



Cite this: *Chem. Sci.*, 2017, 8, 4465

Tris[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]-methyl metal complexes, $[\text{Tism}^{\text{PrBenz}}]\text{M}$: 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)dimethylsilyl]methyl ligand, $[\text{Tism}^{\text{PrBenz}}]$, has been employed to form carbatrane compounds of both the main group metals and transition metals, namely $[\text{Tism}^{\text{PrBenz}}]\text{Li}$, $[\text{Tism}^{\text{PrBenz}}]\text{MgMe}$, $[\text{Tism}^{\text{PrBenz}}]\text{Cu}$ and $[\text{Tism}^{\text{PrBenz}}]\text{NiBr}$. In addition to the formation of atranes, a zinc compound that exhibits κ^3 -coordination, namely $[\kappa^3\text{-Tism}^{\text{PrBenz}}]\text{ZnMe}$, has also been obtained. Furthermore, the $[\text{Tism}^{\text{PrBenz}}]$ ligand may undergo a thermally induced rearrangement to afford a novel tripodal tris(N-heterocyclic carbene) variant, as shown by the conversion of $[\text{Tism}^{\text{PrBenz}}]\text{Cu}$ to $[\kappa^4\text{-C}_4\text{-Tism}^{\text{PrBenz}*}]\text{Cu}$. 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_{atrane} interactions in $[\text{Tism}^{\text{PrBenz}}]\text{Cu}$ and $[\kappa^4\text{-C}_4\text{-Tism}^{\text{PrBenz}*}]\text{Cu}$ are characterized by an “inverted ligand field”, in which the occupied antibonding orbitals are localized more on carbon than on copper.

Received 2nd February 2017

Accepted 27th March 2017

DOI: 10.1039/c7sc00499k

rsc.li/chemical-science

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.^{1–3} A relatively recent development in this area is concerned with the synthesis of metallacarbatranes that feature transannular M–C interactions.⁴ Such compounds are of interest because the M–C bond corresponds to an M–X interaction, in contrast to the

transannular $\text{M} \leftarrow \text{L}^{4,5}$ or $\text{M} \rightarrow \text{Z}^{4,6}$ dative bonds that are more commonly encountered in atranes (Fig. 1).^{7,8} For example, we have recently employed tris(2-pyridylthio)methyl ($[\text{Tptm}]$)^{3,9} and tris(1-methylimidazol-2-ylthio)methyl ($[\text{Titm}^{\text{Me}}]$)¹⁰ as ligands for the construction of metallacarbatranes,¹¹ and have demonstrated that the nature of the heterocyclic nitrogen donor has an impact on the structure of the carbatrane.¹⁰ 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 tetradentate tripodal 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 tripodal tris(N-heterocyclic carbene) derivative.

Results and discussion

We considered the $[\text{Me}_2\text{Si}]$ moiety to be an appealing linker for the construction of analogues of the above tetradentate tripodal ligands because (i) C–Si bonds are typically robust,¹² (ii) methyl substituents on silicon can provide a protective environment for the bridgehead carbon, and (iii) silyl groups lower the pK_a of adjacent C–H groups,¹³ thereby facilitating protolytic cleavage. Furthermore, tripodal molecules of the type $\text{HC}(\text{SiMe}_2\text{X})_3$ are known, *e.g.* $\text{X} = \text{NR},^{14} \text{PR}_2,^{15} \text{CH}_2\text{PR}_2,^{16} \text{S},^{17} \text{Se},^{17}$ and

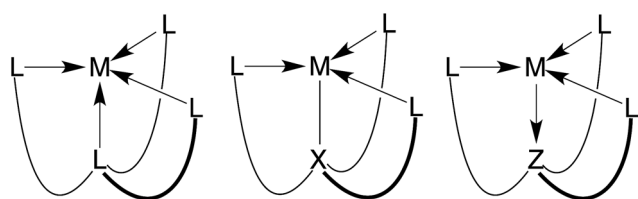


Fig. 1 Three types of atrane molecules classified according to whether the transannular interaction involves an L, X or Z-type binding site.

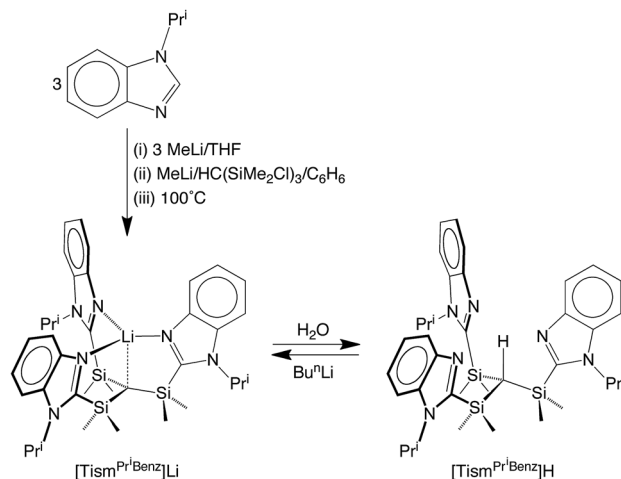
Department of Chemistry, Columbia University, New York 10027, USA. E-mail: parkin@columbia.edu

† Electronic supplementary information (ESI) available: Experimental details. CCDC 1529724–1529731. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc00499k

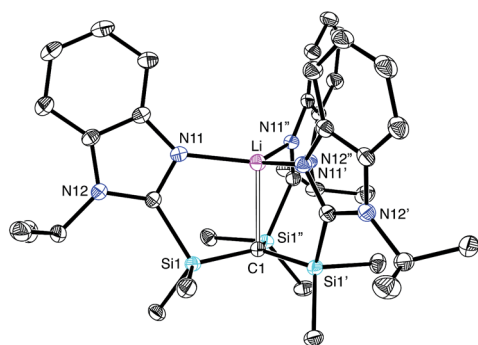


$\text{OC}_2\text{H}_4\text{OMe}$,¹⁸ and thus provide a precedent for the synthesis of variants that include heterocyclic nitrogen donors.

Indeed, tris[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methane, $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{H}$, and the lithium derivative, $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$, may be obtained from 1-isopropylbenzimidazole and $\text{HC}(\text{SiMe}_2\text{Cl})_3$ via the sequence illustrated in Scheme 1.¹⁹ Specifically, treatment of 1-isopropylbenzimidazole with MeLi, followed by addition of $\text{HC}(\text{SiMe}_2\text{Cl})_3$, affords $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$, which is converted to $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{H}$ upon reaction with H_2O ;²⁰ $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$ may also be regenerated by treatment of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{H}$ with Bu^nLi .



Scheme 1

Fig. 2 Molecular structure of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$.

The molecular structure of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$ has been determined by X-ray diffraction (Fig. 2), thereby revealing that the compound possesses an atrane motif²¹ in which the lithium adopts an approximately trigonal monopyramidal²² coordination environment with N–Li–N and C–Li–N bond angles of $118.61(9)^\circ$ and $96.8(2)^\circ$.^{23,24} Trigonal monopyramidal coordination is not common for lithium, but a similar coordination environment is observed for tris(2-pyridylthio)methyl lithium, $[\text{Tptm}]\text{Li}$.^{3,25} An interesting difference between $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$ and $[\text{Tptm}]\text{Li}$, however, pertains to the geometry at the bridgehead carbon atom. Specifically, the $[\text{CSi}_3]$ moiety of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$ adopts a much greater degree of planarity (Table 1) than does the $[\text{CS}_3]$ moiety of $[\text{Tptm}]\text{Li}$, as indicated by the fact that the sum of the Si–C–Si angles of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$ (355.8°)²⁶ is much closer to 360° than is the sum of the S–C–S angles of $[\text{Tptm}]\text{Li}$ (345.2°). Furthermore, the Li–C–Si angles of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$ [$96.87(13)^\circ$] are closer to 90° than are the Li–C–S angles of $[\text{Tptm}]\text{Li}$ [$103.05(7)^\circ$].^{27,28} Since silyl-substituted carbanions are close to planar,²⁹ as illustrated by $[\text{Li}(\text{tmen})_2][\text{C}(\text{SiMe}_2\text{PPh}_2)_3]$,^{30,31,32} the planarity of the $[\text{CSi}_3]$ moiety of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$ 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 [$2.017(2) \text{ \AA}$] are comparable to the sum of the covalent radii (1.99 \AA),³⁶ the Li–C bond length [$2.273(9) \text{ \AA}$] is distinctly longer (by 0.23 \AA) than the sum of covalent radii (2.04 \AA).^{36,37} Moreover, the HOMO of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$ is largely composed of a p-orbital on carbon, similar to that of the planar $[\text{Tism}^{\text{Pr}^i\text{Benz}}]^-$ anion with a comparable conformation (Fig. 3).

$[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{H}$ and $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$ may be employed to form caratrane compounds of the main group and transition metals. For example, $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{H}$ reacts with Me_2Mg via elimination of methane to afford $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$ (Scheme 2). The molecular structure of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$ has been determined by X-ray diffraction (Fig. 4), thereby demonstrating that the $[\text{Tism}^{\text{Pr}^i\text{Benz}}]$ ligand coordinates in a κ^4 -manner such that the molecule possesses a caratrane motif,²¹ but with a Mg–C_{atrane} distance [$2.4925(12) \text{ \AA}$] that is significantly longer (by 0.32 \AA) than both (i) the Mg–CH₃ bond length [$2.1781(13) \text{ \AA}$] and (ii) the sum of covalent radii (2.17 \AA).^{36,38,39} The long Mg–C_{atrane} 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 $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{M}$ derivatives

	$d(\text{M}-\text{C})/\text{\AA}$	$d(\text{M}-\text{C}) - \sum(\text{cov. radii})^a$	$\sum(\text{Si}-\text{C}-\text{Si})^\circ$	$d(\text{C}-[\text{Si}_3])^b/\text{\AA}$
$[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$	2.273(9)	0.23	355.8	0.22
$[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$	2.4925(12)	0.32	347.8	0.37
$[\kappa^3\text{-Tism}^{\text{Pr}^i\text{Benz}}]\text{ZnMe}$	2.171(3)	0.19	346.3	0.40
$[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Cu}$	2.281(7)	0.20	355.2	0.23
$[\kappa^4\text{-C}_4\text{-Tism}^{\text{Pr}^i\text{Benz}}]\text{Cu}$	2.4283(18)	0.35	357.8	0.15
$[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{NiBr}$	2.2197(16)	0.22	347.7	0.38
$[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{H}$	—	—	342.3	0.47

^a Ref. 36. ^b Distance of bridgehead carbon from the $[\text{Si}_3]$ plane.



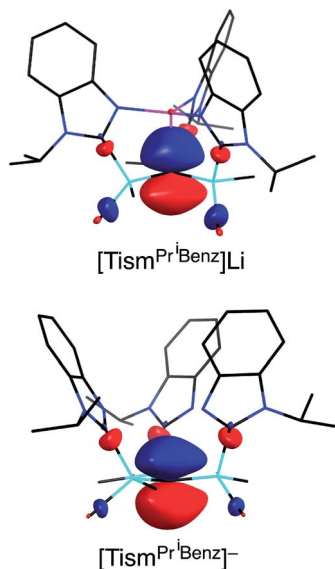
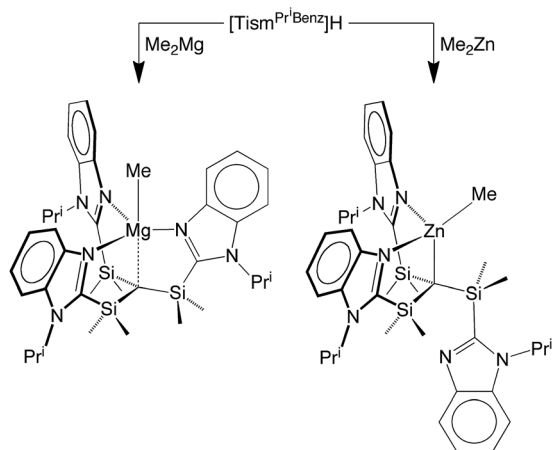


Fig. 3 Comparison of the HOMO of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$ (top) and $[\text{Tism}^{\text{Pr}^i\text{Benz}}]^-$ (bottom).



Scheme 2

effectively a lone pair orbital on carbon, with very little contribution from magnesium (Fig. 5).⁴⁰ As such, the HOMO-1 of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$ is similar in nature to the HOMO of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$. Despite the comparable atrane motifs of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$ and $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$, however, a notable difference is that the $[\text{CSi}_3]$ moiety of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$ is more pyramidal than that of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$, as indicated by the fact that the sum of the Si–C–Si angles of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$ (347.8°) is smaller than that for $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{Li}$ (355.8°).

$[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{H}$ can also be used as a reagent in zinc chemistry. Thus, $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{H}$ reacts with Me_2Zn to afford $[\kappa^3\text{-Tism}^{\text{Pr}^i\text{Benz}}]\text{ZnMe}$ (Scheme 2). Although the reaction is analogous to that between $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{H}$ and Me_2Mg , X-ray diffraction demonstrates that the zinc product, $[\kappa^3\text{-Tism}^{\text{Pr}^i\text{Benz}}]\text{ZnMe}$, has a notably different structure to that of the magnesium counterpart. Specifically, rather than coordinating to zinc in a κ^4 -manner to

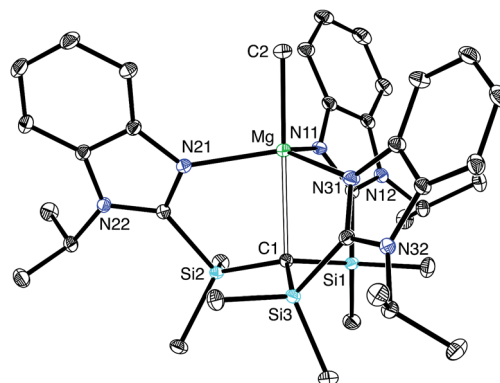


Fig. 4 Molecular structure of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$.

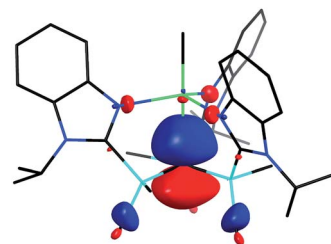


Fig. 5 HOMO-1 of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$.

afford a carbatrane motif, the ligand binds to zinc in a hypodentate⁴¹ κ^3 -manner, such that one of the imidazolyl groups remains uncoordinated (Fig. 6).^{42–44} Also in contrast to the magnesium derivative, $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$, for which the Mg-CH_3 and $\text{Mg-C}_{\text{atrane}}$ bond lengths are very different, the corresponding bonds for $[\kappa^3\text{-Tism}^{\text{Pr}^i\text{Benz}}]\text{ZnMe}$ are more similar: $d(\text{Zn-CH}_3) = 1.989(3) \text{ \AA}$ and $d(\text{Zn-C}_{\text{atrane}}) = 2.171(3) \text{ \AA}$, and the former is comparable to the sum of covalent radii (1.98 \AA).^{36,45,46}

Density functional theory (DFT) calculations on the isomeric forms of $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$ and $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{ZnMe}$ support the experimental observations. Specifically, the DFT calculations demonstrate that the κ^4 -isomer is $1.94 \text{ kcal mol}^{-1}$ more stable than the κ^3 -isomer for $[\text{Tism}^{\text{Pr}^i\text{Benz}}]\text{MgMe}$, whereas the

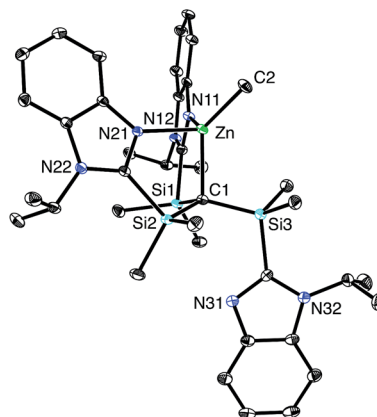


Fig. 6 Molecular structure of $[\kappa^3\text{-Tism}^{\text{Pr}^i\text{Benz}}]\text{ZnMe}$.



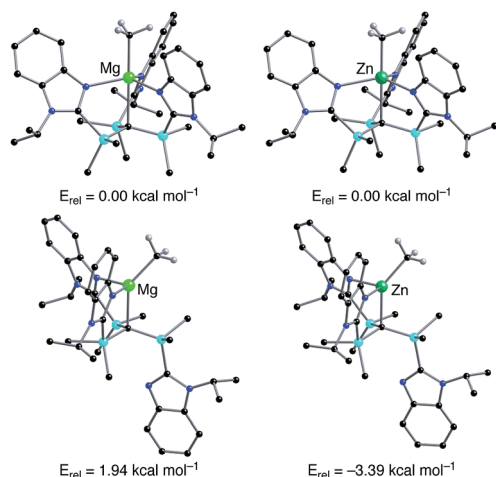


Fig. 7 Relative energies of geometry optimized structures of κ^3 - and κ^4 -[Tism^{PrⁱBenz}]MMe (M = Mg, Zn). Hydrogen atoms on [Tism^{PrⁱBenz}] are omitted for clarity.

κ^3 -isomer is 3.39 kcal mol⁻¹ more stable than the κ^4 -isomer for [Tism^{PrⁱBenz}]ZnMe (Fig. 7).

The lithium compound, [Tism^{PrⁱBenz}]Li, has also been used to synthesize metal complexes *via* metathesis reactions involving metal halides. For example, [Tism^{PrⁱBenz}]Li reacts with [(Me₃P)-CuCl]₄ to give [Tism^{PrⁱBenz}]Cu (Scheme 3), which has been shown by X-ray diffraction (Fig. 8) to possess a trigonal monopyramidal structure similar to that of [Tism^{PrⁱBenz}]Li, with Cu–C and Cu–N distances of 2.281(7) Å and 2.014(3) Å, respectively.^{47,48} As with the lithium and magnesium carbatranes, the Cu–C_{atrane} bond of [Tism^{PrⁱBenz}]Cu is also longer (by 0.20 Å) than the sum of covalent radii (2.08 Å).^{36,49,50}

A distinct difference between [Tism^{PrⁱBenz}]Cu and the lithium and magnesium complexes, [Tism^{PrⁱBenz}]Li and [Tism^{PrⁱBenz}]MgMe, however, is the degree of covalent interaction between copper and the atrane carbon atom. Specifically, overlap between the carbon 2p_z orbital and the copper 3d_{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

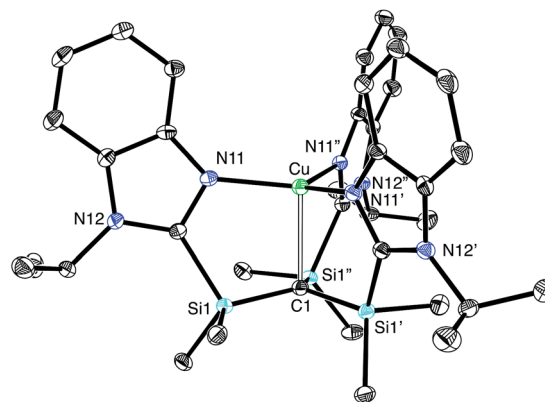


Fig. 8 Molecular structure of [Tism^{PrⁱBenz}]Cu.

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 [Tism^{PrⁱBenz}]Cu classifies the HOMO as a carbon lone pair orbital. This arrangement is counter to that observed for most transition metal compounds with σ -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.^{51,52}

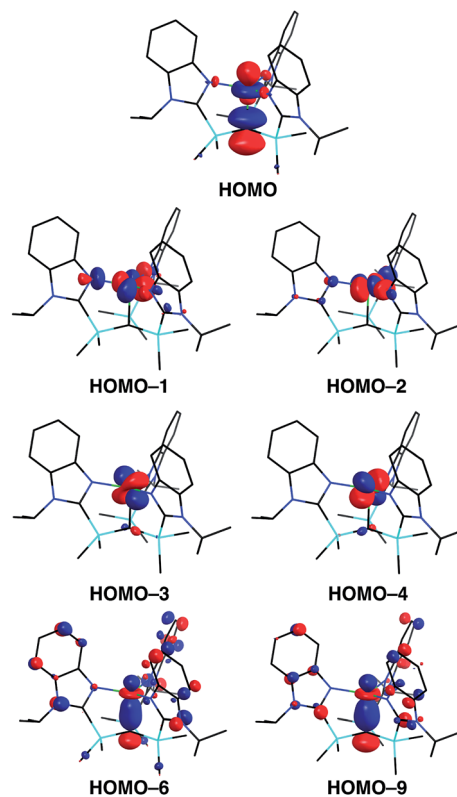
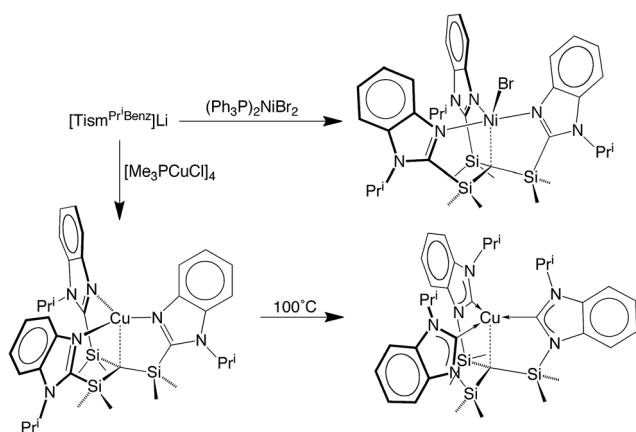


Fig. 9 Frontier orbitals of [Tism^{PrⁱBenz}]Cu. Note that the in-phase interaction between the carbon 2p_z orbital and the copper 3d_{z²} orbital is a component of two molecular orbitals with similar energies (HOMO-6, -0.2169 eV; HOMO-9, -0.2192 eV).



Scheme 3



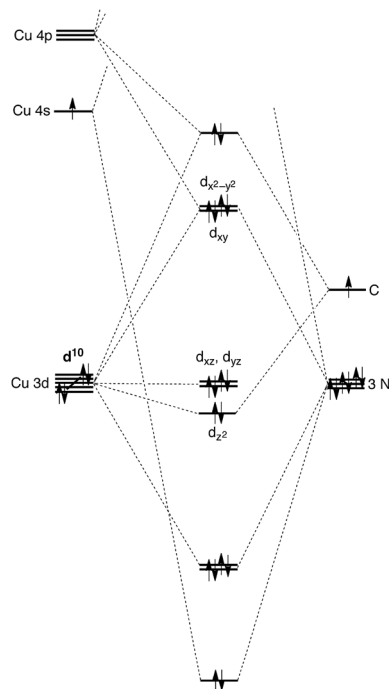


Fig. 10 Qualitative molecular orbital diagram for $[\text{Tism}^{\text{PrBenz}}]\text{Cu}$ with C_{3v} symmetry, with the ligand arbitrarily represented in its neutral form.

However, despite the fact that situations in which the bonding orbital possesses mainly metal character (and the corresponding antibonding orbital possesses mainly ligand character) are not normally encountered in transition metal chemistry, examples of so-called “inverted ligand fields” have recently been discussed.⁵¹ Such circumstances may arise when the ligand σ -orbitals are higher in energy than the metal d orbitals, an occurrence that is more likely at the end of the transition series.⁵¹ A salient example is provided by $[\text{Cu}(\text{CF}_3)_4]^-$, for which the bonding has been investigated both experimentally and computationally.^{51,53–55}

Most interestingly, $[\text{Tism}^{\text{PrBenz}}]\text{Cu}$ undergoes a novel isomerization at 100 °C to afford a tris(N-heterocyclic carbene) derivative, $[\kappa^4\text{-C}_4\text{-Tism}^{\text{PrBenz}}]\text{Cu}$ (Scheme 3),⁵⁶ which has been structurally characterized by X-ray diffraction (Fig. 11).

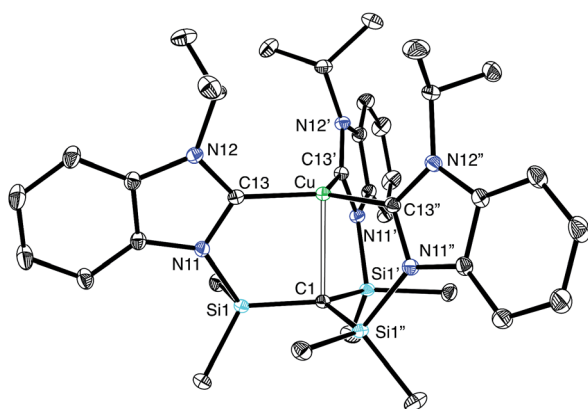


Fig. 11 Molecular structure of $[\kappa^4\text{-C}_4\text{-Tism}^{\text{PrBenz}}]\text{Cu}$.

Although several tripodal tris(N-heterocyclic carbene) ligands have been reported,^{57–59} the formation of $[\kappa^4\text{-C}_4\text{-Tism}^{\text{PrBenz}}]\text{Cu}$ is notable because $[\kappa^4\text{-C}_4\text{-Tism}^{\text{PrBenz}}]$ is an example of such a ligand that also features an additional potential X-type⁷ binding site.⁶⁰ The isomerization of $[\text{Tism}^{\text{PrBenz}}]\text{Cu}$ to $[\kappa^4\text{-C}_4\text{-Tism}^{\text{PrBenz}}]\text{Cu}$ is, however, accompanied by an increase in the axial Cu–C_{atran} 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_{z²} and carbon 2p_z orbitals interact, and the derived bonding and antibonding orbitals are illustrated in Fig. 12. As observed for $[\text{Tism}^{\text{PrBenz}}]\text{Cu}$, the antibonding orbital possesses mainly carbon character such that the bonding situation also corresponds to an “inverted ligand field”.

DFT calculations indicate that $[\kappa^4\text{-C}_4\text{-Tism}^{\text{PrBenz}}]\text{Cu}$ is more stable than $[\text{Tism}^{\text{PrBenz}}]\text{Cu}$ by 4.18 kcal mol^{−1}, which is in accord with the experimental observations. In contrast, isomerization of the structurally analogous lithium derivative, $[\text{Tism}^{\text{PrBenz}}]\text{Li}$, to $[\kappa^4\text{-C}_4\text{-Tism}^{\text{PrBenz}}]\text{Li}$ is predicted to be thermodynamically unfavorable by 35.3 kcal mol^{−1}.⁶² The different thermodynamic trends reflect, *inter alia*, (i) the intrinsic stability of $[\text{Tism}^{\text{PrBenz}}]$ versus $[\text{Tism}^{\text{PrBenz}}]$ and (ii) the relative preferences of copper and lithium to coordinate to a N-heterocyclic carbene versus an imidazole donor.⁶³ With respect to the former, the tris(N-heterocyclic carbene), $[\text{Tism}^{\text{PrBenz}}]\text{H}$, is calculated to be 41.1 kcal mol^{−1} higher in energy than the tris(imidazole), $[\text{Tism}^{\text{PrBenz}}]\text{H}$, with the 3 : 0 conformation⁶⁴ that is used for κ^4 -coordination.^{65,66} 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 imidazoles to a C-coordinated ligand at a metal center has been previously observed,^{68–70} we are unaware of the corresponding transformation involving migration of a silyl group rather than a hydrogen atom.⁷¹ Furthermore, the formation of $[\kappa^4\text{-C}_4\text{-Tism}^{\text{PrBenz}}]\text{Cu}$ is also noteworthy because C-coordination has been predicted to be less favorable than N-coordination of imidazole to CuCl.^{66a,b}

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

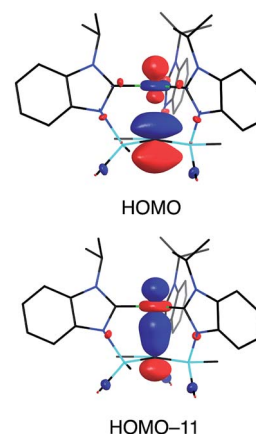


Fig. 12 The HOMO and HOMO-11 of $[\kappa^4\text{-C}_4\text{-Tism}^{\text{PrBenz}}]\text{Cu}$.



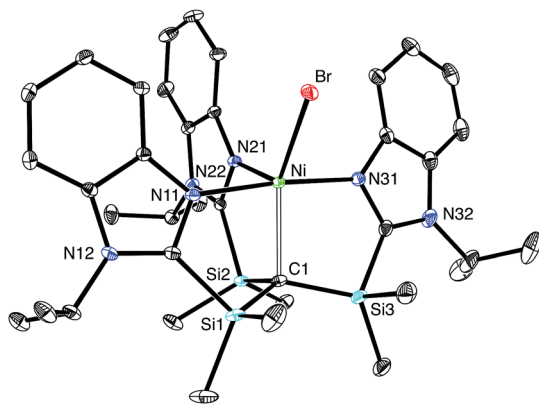


Fig. 13 Molecular structure of $[\text{Tism}^{\text{Pr}^{\text{Benz}}}] \text{NiBr}$.

Although the $[\text{Tism}^{\text{Pr}^{\text{Benz}}}]$ ligand binds in a κ^4 -manner (Fig. 13), with a Ni–C bond length of 2.2197(16) Å and Ni–N bond lengths in the range 2.0093(14)–2.1230(14) Å,⁷² the molecule does not adopt a trigonal bipyramidal structure akin to that of $[\text{Tism}^{\text{Pr}^{\text{Benz}}}] \text{MgMe}$. Specifically, rather than possess three N–Ni–N angles of approximately 120°, the three nitrogen atoms of $[\text{Tism}^{\text{Pr}^{\text{Benz}}}] \text{NiBr}$ adopt a T-shaped arrangement, with N–Ni–N bond angles of 89.36(5)°, 90.34(6)° and 174.72(5)°; despite the different placement of the imidazole donors, however, the three C–Ni–N angles retain values of approximately 90°, namely 87.18(6)°, 87.63(6)° and 96.75(6)°.⁷² Thus, in addition to coordinating with a local C_3 geometry, the $[\text{Tism}^{\text{Pr}^{\text{Benz}}}]$ ligand is flexible and may also coordinate with an idealized 90° seesaw geometry.²³ Although the latter coordination mode of the $[\text{Tism}^{\text{Pr}^{\text{Benz}}}]$ ligand could support a square pyramidal structure, the location of the bromine is such that the coordination geometry of nickel is intermediate between square pyramidal and trigonal bipyramidal,⁷³ as indicated by a τ_5 five coordinate index of 0.44.^{74–76} As observed for the above carbatrane compounds, the Ni–C bond length [2.2197(16) Å] is also longer (by 0.22 Å) than the sum of covalent radii (2.00 Å).^{36,77}

Conclusions

In summary, $[\text{Tism}^{\text{Pr}^{\text{Benz}}}]$ is a flexible ligand that can coordinate to a metal center in both κ^3 and κ^4 -manners, with the latter affording a carbatrane motif. Furthermore, when coordinating in a κ^4 -manner, the $[\text{Tism}^{\text{Pr}^{\text{Benz}}}]$ ligand can adopt either a trigonal monopyramidal geometry or a seesaw geometry. Interestingly, we have also demonstrated that the $[\text{Tism}^{\text{Pr}^{\text{Benz}}}]$ ligand may undergo a thermally induced rearrangement to afford a novel tripodal tris(N-heterocyclic carbene) ligand, as demonstrated by the conversion of $[\text{Tism}^{\text{Pr}^{\text{Benz}}}] \text{Cu}$ to $[\kappa^4\text{-C}_4\text{-Tism}^{\text{Pr}^{\text{Benz}}}] \text{Cu}$. 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 $[\text{Tism}^{\text{Pr}^{\text{Benz}}}] \text{Cu}$ and $[\kappa^4\text{-C}_4\text{-Tism}^{\text{Pr}^{\text{Benz}}}] \text{Cu}$ is that Cu–C_{atrance} 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

- (a) J. G. Verkade, *Coord. Chem. Rev.*, 1994, **137**, 233–295; (b) J. G. Verkade, *Acc. Chem. Res.*, 1993, **26**, 483–489.
- (a) M. G. Voronkov, *Pure Appl. Chem.*, 1966, **13**, 35–59; (b) M. G. Voronkov and V. P. Baryshok, *J. Organomet. Chem.*, 1982, **239**, 199–249; (c) M. G. Voronkov, G. I. Seltshan, A. Lapsina and W. A. Pestunowitschich, *Z. Chem.*, 1968, **8**, 214–217.
- Although the term “atrane” 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.
- I. Kuzu, I. Krummenacher, J. Meyer, F. Armbruster and F. Breher, *Dalton Trans.*, 2008, 5836–5865.
- (a) A. G. Blackman, *Polyhedron*, 2005, **24**, 1–39; (b) A. G. Blackman, *Eur. J. Inorg. Chem.*, 2008, 2633–2647.
- (a) H. Kameo and H. Nakazawa, *Chem.-Asian J.*, 2013, **8**, 1720–1734; (b) H. Braunschweig and R. D. Dewhurst, *Dalton Trans.*, 2011, **40**, 549–558; (c) H. Braunschweig, R. D. Dewhurst and A. Schneider, *Chem. Rev.*, 2010, **110**, 3924–3957; (d) F. G. Fontaine, J. Boudreau and M. H. Thibault, *Eur. J. Inorg. Chem.*, 2008, 5439–5454; (e) A. Amgoune and D. Bourissou, *Chem. Commun.*, 2011, **47**, 859–871; (f) G. Parkin, *Organometallics*, 2006, **25**, 4744–4747; (g) G. Bouhadir, A. Amgoune and D. Bourissou, *Adv. Organomet. Chem.*, 2010, **58**, 1–107.
- For the classification of ligands as L, X or Z, see: (a) M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127–148; (b) G. Parkin, *Comprehensive Organometallic Chemistry III*, ed. R. H. Crabtree and D. M. P. Mingos, Elsevier, Oxford, 2006, ch. 1, vol. 1; (c) M. L. H. Green and G. Parkin, *J. Chem. Educ.*, 2014, **91**, 807–816.
- While Fig. 1 depicts three equatorial L-type donors, variants with X-type donors are also known. See, for example, ref. 1, 2 and (a) L. H. Gade, *Acc. Chem. Res.*, 2002, **35**, 575–582; (b) R. R. Schrock, *Pure Appl. Chem.*, 1997, **69**, 2197–2203; (c) R. R. Schrock, *Acc. Chem. Res.*, 1997, **30**, 9–16; (d) H. Kawaguchi and T. Matsuo, *J. Organomet. Chem.*, 2004, **689**, 4228–4243; (e) B. V. Kelly, E. C. Weintrob, D. Buccella, J. M. Tanski and G. Parkin, *Inorg. Chem. Commun.*, 2007, **10**, 699–704; (f) L. H. Tong, Y. L. Wong, H. K. Lee and J. R. Dilworth, *Inorg. Chim. Acta*, 2012, **383**, 91–97; (g) S. Worl, D. Hellwinkel, H. Pritzkow, M. Hofmann and R. Kramer, *Dalton Trans.*, 2004, 2750–2757; (h)



- J. Kobayashi, K. Goto, T. Kawashima, M. W. Schmidt and S. Nagase, *J. Am. Chem. Soc.*, 2002, **124**, 3703–3712; (i) S. Banerjee, P. Halder and T. K. Paine, *Z. Anorg. Allg. Chem.*, 2014, **640**, 1168–1176; (j) Y. Nakanishi, Y. Ishida and H. Kawaguchi, *Dalton Trans.*, 2016, **45**, 15879–15885; (k) F. Akagi, Y. Ishida, T. Matsuo and H. Kawaguchi, *Dalton Trans.*, 2011, **40**, 2375–2382; (l) F. Akagi, T. Matsuo and H. Kawaguchi, *J. Am. Chem. Soc.*, 2005, **127**, 11936–11937.
- 9 (a) W. Sattler and G. Parkin, *J. Am. Chem. Soc.*, 2011, **133**, 9708–9711; (b) W. Sattler and G. Parkin, *J. Am. Chem. Soc.*, 2012, **134**, 17462–17465; (c) W. Sattler, S. Ruccolo and G. Parkin, *J. Am. Chem. Soc.*, 2013, **135**, 18714–18717; (d) W. Sattler, S. Ruccolo, M. R. Chaijan, T. N. Allah and G. Parkin, *Organometallics*, 2015, **34**, 4717–4731; (e) W. Sattler and G. Parkin, *Catal. Sci. Technol.*, 2014, **4**, 1578–1584; (f) W. Sattler and G. Parkin, *Chem. Sci.*, 2012, **3**, 2015–2019.
- 10 S. Ruccolo, W. Sattler, Y. Rong and G. Parkin, *J. Am. Chem. Soc.*, 2016, **138**, 14542–14545.
- 11 For other examples of metallacarbatranes, see ref. 8i–l and (a) Y. Rong and G. Parkin, *Aust. J. Chem.*, 2013, **66**, 1306–1310; (b) A. Al-Harbi, Y. Rong and G. Parkin, *Dalton Trans.*, 2013, **42**, 14053–14057; (c) I. Kinoshita, L. J. Wright, S. Kubo, K. Kimura, A. Sakata, T. Yano, R. Miyamoto, T. Nishioka and K. Isobe, *Dalton Trans.*, 2003, 1993–2003; (d) R. Miyamoto, R. Santo, T. Matsushita, T. Nishioka, A. Ichimura, Y. Teki and I. Kinoshita, *Dalton Trans.*, 2005, 3179–3186; (e) R. Miyamoto, R. T. Hamazawa, M. Hirotsu, T. Nishioka, I. Kinoshita and L. J. Wright, *Chem. Commun.*, 2005, 4047–4049; (f) R. Santo, R. Miyamoto, R. Tanaka, T. Nishioka, K. Sato, K. Toyota, M. Obata, S. Yano, I. Kinoshita, A. Ichimura and T. Takui, *Angew. Chem., Int. Ed.*, 2006, **45**, 7611–7614; (g) Y. Yoshida, R. Miyamoto, T. Nishioka, H. Hashimoto and I. Kinoshita, *Chem. Lett.*, 2009, **38**, 366–367; (h) I. Kinoshita, H. Hashimoto, T. Nishioka, R. Miyamoto, N. Kuwamura and Y. Yoshida, *Photosynth. Res.*, 2008, **95**, 363–371; (i) Y. Yoshida, R. Miyamoto, A. Nakato, R. Santo, N. Kuwamura, K. Gobo, T. Nishioka, M. Hirotsu, A. Ichimura, H. Hashimoto and I. Kinoshita, *Bull. Chem. Soc. Jpn.*, 2011, **84**, 600–611; (j) K. Kitano, N. Kuwamura, R. Tanaka, R. Santo, T. Nishioka, A. Ichimura and I. Kinoshita, *Chem. Commun.*, 2008, 1314–1316; (k) F. T. Vieira, G. M. de Lima, J. L. Wardell, S. M. S. V. Wardell, K. Krambrock and A. F. d. C. Alcântara, *J. Organomet. Chem.*, 2008, **693**, 1986–1990; (l) N. Kuwamura, R. Kato, K. Kitano, M. Hirotsu, T. Nishioka, H. Hashimoto and I. Kinoshita, *Dalton Trans.*, 2010, **39**, 9988–9993; (m) S. E. Creutz and J. C. Peters, *J. Am. Chem. Soc.*, 2014, **136**, 1105–1115; (n) J. Rittle and J. C. Peters, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 15898–15903; (o) P. Halder, S. Paria and T. K. Paine, *Chem.–Eur. J.*, 2012, **18**, 11778–11787; (p) Y. Yuki, M. Riichi, N. Takanori, H. Hideki and K. Isamu, *Chem. Lett.*, 2009, **38**, 366–367.
- 12 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.
- 13 (a) A. Streitwieser, L. Xie, P. Wang and S. M. Bachrach, *J. Org. Chem.*, 1993, **58**, 1778–1784; (b) S. Durmaz, *J. Organomet. Chem.*, 1975, **96**, 331–334; (c) B. Romer, G. G. Gatev, M. L. Zhong and J. I. Brauman, *J. Am. Chem. Soc.*, 1998, **120**, 2919–2924; (d) E. A. Brinkman, S. Berger and J. I. Brauman, *J. Am. Chem. Soc.*, 1994, **116**, 8304–8310; (e) D. M. Wetzel and J. I. Brauman, *J. Am. Chem. Soc.*, 1988, **110**, 8333–8336; (f) P. v. R. Schleyer, T. Clark, A. J. Kos, G. W. Spitznagel, C. Rohde, D. Arad, K. N. Houk and N. G. Rondan, *J. Am. Chem. Soc.*, 1984, **106**, 6467–6475.
- 14 See, for example, ref. 8a.
- 15 (a) D. M. Friesen, R. McDonald and L. Rosenberg, *Can. J. Chem.*, 1999, **77**, 1931–1940; (b) A. Avent, D. Bonafoux, C. Eaborn, S. K. Gupta, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1999, 831–834; (c) D. M. Friesen, O. J. Bowles, R. McDonald and L. Rosenberg, *Dalton Trans.*, 2006, 2671–2682.
- 16 Ref. 11n and A. G. Avent, D. Bonafoux, C. Eaborn, M. S. Hill, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 2000, 2183–2190.
- 17 U. Herzog, G. Rheinwald and H. Borrmann, *J. Organomet. Chem.*, 2002, **660**, 27–35.
- 18 (a) H. Li, A. J. A. Aquino, D. B. Cordes, F. Hung-Low, W. L. Hase and C. Krempner, *J. Am. Chem. Soc.*, 2013, **135**, 16066–16069; (b) H. Li, A. J. A. Aquino, D. B. Cordes, W. L. Hase and C. Krempner, *Chem. Sci.*, 2017, **8**, 1316–1328.
- 19 Unless otherwise specified, the abbreviation [Tism^{PrBenz}] refers to coordination to a metal *via* a nominal κ^4 -N₃C manner.
- 20 For related synthetic approaches, see ref. 16 and (a) J. Ohshita, Y. Hatanaka, S. Matsui, T. Mizumo, Y. Kunugi, Y. Honsho, A. Saeki, S. Seki, J. Tibbelin, H. Ottosson and T. Takeuchi, *Dalton Trans.*, 2010, **39**, 9314–9320; (b) C. L. Lund, O. Stanga, J. W. Quail and J. Muller, *Can. J. Chem.*, 2007, **85**, 483–490; (c) P. Jutzi and W. Sakriss, *Chem. Ber.*, 1973, **106**, 2815–2824.
- 21 To the extent that M–C_{atranes} distances are larger than the sum of the covalent radii, the compounds may be better described as quasi-atranes (see ref. 1).
- 22 Note that “trigonal pyramidal” is not synonymous with “trigonal monopyramidal” since the former refers to three-coordinate geometries, while the latter refers to four-coordinate geometries. See, for example, ref. 3 and: (a) P. A. W. Dean, J. J. Vittal and N. C. Payne, *Inorg. Chem.*, 1984, **23**, 4232–4236; (b) K. Izod, J. Stewart, E. R. Clark, W. McFarlane, B. Allen, W. Clegg and R. W. Harrington, *Organometallics*, 2009, **28**, 3327–3337; (c) S. Yamana, *J. Chem. Educ.*, 1988, **65**, 1074–1074; (d) C. C. Cummins, J. Lee, R. R. Schrock and W. D. Davis, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1501–1503; (e) M. Ray, B. S. Hammes, G. P. A. Yap, A. L. Rheingold and A. S. Borovik, *Inorg. Chem.*, 1998, **37**, 1527–1532; (f) C. E. Searls, S. T. Kleespies, M. L. Eppright, S. C. Schwartz, G. P. A. Yap and R. C. Scarrow, *Inorg. Chem.*, 2010, **49**, 11261–11263; (g) D. S. Kuiper, R. E. Douthwaite, A. R. Mayol, P. T. Wolczanski, E. B. Lobkovsky, T. R. Cundari, O. P. Lam and K. Meyer, *Inorg. Chem.*, 2008, **47**, 7139–7153;



- (h) S. Suzuki, T. Sakurai, A. Nakahara, M. Masuko and H. Iwasaki, *Biochim. Biophys. Acta*, 1985, **827**, 190–192; (i) H. Schumann, U. Hartmann, A. Dietrich and J. Pickardt, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1077–1078.
- 23 Correspondingly, the four-coordinate τ_4 (0.87) and $\tau_{4\delta}$ (0.87) geometry indices are close to the idealized value for a trigonal monopyramid (0.85). $\tau_4 = [360 - (\alpha + \beta)]/141$, where α and β are the two largest angles, and $\tau_{4\delta} = \tau_4(\beta/\alpha)$, where $\alpha > \beta$. 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(SiMe₂)₃ 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 [CSi₃] moiety of the related phosphine derivative, [κ⁴-C(SiMe₂CH₂PPh₂)₃]Li, with Li–C–Si angles in the range 103.4–104.9°, and $\sum(\text{Si–C–Si}) = 343.2^\circ$, is much less planar than that of [Tism^{PrⁱBenz}]Li. See ref. 16.
- 28 In contrast to [Tism^{PrⁱBenz}]Li, the protonated derivative, [Tism^{PrⁱBenz}]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 [CSi₃] 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^* Si–C bonds. See, for example, ref. 13b–f.
- 30 A. G. Avent, D. Bonafoux, C. Eaborn, S. K. Gupta, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1999, 831–834.
- 31 (a) C. Eaborn, K. Izod and J. D. Smith, *J. Organomet. Chem.*, 1995, **500**, 89–99; (b) S. S. Al-Juaid, C. Eaborn, P. B. Hitchcock, K. Izod, M. Mallien and J. D. Smith, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1268–1270; (c) C. Eaborn, P. B. Hitchcock, K. Izod, A. J. Jaggar and J. D. Smith, *Organometallics*, 1994, **13**, 753–754.
- 32 For examples of formally zwitterionic compounds with a planar [C(SiMe₂X)₃] moiety, see ref. 18b and: (a) C. Eaborn, A. Farook, P. B. Hitchcock and J. D. Smith, *Organometallics*, 1998, **17**, 3135–3137; (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, *Organometallics*, 1997, **16**, 503–504.
- 33 R. Chauvin, *Eur. J. Inorg. Chem.*, 2000, 577–591.
- 34 For other carbatranes with formally zwitterionic character, see ref. 10.
- 35 For examples of metal compounds with formally three-coordinate anionic carbon centers in which the lone pair on carbon is directed away from the metal center, see: (a) S. O. Grim, P. H. Smith, S. Nittolo, H. L. Ammon, L. C. Satek, S. A. Sangokoya, R. K. Khanna, I. J. Colquhoun, W. McFarlane and J. R. Holden, *Inorg. Chem.*, 1985, **24**, 2889–2895; (b) S. O. Grim, S. A. Sangokoya, A. L. Rheingold, W. McFarlane, I. J. Colquhoun and R. D. Gilardi, *Inorg. Chem.*, 1991, **30**, 2519–2522; (c) M. Valderrama, R. Contreras, V. Arancibia, P. Muñoz, D. Boys, M. P. Lamata, F. Viguri, D. Carmona, F. J. Lahoz, J. A. López and L. A. Oro, *J. Organomet. Chem.*, 1997, **545**, 507–517; (d) M. C. Gimeno, P. G. Jones, A. Laguna and M. D. Villacampa, *Chem. Ber.*, 1996, **129**, 585–588; (e) F. Breher, J. Grunenberger, S. C. Lawrence, P. Mountford and H. Rüegger, *Angew. Chem., Int. Ed.*, 2004, **43**, 2521–2524; (f) R. Lalrempuia, A. Stasch and C. Jones, *Chem.-Asian J.*, 2015, **10**, 447–454; (g) C. Müller, A. Koch, H. Görls, S. Kriek and M. Westerhausen, *Inorg. Chem.*, 2015, **54**, 635–645; (h) I. Kuzu, I. Krummenacher, I. J. Hewitt, Y. Lan, V. Mereacre, A. K. Powell, P. Höfer, J. Harmer and F. Breher, *Chem.-Eur. J.*, 2009, **15**, 4350–4365; (i) S. González-Gallardo, I. Kuzu, P. Oña-Burgos, T. Wolfer, C. Wang, K. W. Klinkhammer, W. Kloppe, S. Bräse and F. Breher, *Organometallics*, 2014, **33**, 941–951; (j) J. Meyer, I. Kuzu, S. González-Gallardo and F. Breher, *Z. Anorg. Allg. Chem.*, 2013, **639**, 301–307; (k) D. Kratzert, D. Leusser, D. Stern, J. Meyer, F. Breher and D. Stalke, *Chem. Commun.*, 2011, **47**, 2931–2933.
- 36 B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.*, 2008, 2832–2838.
- 37 For examples of lithium alkyl compounds with Li–C bond lengths comparable to the sum of the covalent radii, see: (a) M. Hülsmann, A. Mix, B. Neumann, H.-G. Stämmler and N. W. Mitzel, *Eur. J. Inorg. Chem.*, 2014, **2014**, 46–50; (b) C. Strohmman, V. H. Gessner and A. Damme, *Chem. Commun.*, 2008, 3381–3383.
- 38 For examples of magnesium alkyl compounds with Mg–C bond lengths comparable to the sum of the covalent radii, see: (a) P. J. Bailey, D. Lorono-Gonzalez and S. Parsons, *Chem. Commun.*, 2003, 1426–1427; (b) V. Balasanthiran, M. H. Chisholm, K. Choojun, C. B. Durr and P. M. Wambua, *Polyhedron*, 2016, **103**, 235–240; (c) R. Han, A. Looney and G. Parkin, *J. Am. Chem. Soc.*, 1989, **111**, 7276–7278; (d) R. Han and G. Parkin, *Organometallics*, 1991, **10**, 1010–1020.
- 39 In contrast, the Mg–CH₃ [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–CH₃ moiety.
- 41 E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67–138.
- 42 Despite this different coordination mode, the sum of the three Si–C–Si angles of [κ³-Tism^{PrⁱBenz}]ZnMe (346.30°) is similar to that for [Tism^{PrⁱBenz}]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 κ^3 coordination mode are observed at -70°C .
- 44 The κ^3 -coordination mode is also observed for tris(2-pyridylthio)methyl and tris(1-methylimidazol-2-ylthio)-methyl compounds, $[\kappa^3\text{-Tptm}]\text{ZnMe}^{9a}$ and $[\kappa^3\text{-Titm}^{\text{Me}}]\text{ZnMe}^{10}$.
- 45 For examples of zinc alkyl compounds with Zn–C bond lengths comparable to the sum of the covalent radii, see: (a) C. Romain, V. Rosa, C. Fliedel, F. Bier, F. Hild, R. Welter, S. Dagorne and T. Aviles, *Dalton Trans.*, 2012, **41**, 3377–3379; (b) A. Stasch, *Chem.–Eur. J.*, 2012, **18**, 15105–15112; (c) J. G. Melnick, A. Docrat and G. Parkin, *Chem. Commun.*, 2004, 2870–2871; (d) I. B. Gorrell, A. Looney and G. Parkin, *J. Chem. Soc., Chem. Commun.*, 1990, 220–222; (e) A. Looney, R. Han, I. B. Gorrell, M. Cornebise, K. Yoon, G. Parkin and A. L. Rheingold, *Organometallics*, 1995, **14**, 274–288.
- 46 The Zn–N bond lengths [2.088(2) Å and 2.091(2) Å] are also close to the sum of covalent radii (1.93 Å).
- 47 For an example of trigonal monopyramidal Cu(I) compound with three imidazole donors, see: J. K. Voo, K. C. Lam, A. L. Rheingold and C. G. Riordan, *J. Chem. Soc., Dalton Trans.*, 2001, 1803–1805.
- 48 For an example of a structurally related anionic boratrane derivative, see: M. E. Moret, L. M. Zhang and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 3792–3795.
- 49 For examples of copper alkyl compounds with Cu–C bond lengths comparable to the sum of the covalent radii, see: (a) F. Schaper, S. R. Foley and R. F. Jordan, *J. Am. Chem. Soc.*, 2004, **126**, 2114–2124; (b) G. Boche, F. Bosold, M. Marsch and K. Harms, *Angew. Chem., Int. Ed.*, 1998, **37**, 1684–1686.
- 50 It is also worth noting that copper carborane 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.
- 51 R. Hoffmann, S. Alvarez, C. Mealli, A. Falceto, T. J. Cahill, T. Zeng and G. Manca, *Chem. Rev.*, 2016, **116**, 8173–8192.
- 52 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.
- 53 R. C. Walroth, J. T. Lukens, S. N. MacMillan, K. D. Finkelstein and K. M. Lancaster, *J. Am. Chem. Soc.*, 2016, **138**, 1922–1931.
- 54 (a) J. P. Snyder, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 80–81; (b) M. Kaupp and H. G. Vonscherner, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 986–986; (c) S. Alvarez, R. Hoffmann and C. Mealli, *Chem.–Eur. J.*, 2009, **15**, 8358–8373; (d) G. Aullón and S. Alvarez, *Theor. Chem. Acc.*, 2009, **123**, 67–73.
- 55 It is worth noting that inverted ligand field patterns can also be obtained due to molecular distortions. For example, the axial distortion of a tetrahedron can result in a “two-above-three” pattern of d orbitals, rather than the “three-above-two” pattern that is associated with tetrahedral symmetry. See, for example: (a) D. M. Jenkins, A. J. Di Bilio, M. J. Allen, T. A. Betley and J. C. Peters, *J. Am. Chem. Soc.*, 2002, **124**, 15336–15350; (b) D. M. Jenkins and J. C. Peters, *J. Am. Chem. Soc.*, 2005, **127**, 7148–7165; (c) S. D. Brown and J. C. Peters, *J. Am. Chem. Soc.*, 2005, **127**, 1913–1923.
- 56 For related isomerization reactions of tripodal compounds, see: (a) P. Halder and T. K. Paine, *Inorg. Chem.*, 2011, **50**, 708–710; (b) N. Kuwamura, K. Kitano, M. Hirotsu, T. Nishioka, Y. Teki, R. Santo, A. Ichimura, H. Hashimoto, L. J. Wright and I. Kinoshita, *Chem.–Eur. J.*, 2011, **17**, 10708–10715; (c) C. Gwengo, R. M. Silva, M. D. Smith, S. V. Lindeman and J. R. Gardinier, *Inorg. Chim. Acta*, 2009, **362**, 4127–4136; (d) D. L. Reger, T. C. Grattan, K. J. Brown, C. A. Little, J. J. S. Lamba, A. L. Rheingold and R. D. Sommer, *J. Organomet. Chem.*, 2000, **607**, 120–128; (e) A. Al-Harbi, Y. Rong and G. Parkin, *Dalton Trans.*, 2013, **42**, 14053–14057; (f) J. M. White, V. W. L. Ng, D. C. Clarke, P. D. Smith, M. K. Taylor and C. G. Young, *Inorg. Chim. Acta*, 2009, **362**, 4570–4577 and references therein.
- 57 (a) C. Santini, M. Marinelli and M. Pellei, *Eur. J. Inorg. Chem.*, 2016, **2016**, 2312–2331; (b) X. Hu and K. Meyer, *J. Organomet. Chem.*, 2005, **690**, 5474–5484; (c) K. Meyer and S. C. Bart, *Adv. Inorg. Chem.*, 2008, **60**, 1–30; (d) J. Smith, *Comments Inorg. Chem.*, 2008, **29**, 189–233; (e) J. A. Mata, M. Poyatos and E. Peris, *Coord. Chem. Rev.*, 2007, **251**, 841–859.
- 58 (a) H. V. R. Dias and W. C. Jin, *Tetrahedron Lett.*, 1994, **35**, 1365–1366; (b) H. Nakai, Y. J. Tang, P. Gantzel and K. Meyer, *Chem. Commun.*, 2003, 24–25; (c) X. Hu, Y. Tang, P. Gantzel and K. Meyer, *Organometallics*, 2003, **22**, 612–614; (d) H. Kropp, A. Scheurer, F. W. Heinemann, J. Bendix and K. Meyer, *Inorg. Chem.*, 2015, **54**, 3562–3572; (e) S. B. Muñoz, W. K. Foster, H.-J. Lin, C. G. Margarit, D. A. Dickie and J. M. Smith, *Inorg. Chem.*, 2012, **51**, 12660–12668.
- 59 For some reviews pertaining to the coordination chemistry of N-heterocyclic carbenes, see: (a) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39–91; (b) D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723–6753.
- 60 For an example of a tripodal tris(N-heterocyclic carbene) coordinated to Cu(I), see: X. Hu, I. Castro-Rodriguez and K. Meyer, *J. Am. Chem. Soc.*, 2003, **125**, 12237–12245.
- 61 This variation is also reproduced by DFT calculations, although the magnitude of the increase (0.32 Å) is greater than that observed experimentally (0.15 Å).
- 62 For examples of N-heterocyclic carbene complexes of the main group metals, see: (a) S. Bellemin-Laponnaz and S. Dagorne, *Chem. Rev.*, 2014, **114**, 8747–8774; (b) C. E. Williams, *Organomet. Chem.*, 2010, **36**, 1–28.
- 63 In addition, energy changes associated with the different $\text{Cu}\cdots\text{C}_{\text{atrane}}$ interactions also play a role in dictating the relative stabilities of the two isomers.
- 64 For a discussion of the conformational classifications of tripodal ligands, see: A. Kreider-Mueller, Y. Rong, J. S. Owen and G. Parkin, *Dalton Trans.*, 2014, **43**, 10852–10865.



- 65 A similar difference in energy (40.9 kcal mol⁻¹) is also calculated for [Tism^{PrBenz*}]H and [Tism^{PrBenz}]H with a 1 : 2 conformation akin to that of the solid state structure of the latter. In addition, the [Tism^{PrBenz*}]⁻ anion is 25.6 kcal mol⁻¹ higher in energy than the tris(imidazole) counterpart, [Tism^{PrBenz}]⁻, with the 3 : 0 conformation that is used for κ^4 -coordination.
- 66 Indeed, calculations on the parent imidazole demonstrate that the tautomer with one NH moiety is more stable than the tautomer with two NH groups. See: (a) G. Sini, O. Eisenstein and R. H. Crabtree, *Inorg. Chem.*, 2002, **41**, 602–604; (b) R. Tonner, G. Heydenrych and G. Frenking, *Chem.-Asian J.*, 2007, **2**, 1555–1567; (c) G. A. McGibbon, C. Heinemann, D. J. Lavorato and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1478–1481; (d) C. Heinemann and W. Thiel, *Chem. Phys. Lett.*, 1994, **217**, 11–16; (e) H. Basch, M. Krauss and W. J. Stevens, *Int. J. Quantum Chem.*, 1987, **31**, 405–415.
- 67 In this regard, it is pertinent to note that, whereas the geometry optimized Cu–C_{Het} bond length (2.005 Å) of [κ^4 -C₄-Tism^{PrBenz*}]Cu is shorter than the Cu–N bond lengths (2.073 Å) of [Tism^{PrBenz}]Cu, the opposite is observed for the lithium system, with the Li–C_{Het} distance (2.103 Å) being longer than the Li–N interaction (2.024 Å).
- 68 (a) R. J. Sundberg, R. F. Bryan, I. F. Taylor and H. Taube, *J. Am. Chem. Soc.*, 1974, **96**, 381–392; (b) M. Brill, J. Diaz, M. A. Huertos, R. Lopez, J. Perez and L. Riera, *Chem.-Eur. J.*, 2011, **17**, 8584–8595; (c) B. Eguillor, M. A. Esteruelas, J. Garcia-Raboso, M. Olivan, E. Onate, I. M. Pastor, I. Penafiel and M. Yus, *Organometallics*, 2011, **30**, 1658–1667; (d) M. H. Yu, H. H. Yang, A. R. Naziruddin, S. Kanne, B. H. Wang, F. C. Liu, I. J. B. Lin and G. H. Lee, *Eur. J. Inorg. Chem.*, 2016, 4829–4834; (e) M. A. Huertos, J. Perez, L. Riera, J. Diaz and R. Lopez, *Chem.-Eur. J.*, 2010, **16**, 8495–8507; (f) M. A. Huertos, J. Perez, L. Riera and A. Menedez-Veldazquez, *J. Am. Chem. Soc.*, 2008, **130**, 13530–13531; (g) M. A. Huertos, J. Perez, L. Riera, J. Diaz and R. Lopez, *Angew. Chem., Int. Ed.*, 2010, **49**, 6409–6412; (h) J. Ruiz and B. F. Perandones, *J. Am. Chem. Soc.*, 2007, **129**, 9298–9299.
- 69 Examples of the transformation of a C-coordinated ligand to a N-coordinated imidazole ligand have also been observed. See: (a) S. Burling, M. F. Mahon, R. E. Powell, M. K. Whittlesey and J. M. J. Williams, *J. Am. Chem. Soc.*, 2006, **128**, 13702–13703; (b) L. J. L. Haller and S. A. Macgregor, *Eur. J. Inorg. Chem.*, 2009, 2000–2006.
- 70 The isomerization of 2-substituted pyridines to afford N-heterocyclic carbene derivatives is also known. See, for example: (a) S. Conejero, J. Lopez-Serrano, M. Paneque, A. Petronilho, M. L. Poveda, F. Vattier, E. Alvarez and E. Carmona, *Chem.-Eur. J.*, 2012, **18**, 4644–4664; (b) F. Vattier, V. Salazar, M. Paneque, M. L. Poveda and E. Alvarez, *Organometallics*, 2014, **33**, 498–510.
- 71 For the formal 1,2-migration of silyl groups from nitrogen to carbon in N-heterocyclic carbenes, see: S. Sole, H. Gornitzka, O. Guerret and G. Bertrand, *J. Am. Chem. Soc.*, 1998, **120**, 9100–9101.
- 72 These data are for crystals of [Tism^{PrBenz}]NiBr·THF obtained from a solution in THF. A different crystalline form, [Tism^{PrBenz}]NiBr·C₆H₆, with similar bond lengths and angles, has also been obtained.
- 73 Note that the idealized trigonal bipyramidal structure of [Tism^{PrBenz}]NiBr is one in which the Br is in an equatorial site, which contrasts with the structure of [Tism^{PrBenz}]-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, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.
- 75 Distortions of this type are not uncommon for 5-coordinate d⁸ nickel centers. See, for example: (a) C. Janiak, L. Uehlin, H. P. Wu, P. Klufers, H. Piotrowski and T. G. Scharmann, *J. Chem. Soc., Dalton Trans.*, 1999, 3121–3131; (b) M. D. Santana, G. Garcia, A. A. Lozano, G. Lopez, J. Tudela, J. Perez, L. Garcia, L. Lezama and T. Roj, *Chem.-Eur. J.*, 2004, **10**, 1738–1746; (c) S. Zai, H. Gao, Z. Huang, H. Hu, H. Wu and Q. Wu, *ACS Catal.*, 2012, **2**, 433–440; (d) P. Chavez, I. G. Rios, A. Kermagoret, R. Pattacini, A. Meli, C. Bianchini, G. Giambastiani and P. Braunstein, *Organometallics*, 2009, **28**, 1776–1784; (e) F. Speiser, P. Braunstein, L. Saussine and R. Welter, *Organometallics*, 2004, **23**, 2613–2624; (f) R. Gao, M. Zhang, T. L. Liang, F. S. Wang and W. H. Sun, *Organometallics*, 2008, **27**, 5641–5648; (g) X. Hou, T. L. Liang, W.-H. Sun, C. Redshaw and X. Chen, *J. Organomet. Chem.*, 2012, **708**, 98–105; (h) J. Hou, W.-H. Sun, S. Zhang, H. Ma, Y. Deng and X. Lu, *Organometallics*, 2006, **25**, 236–244.
- 76 For a review of the structures of 5-coordinate nickel(II) compounds, see: D. M. Roddick and D. Zargarian, *Inorg. Chim. Acta*, 2014, **422**, 251–264.
- 77 For examples of nickel alkyl compounds with Ni–C bond lengths comparable to the sum of the covalent radii, see: (a) J. Cámpora, I. Matas, P. Palma, C. Graiff and A. Tiripicchio, *Organometallics*, 2005, **24**, 2827–2830; (b) C. Yoo, S. Oh, J. Kim and Y. Lee, *Chem. Sci.*, 2014, **5**, 3853–3858.

