(SiMe3)4] moiety of the related phosphine derivative, \([k^1-C(SiMe_3)_4PPh_2]_2\)Li, with Li–C–Si angles in the range 103.4°–104.9°, and \(\sum\text{Si–C–Si} = 343.2°\), is much less planar than that of [Tism\(^{Pr\text{Benz}}\)ZnMe]. See ref. 16.

28 In contrast to [Tism\(^{Pr\text{Benz}}\)ZnMe], the protonated derivative, \([k^1-C(SiMe_3)_4PPh_2]_2\)H, possesses H–C–Si [102.2(15)°, 102.6(15)°, and 108.0(15)°] angles and Si–C–Si [112.32(9)°, 114.34(9)°, and 115.60(9)°] angles which are in accord with a pyramidal geometry for the [C(SiMe3)4] moiety.

29 α-Silyl groups are also known to stabilize carbanions via negative hyperconjugation involving delocalization of electron density from the carbon p-orbital into low energy σ*–C bonds. See, for example, ref. 13b–f.


32 For examples of formally zwitterionic compounds with a planar \([C(SiMe_X_3)]_2\) moiety, see ref. 18b and: (a) C. Eaborn, A. Farook, P. B. Hitchcock and J. D. Smith, *Organometalics*, 1998, 17, 3133–3137; (b) F. Adam, C. Eaborn, P. B. Hitchcock and J. D. Smith, *Chem. Commun.*, 1996, 741–742; (c) C. Eaborn, A. Farook, P. B. Hitchcock and J. D. Smith, *Organometalics*, 1997, 16, 503–504.


34 For other carbatranes with formally zwitterionic character, see ref. 10.


39 In contrast, the Mg–CH\(_3\) [2.1781(13) Å] and Mg–N [2.1890(11) Å, 2.2156(11) Å, 2.2238(11) Å] bonds correspond closely to the respective sums of covalent radii (2.17 Å and 2.12 Å).

40 The HOMO is highly localized on the carbon atom of the Mg–CH\(_3\) moiety.


42 Despite this different coordination mode, the sum of the three Si–C–Si angles of \([k^3-\text{Tism}^{Pr\text{Benz}}\text{ZnMe}] (346.30°)\) is similar to that for \([\text{Tism}^{Pr\text{Benz}}\text{MgMe}] (347.84°)\)
43 The compound is, however, fluxional in solution, such that the imidazolyl groups are rendered chemically equivalent at room temperature. Decoalescence occurs upon lowering the temperature, such that broad signals indicative of a \( \kappa^3 \) coordination mode are observed at \(-70^\circ C\).

44 The \( \kappa^3 \)-coordination mode is also observed for tris(2-pyridylthio)methyl and tris(1-methylimidazol-2-ylthio)methyl compounds, \([\kappa^3\text{Tptm}]\text{ZnMe}^m\) and \([\kappa^3\text{Ttmm}]\text{ZnMe}^m\)\(^{19}\).


46 The Zn–N bond lengths \([2.088(2)\ \AA\ \text{and}\ 2.091(2)\ \AA\]\) are also close to the sum of covalent radii \((1.93\ \AA)\).


48 This variation is also reproduced by DFT calculations, although the magnitude of the increase \((0.32\ \AA)\) is greater than that observed experimentally \((0.15\ \AA)\).


53 It is also worth noting that copper carbanato compounds of the type \([\text{Tptm}]\text{CuX}\) possess Cu–C bond lengths that are comparable to the sum of the covalent radii. See, for example, ref. 11c–h.


55 In contrast, the opposite situation is observed for Lewis acidic ligands in which the unoccupied acceptor orbitals are higher in energy than the occupied metal orbitals. See, for example, ref. 4 and 6.


58 In addition, energy changes associated with the different Cu⋯C\text{arane} interactions also play a role in dictating the relative stabilities of the two isomers.

65 A similar difference in energy (40.9 kcal mol\(^{-1}\)) is also calculated for \([\text{Tism}^{\text{PrBenz}}]H\) and \([\text{Tism}^{\text{ThBenz}}]H\) with a 1:2 conformation akin to that of the solid state structure of the latter. In addition, the \([\text{Tism}^{\text{PrBenz}}]^-\) anion is 25.6 kcal mol\(^{-1}\) higher in energy than the tris(imidazole) counterpart, \([\text{Tism}^{\text{PrBenz}}]^-\), with the 3:0 conformation that is used for \(\kappa^4\)-coordination.


67 In this regard, it is pertinent to note that, whereas the geometry optimized Cu–C_\text{Het} bond length (2.005 Å) of \([\text{Cu}^{\text{Tism}^{\text{PrBenz}}}]\) is shorter than the Cu–N bond lengths (2.073 Å) of \([\text{Cu}^{\text{Tism}^{\text{PrBenz}}}]\), the opposite is observed for the lithium system, with the Li–C_\text{Het} distance (2.103 Å) being longer than the Li–N interaction (2.024 Å).


72 These data are for crystals of \([\text{Tism}^{\text{PrBenz}}]\text{NiBr}_2\)-THF obtained from a solution in THF. A different crystalline form, \([\text{Tism}^{\text{PrBenz}}]\text{NiBr}_2\text{C}_6\text{H}_4\), with similar bond lengths and angles, has also been obtained.

73 Note that the idealized trigonal bipyramidal structure of \([\text{Tism}^{\text{PrBenz}}]\text{NiBr}_2\) is one in which the Br is in an equatorial site, which contrasts with the structure of \([\text{Tism}^{\text{PrBenz}}]\text{MgMe}\) in which the methyl group is in an axial site.

74 \(\tau_5 = (\beta - \alpha)/60\), where \(\beta - \alpha\) is the difference between the two largest angles. Idealized trigonal bipyramidal and square pyramidal geometries are characterized by values of 1.00 and 0.00, respectively. See: A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, \textit{J. Chem. Soc., Dalton Trans.}, 1984, 1349–1356.

