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Syntheses, Reactivity and DFT Studies of Group 2 and Group 12 Metal Complexes of Tris(pyrazolyl)methanides Featuring "Free" Pyramidal Carbanions

Helen R. Bigmore,[b] Jens Meyer,[a] Ivo Krummenacher,[a, d] Heinz Rüegger,[d] Eric Clot,[c] Philip Mountford,*[b] and Frank Breher*[a]

Abstract: Reactions of $HC(Me_2pz)_3$ with Grignard reagents, dialkyl magnesium compounds and dimethylzinc are reported, together with a DFT study on some of the aspects of this chemistry. Reactions of $HC(Me_2pz)_3$ with MeMgX (X = Cl or Br) gave the half-sandwich zwitterionic compounds $[Mg({}^{Me}Tpmd)X]$ (X = Cl (**2**) or Br (**3**); ${}^{Me}Tpmd^- = [C(Me_2pz)_3]^-$). Addition of HCl to **2** gave the structurally characterised half-sandwich compound $[Mg\{HC(Me_2pz)_3\}Cl_2(thf)]$ (**4**). The zwitterionic sandwich compound $[Mg({}^{Me}Tpmd)_2]$ (**5**) formed in low yields in the reaction of MeMgX with $HC(Me_2pz)_3$ but was readily prepared from $HC(Me_2pz)_3$ and either $Mg\mathit{n}Bu_2$ or $MgPh_2$. The structurally characterised compound **5** contains two "naked" sp^3-hybridised carbanions fully separated from the dicationic metal centre. Only by using $MgPh_2$ as starting material could the half-sandwich compound $[Mg({}^{Me}Tpmd)Ph(thf)]$ (**6**) be isolated. The zwitterionic sandwich compound **5** reacted with HOTf ($OTf^- = [O_3SCF_3]^-$) to form the dication $[Mg\{HC(Me_2pz)_3\}_2]^{2+}$ ($\mathbf{7}^{2+}$), which was structurally characterised. Pulsed field gradient spin-echo (PGSE) diffusion NMR spectroscopy revealed both compounds to be intact in solution. In contrast to the magnesium counterparts, $HC(Me_2pz)_3$ reacted only slowly with $ZnMe_2$ (and not at all with $ZnPh_2$) to form the half-sandwich zwitterion $[Zn({}^{Me}Tpmd)Me]$ (**8**), which contains a cationic methylzinc moiety separated from a single sp^3-hybridised carbanion. Density functional calculations on the zwitterions $[M({}^{Me}Tpmd)Me]$ and $[M({}^{Me}Tpmd)_2]$ (M = Mg, Zn) revealed that the HOMO in each case is a ^{Me}Tpmd-based carbanion lone pair. The κ^1C isomers of $[M({}^{Me}Tpmd)Me]$ were calculated to be considerably less stable than their κ^3N-bound counterparts, with the largest gain in energy for Mg due to the greater ease of electron transfer from metal to the ^{Me}Tpmd apical carbon atom on formation of the zwitterion. Moreover, the computed M–C bond dissociation enthalpies of the κ^1C isomers of $[M({}^{Me}Tpmd)Me]$ are considerably higher than expected by simple extrapolation from the corresponding computed H–C bond dissociation enthalpy.

Keywords: density functional calculations · magnesium · tripodal ligands · zinc · zwitterions

Introduction

Multidentate ligands with dual functionality have attracted considerable interest in the last decades. The modification of "classical" chelating ligands by implementing additional coordination sites furnished novel flexible, ambidentate ligand systems. By analogy to Janus, the Roman mythological god of gates and doors, who is commonly depicted with two faces placed back to back, the term Janus-head ligands was coined years ago for such ambidentate ligand systems.[1]

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[a] J. Meyer, I. Krummenacher, Prof. Dr. F. Breher
Institut für Anorganische Chemie
Universität Karlsruhe (TH)
Engesserstrasse 15, 76131 Karlsruhe (Germany)
Fax: (+49) 721-608-84-40
E-mail: breher@aoc1.uni-karlsruhe.de

[b] Dr. H. R. Bigmore, Prof. Dr. P. Mountford
Chemistry Research Laboratory, University of Oxford
Mansfield Road, Oxford OX1 3TA (UK)
Fax: (+44) 1865-285-141
E-mail: philip.mountford@chem.ox.ac.uk

[c] Dr. E. Clot
Institut Charles Gerhardt Montpellier
UMR 5253 CNRS-UM2-UM1-ENSCM, cc 1501
Place Eugène Bataillon, 34095 Montpellier cedex 5 (France)

[d] I. Krummenacher, Dr. H. Rüegger
Laboratorium für Anorganische Chemie
Departement Chemie und Angewandte Biowissenschaften
ETH Zürich, 8093 Zürich (Switzerland)

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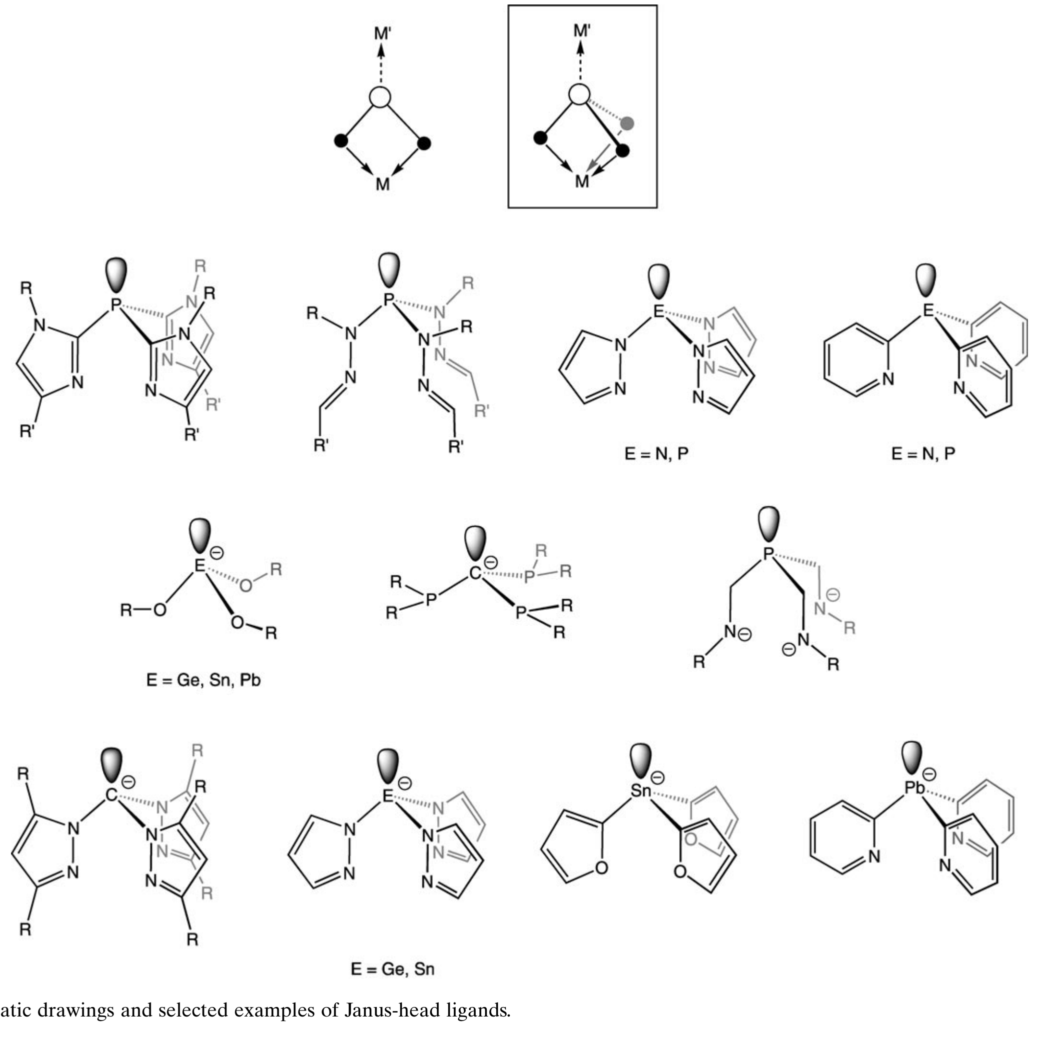
Particular interest in this class of ligands arises from the possibility of forming heterobimetallic complexes of general formula [M(μ-ligand)M′] with both metal atoms arranged in close spatial proximity in order to elucidate communication pathways between the metal centres, for instance. Schematic drawings and selected examples are shown in Scheme 1.

Apart from interesting systems featuring two pendant arms (indicated by ● in the schematic drawing in Scheme 1) and a second coordination site (○),[2] several tripodal molecular "claw" ligands[3] consisting of a κ^3-coordinating six-electron-donor pocket (●) alongside a two electron donor in the ligand backbone (○) can be found in the literature. Typical highly symmetric neutral ligands are, for instance, the well-known tris(imidazoyl)phosphines and their derivatives,[4] tris(hydrazonyl)phosphines,[5] as well as tris(pyrazolyl)-[6] and tris(pyridyl)amines and -phosphines.[7–10] Anionic systems such as $[E(OR)_3]^-$ (with E = Ge, Sn, Pb) and their metal complexes were developed some years ago by Veith et al.[11] Tris(phosphanyl)methanides are known from the work of Karsch and co-workers,[12] and only recently the tris(amido)phosphine ligand was employed by Johnson et al.[13] However, anionic systems featuring a more rigid ligand framework, that is, incorporating heterocyclic rings (and hence preorganised coordination sites) are comparatively rare. Among these the tris(pyrazolyl)germanides and -stannides of Stalke and Steiner,[14] the triorganotin derivative of Veith et al.[15] and the analogous tris(2-pyridyl)plumbate of Wright et al.[16] merit attention.

Recently, we reported on the synthesis, structures and/or computational studies of titanium(IV),[17] lithium,[18] copper(I), silver(I) and gold(I)[19] complexes of the tris(pyrazolyl)methanide ligand $[C(Me_2pz)_3]^-$ (^{Me}Tpmd$^-$),[20] which contains a potential two-electron-donor carbanion centre[21] in the apical position. Indeed, one interest[22] in this class of anionic ligands arises from this potentially reactive carbanion. Therefore, whereas "classical" tripodal ligands like the tris(pyrazolyl)hydroborates ($[HB(R_2pz)_3]^-$, Tp^R)[23] or their neutral analogues the tris(pyrazolyl)methanes ($HC(R_2pz)_3$, ^{R}Tpm),[24] have only pyrazolyl-based nitrogen lone pairs, ambidentate C^-/N ligands like ^{R}Tpmd may alternatively (or simultaneously) act as C-donor Lewis bases due to the carbanionic centre. This coordination mode was first observed by Stone et al. in the early 1990s for the Au^I complex $[Au(^HTpmd)C_6F_5]^-$.[25] In contrast, the lithium compound



Scheme 1. Schematic drawings and selected examples of Janus-head ligands.

[Li(^{Me}Tpmd)(thf)] (**1**) and the titanium complexes [Ti(^{Me}Tpmd)(NR)Cl(L)] (L = thf, py) are well-defined four- or six-coordinate monomeric zwitterions featuring κ^3N-coordinated ^{Me}Tpmd ligands with "naked", formally sp^3-hybridised apical carbanions. Interestingly, among the aforementioned Group 11 metal complexes [M(^{Me}Tpmd)PR$_3$] (M = Cu, Ag, Au; R = Ph, OMe),[19] the Cu^I and Ag^I complexes have a tetrahedral geometry in which the ^{Me}Tpmd ligands act as face-capping, κ^3N donors, whereas the Au^I congener is coordinated only by the apical carbanion of ^{Me}Tpmd, which results in a linear two-coordinate complex with a covalent Au−C bond. This different behaviour between Au^I and the other metals is seemingly in accord with the HSAB (hard/soft acids/bases) principle, which predicts that small, non-polarisable metal centres are expected to be coordinated by the "hard" N donors and softer metal centres by the carbanionic centre. It is also consistent with the well-known preference of Au^I for linear coordination.[26]

Here we extend our studies of the chemistry of the ^{Me}Tpmd ligand to the first sandwich and half-sandwich derivatives[27] of two representative divalent metals, namely, Mg and Zn, differing in size and electronegativity. In addition to a comparison of the bonding in the half-sandwich systems [M(^{Me}Tpmd)Me] we describe DFT studies on thermodynamic aspects of C−H bond metathesis reactions of HC(Me$_2$pz)$_3$ with two series of model metal alkyls [M(R)Me] (M = Mg or Zn; R = alkyl or Ph) to compare with recent results for the transition metals and certain zinc dialkyls.[28,29,58b,66]

Results

Experimental results

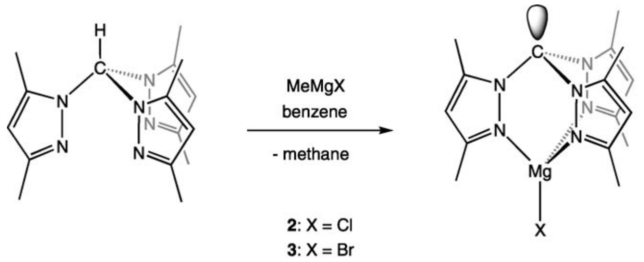
In preliminary studies, reactions with unsubstituted tris(pyrazolyl)methane HC(pz)$_3$ led to poorly soluble and highly sensitive materials. In all of the subsequent studies we therefore focused exclusively on the hexamethyl-substituted compound HC(Me$_2$pz)$_3$.

Reactions of HC(Me$_2$pz)$_3$ with Grignard reagents: In the reaction of HC(Me$_2$pz)$_3$ with Grignard reagents such as MeMgCl two principle reaction patterns may be anticipated [Eqs. (1) and (2)]. Equation (1) represents a simple deprotonation reaction to form a ^{Me}Tpmd halide complex of magnesium [Mg(^{Me}Tpmd)X]$_n$. In principle, the Schlenk equilibrium shown in Equation (2) could then be subsequently shifted to the right due to strong coordination of the anionic Tpmd ligand and thermodynamic (lattice energy) driving force for forming the MgX$_2$ side product.

$$\mathrm{HC(Me_2pz)_3 + MeMgX \rightarrow CH_4 + [Mg(^{Me}Tpmd)X]_n} \quad (1)$$

$$\mathrm{2\,[Mg(^{Me}Tpmd)X] \rightleftharpoons [Mg(^{Me}Tpmd)_2] + MgX_2} \quad (2)$$

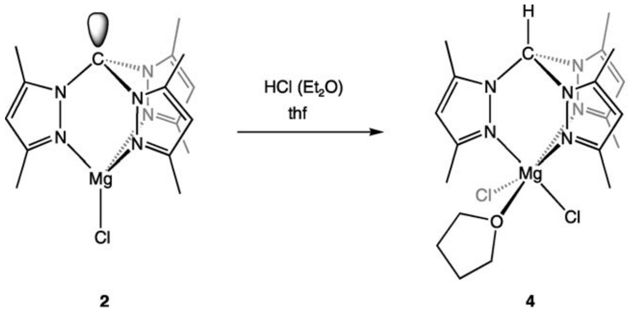
Reaction of HC(Me$_2$pz)$_3$ with one equivalent of ethereal solutions of MeMgX (with X = Br, Cl) in benzene formed highly insoluble colourless solids, which were isolated and characterised. Their elemental analyses were consistent with the composition "[Mg(^{Me}Tpmd)X]" [Scheme 2, X = Cl (**2**) or Br (**3**)]. The IR spectra (Nujol) showed the characteristic stretching frequencies of the pyrazolyl rings at 1551 (**2**) and 1555 cm^{-1} (**3**). Unfortunately, we were not able to obtain NMR data or single crystals of these highly insoluble materials. The analytical data alone do not rule out the possibility that **2** and **3** may be aggregated redistribution products of general composition "[Mg(^{Me}Tpmd)$_2$][MgX$_2$]", formed according to the Schlenk equilibrium [Eq. (2)]. However, the EI mass spectra showed no peaks above about *m/z* 321 (20%), which corresponds to the expected value and isotope distribution for [Mg(^{Me}Tpmd)]$^+$, that is, [*M*−X]$^+$. The independently synthesised sandwich compound [Mg(^{Me}Tpmd)$_2$] readily forms a molecular ion envelope centred at *m/z* 618 (see below). The absence of such a peak in the mass spectra of **2** and **3** suggests that these compounds do not contain [Mg(^{Me}Tpmd)$_2$] moieties. However, although it is reasonable to conclude that **2** and **3** are indeed half-sandwich species of the type "[Mg(^{Me}Tpmd)X]", they most likely exist as halogen-bridged dimers[30] or oligomers in the solid-state with magnesium coordination numbers of five or six (as found in the protonation product [Mg{HC(Me$_2$pz)$_3$}Cl$_2$(thf)] (**4**); vide infra).



Scheme 2. Synthesis of [Mg(^{Me}Tpmd)X] [X = Cl (**2**) or Br (**3**)].

We have shown previously that the apical carbanion of a metal-bound ^{Me}Tpmd ligand may be readily protonated to form the corresponding tris(pyrazolyl)methane complex.[17a] No tris(pyrazolyl)methane complexes of magnesium have yet been prepared, and we speculated that protonation of the apical carbanion in **2** with a suitable Brønsted acid would provide a suitable entry point. On reaction of a suspension of **2** in THF with ethereal HCl the appearance of the suspension immediately changed and we were able to isolate the poorly soluble tris(3,5-dimethylpyrazolyl)methane complex [Mg{HC(Me$_2$pz)$_3$}Cl$_2$(thf)] (**4**) in 29% yield after standard work-up procedures (Scheme 3).

The molecular structure of **4** is shown in Figure 1 (space group *P*2$_1$/*c*).[31] Compound **4**, which contains a CH group in the apical position of the ligand instead of the carbanion in **2**, is the first reported tris(pyrazolyl)methane complex of magnesium, and the first half-sandwich tris(pyrazolyl)methane complex of any Group 2 metal.[24] The Mg atom is oc-



Scheme 3. Synthesis of [Mg{HC(Me$_2$pz)$_3$}Cl$_2$(thf)] (**4**).

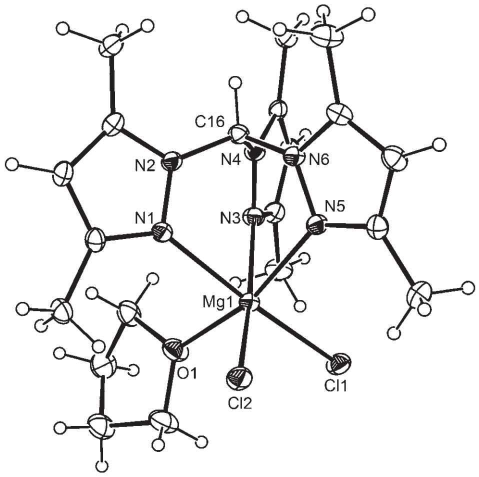


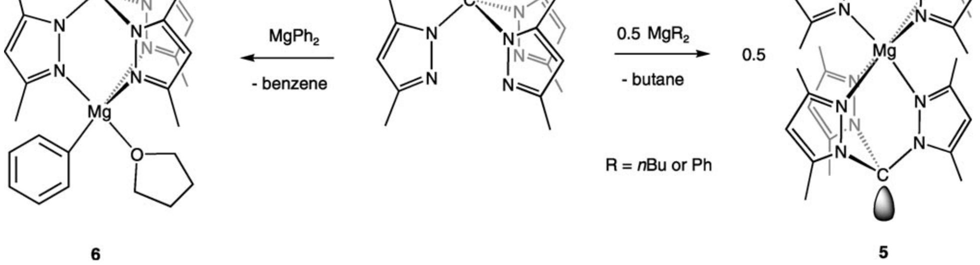
Figure 1. Molecular structure of [Mg{HC(Me$_2$pz)$_3$}Cl$_2$(thf)] (**4**). Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths [pm] and angles [°]: Mg1–N1 226.4(2), Mg1–N3 232.5(2), Mg1–N5 222.5(2), Mg1–Cl1 241.47(8), Mg1–Cl2 241.59(8), Mg1–O1 210.0(2), Mg1···C16 327.3, C16–N2 143.9(2), C16–N4 144.6(2), C16–N6 144.6(3); N2-C16-N4 111.9(2), N2-C16-N6 111.7(2), N4-C16-N6 111.0(2).

tahedrally coordinated by three pyrazolyl nitrogen donor atoms, two chloride ligands, and one THF donor molecule. The coordination sphere around Mg is strongly distorted. While comparatively narrow N-Mg-N angles (78.78(6)–83.06(6)°) are observed, the remaining ligands (Cl and THF) adopt angles of 97.21(3) (Cl1-Mg1-Cl2), 91.73(5) (Cl1-Mg1-O1), and 97.25(5)° (Cl2-Mg1-O1) between each other. The average Mg–N distance of 227.1 pm[32] is slightly longer than those found for other magnesium N-donor ligand complexes.[33] The Mg–Cl distances of 241.59(8) and 241.47(8) pm are comparable with those found in the literature.[34]

Although the insoluble compounds [Mg(^{Me}Tpmd)X] [X = Cl (**2**) or Br (**3**)] are the major products of the reaction of HC(Me$_2$pz)$_3$ with MeMgX, ^{1}H NMR monitoring of the reactions in C_6D_6 showed the characteristic signals for Me$_2$pz groups, the chemical shifts of which were identical regardless of the nature of X in the Grignard reagent. No apical CH proton was observed in either case. Although these observations are in principle consistent with the presence of solubilised traces of [Mg(^{Me}Tpmd)X] (**2** or **3**), on the basis of further studies described below we found they correspond to the formation of a zwitterionic sandwich complex [Mg(^{Me}Tpmd)$_2$] (**5**). Compound **5** is presumably formed through a Schlenk equilibrium, either according to Equation (2) above, or between solvated MeMgX and MgCl$_2$ and MgMe$_2$ followed by subsequent reaction of the latter with HC(Me$_2$pz)$_3$ (vide infra).

The sandwich complex [Mg(^{Me}Tpmd)$_2$] (**5**) was obtained on a preparative scale by addition of dioxane to the benzene-soluble portion obtained from a synthesis of [Mg(^{Me}Tpmd)Cl]. This yielded a colourless precipitate of [MgCl$_2$·dioxane]$_\infty$, and **5** was isolated from the organic phases in 18% yield. The ^{1}H and ^{13}C NMR and mass spectrometric (correct $[M]^+$) data and elemental analysis (no chlorine was detected) strongly supported the formation of **5**. The considerably higher solubility of **5** in hydrocarbon solvents compared to the monohalide species **2** and **3** is consistent with its formulation as a monomeric sandwich compound, confirmed by X-ray crystallography (vide infra).

Reactions of HC(Me$_2$pz)$_3$ with dialkyl magnesium reagents: In view of the low yield when prepared from Grignard reagents RMgX, we decided to prepare **5** in a more convenient way (Scheme 4). Thus, reaction of two equivalents of HC(Me$_2$pz)$_3$ with one equivalent of a heptane solution of Mg*n*Bu$_2$ in diethyl ether directly afforded **5** as a crystalline material in good yield (ca. 75% isolated product). The same results are obtained by using an ethereal solution of MgPh$_2$



Scheme 4. Synthesis of [Mg(^{Me}Tpmd)$_2$] (**5**) and [Mg(^{Me}Tpmd)Ph(thf)] (**6**).

(stoichiometry 2:1). Attempts to form half-sandwich compounds of the type [Mg(^{Me}Tpmd)R] (R = *n*Bu or Ph) by using a stoichiometric ratio of 1:1 ($HC(Me_2pz)_3$:MgR_2) only succeeded with $MgPh_2$ as starting material. However, even if the reaction is carried out at low temperature and an excess of $MgPh_2$ is used, the half-sandwich compound [Mg(^{Me}Tpmd)Ph(thf)] (**6**) only forms in low yields, and considerable amounts of **5** must be separated by fractional crystallisation.[35] Even though the crystallisation procedure was repeated several times, the isolated portions of **6** all contained impurities of $MgPh_2$. The latter had to be used in excess in order to suppress formation of sandwich complex **5**. As already mentioned, considerable amounts of **5** are formed if the stoichiometric ratio of 1:1 is used. From this behaviour it must be concluded that half-sandwich complex **6** is quite reactive and barely isolable prior to subsequent reaction with a second equivalent of $HC(Me_2pz)_3$. Although the impurities prevented full characterisation of **6** (vide infra) it is clearly an important intermediate formed en route to **5**. As shown below, a half-sandwich zwitterionic compound of zinc is readily available and does not form zwitterionic sandwich compounds [Zn(^{Me}Tpmd)$_2$].

Compound **5** is a colourless crystalline solid that is very sensitive to air and moisture but thermally stable with decomposition points in excess of 150 °C. The IR spectrum shows the characteristic stretching frequencies of the pyrazolyl rings at 1551 cm^{-1}. The ^1H NMR spectrum shows the pyrazolyl ring resonance at $\delta = 5.62$ ppm, whereas two further singlets at $\delta = 1.69$ and 2.52 ppm belong to the methyl substituents of ^{Me}Tpmd ($|\Delta\delta_{3,5}| = 0.83$).[36] The ^{13}C NMR resonance of the carbanionic moiety of **5** shows more or less the same chemical shift ($\delta = 73.7$) found for other κ^3N-^{Me}Tpmd complexes. The X-ray structure of **5** is discussed below.

The zwitterionic sandwich complex **5** is unique in organomagnesium chemistry in having no Mg–C bond and instead featuring two "naked" sp^3-hybridised carbanionic centres[37] fully separated from a Mg^{2+} cation, and we have investigated its solution behaviour in more detail. Pulsed field gradient spin-echo (PGSE) NMR measurements and determination of the diffusion coefficient for **5** ($D = 6.29 \times 10^{-10}\ m^2 s^{-1}$ in C_6D_6) revealed the compound to be monomeric (i.e., zwitterionic) in solution (see Figure 2).[38,39] The hydrodynamic radius ($r_H(\mathbf{5}) = 5.76$ Å) and volume ($V_H(\mathbf{5}) = 802$ Å^3)[40] were obtained by using the experimental *D* values together with the Stokes–Einstein equation. The latter value is in excellent agreement with the volume ($V_{X\text{-ray}} = 806$ Å^3) for an individual [Mg(^{Me}Tpmd)$_2$] complex obtained by X-ray crystallography (vide infra). Clearly, the Mg^{2+} ion is fixed within the pyrazolyl pockets in solution, showing the same behaviour as observed for the lithium derivative **1**.[18]

The molecular structure of [Mg(^{Me}Tpmd)$_2$] (**5**) is shown in Figure 3 and confirms the formation of a monomeric magnesium(II) complex in which the metal cation is coordinated by six pyrazolyl nitrogen atoms. Compound **5** crystallises in the trigonal space group $R\bar{3}$[31] with the magnesium atom on a special crystallographic position and three molecules in the unit cell. It can formally be described as zwitterion containing spatially separated carbanions (C1 and C1‴) and a dication (Mg1). The N-C1-N angles (108.9°) are in agreement with a (pseudo)tetrahedral environment at the sp^3-hybridised carbanionic centre and compare well with those found for other tris(3,5-dimethylpyrazolyl)methanide com-

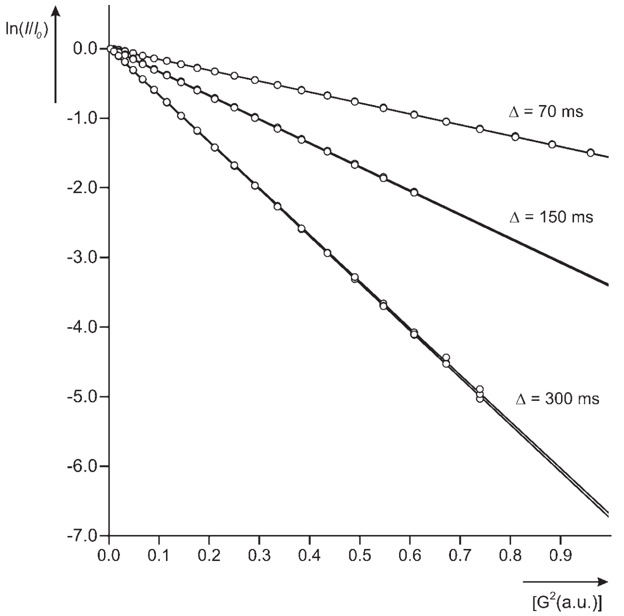


Figure 2. Plot of ln(I/I_o) versus arbitrary units proportional to the square of the gradient amplitude for ^1H PGSE NMR diffusion measurements on approximately 60 mM samples of [Mg(^{Me}Tpmd)$_2$] (**5**) at ambient temperature in C_6D_6 (^1H: $\Delta = 70$ ms (top), 150 ms (middle) and 300 ms (bottom); $D = 6.29 \times 10^{-10}\ m^2 s^{-1}$). Each experiment (open circles) was performed for each of the three proton resonances of **5**.

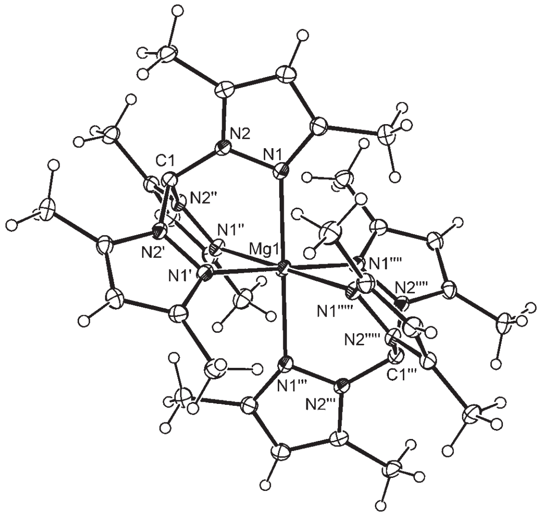


Figure 3. Molecular structure of [Mg(^{Me}Tpmd)$_2$] (**5**). Displacement ellipsoids drawn at the 30 % probability level. Selected bond lengths [pm] and angles [°]: Mg1–N1 218.9(1), C1–Mg1 319.8; N2-C1-N2′ 108.9(1), N1–Mg1-N1′ 84.42(5), N1-Mg1-N1⁗ 95.58(5). Equivalent atoms are generated by $-x+1, x-y+1, z$; $-x+y, -x+1, z$; $-x+2/3, -y+1/3, -z+1/3$; $y-1/3, -x+y+1/3, -z+1/3$; $x-y+2/3, x+1/3, -z+1/3$.

plexes.[17,18,19] The six nitrogen atoms of **5** span a trigonally distorted octahedron (approximately D_{3d} symmetry) around the Mg atom with independent values of 84.42(5) and 95.58(5)° for the N-Mg-N angles. The average Mg–N distance of 218.9(1) pm compares well with those for other magnesium complexes of N-donor ligands in the literature.[33] It is particularly relevant to compare the structural parameters of **5** with those of the tris(pyrazolyl)hydroborate analogue [Mg{HB(Me$_2$pz)$_3$}$_2$], which also has a sandwich structure.[41] In this complex the average Mg–N distance is 218.6 pm (cf. 218.9(1) pm in **5**) and the Mg···B distance is 320.2 pm (cf. Mg···C 319.8 pm in **5**).

The C1···Mg1 distance is about 100–110 pm longer[42] than usually observed in organomagnesium compounds featuring a direct Mg–C bond.[43] Any interaction between C1 and Mg1 must therefore be predominantly electrostatic in nature between the regions of negative and positive charge. For the six-coordinate complex [Mg{HC(Me$_2$pz)$_3$}Cl$_2$(thf)] (**4**) containing a neutral HC(Me$_2$pz)$_3$ ligand the Mg···CH distance is slightly longer (Mg1···C16 327.3(2) pm) than in **5**. This is consistent with DFT calculations previously performed for the lithium derivative **1**, for which small electrostatic interactions between the cation and anion were inferred from the calculated compliance constants.[18,44]

As mentioned above, crystalline portions of **6** always contained impurities of MgPh$_2$, which impeded precise assignment of the aryl ^{1}H and ^{13}C NMR resonances of **6** due to overlapping signals. Nonetheless, the ^{1}H NMR spectrum (C$_6$D$_6$) shows the typical resonances with chemical shifts of $\delta = 5.42$ ppm (CH$_{pz}$) and $\delta = 2.37$ and 2.06 ppm. The latter belong to the methyl substituents of ^{Me}Tpmd showing a separation $|\Delta\delta_{3,5}|$ of 0.31 ppm. Again we found a characteristic ^{13}C NMR resonance of the carbanion at $\delta = 73.3$. Heating a C$_6$D$_6$ solution of **6** and ^{1}H NMR spectroscopic monitoring did not show any formation of further amounts of MgPh$_2$ or sandwich compound **5**, which would have been the case if **6** were unstable with respect to a conceivable Schlenk equilibrium [Eq. (2) with X = Ph]. Furthermore, we were not able to detect the resonances of **6** upon heating a 1:1 mixture of MgPh$_2$·2 thf and **5** in [D$_8$]THF for 25 min at 60 °C in an NMR spectrometer.[45] Note that such a Schlenk equilibrium reaction was observed by Parkin et al. for the analogous Tp complexes [Mg{HB(Me$_2$pz)$_3$}R], which transform into the homoleptic species [Mg{HB(Me$_2$pz)$_3$}$_2$] and MgR$_2$ at 80–120 °C to about 90 % completion.[33j]

Although the crystalline portions of **6** are contaminated with MgPh$_2$ we were able to select a few single crystals of [Mg(^{Me}Tpmd)Ph(thf)] (**6**) suitable for X-ray diffraction (space group *C*2/c,[31] Figure 4). The X-ray structure confirms the formation of the half-sandwich complex with the magnesium cation pentacoordinated by one κ^3N-^{Me}Tpmd ligand, one Ph substituent, and one THF solvent molecule. Overall, the coordination geometry around magnesium can be described as distorted trigonal-bipyramidal. The three nitrogen donor atoms of the ^{Me}Tpmd ligand occupy two equatorial and one axial position. As was observed earlier, the strongest ligand occupies the equatorial sites in trigonal-bipyramidal coordination compounds, and therefore the phenyl substituent resides in the equatorial positions.[33b] The remaining thf donor coordinates axially. The zwitterionic half-sandwich compound shows both a direct M–C$_{Ph}$ bond (formally sp^2) and a non-coordinated, formally sp^3 hybridised apical carbanion that shows no bonding interaction with the metal centre. This structural motif is again very unusual for magnesium organyls.[37]

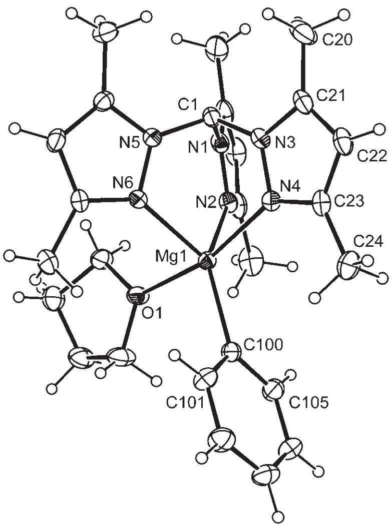
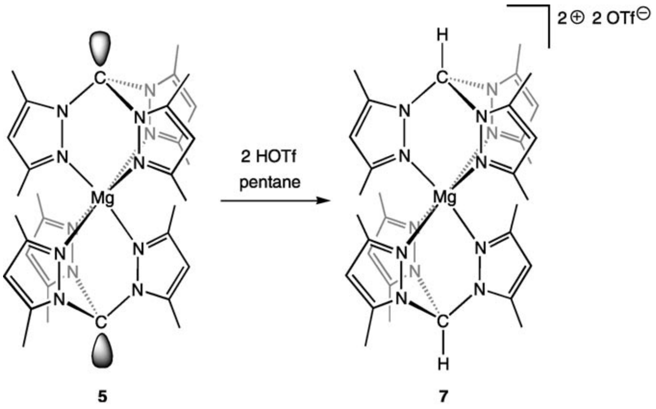


Figure 4. Molecular structure of [Mg(^{Me}Tpmd)Ph(thf)] (**6**). Displacement ellipsoids drawn at the 30 % probability level. Selected bond lengths [pm] and angles [°]: Mg1–N2 209.6(2), Mg1–N4 219.0(2), Mg1–N6 212.2(2), C1–Mg1 315.1, Mg1–O1 220.5(2), Mg1–C100 214.1(3); N1-C1-N3 109.1(2), N3-C1-N5 108.7(2), N1-C1-N5 109.3(2), C101-C100-C105 113.3(2), N2-Mg1-N6 90.93(8), N2-Mg1-C100 138.9(1), N6-Mg1-C100 129.94(9), N4-Mg1-O1 164.97(7).

The N-C1-N angles at the carbanionic centre (av 109.0°) fall in the typical range found for the ^{Me}Tpmd ligand. The intramolecular C1···Mg1 distance of 315.1 pm is shorter than that in the comparable sandwich compound **5** (cf. 319.8 pm), which might be attributed to the lower coordination number of Mg^{II} (five in **6**, six in **5**). The same shortening is observed for the average magnesium–nitrogen distance of 213.6(2) pm, which is again shorter than in hexacoordinate magnesium complex **5** (cf. 218.9(1) pm). Comparable bond lengths are known from the literature for some tetracoordinate magnesium alkyl complexes containing Tp-type ligands.[46] In **6**, however, the difference between the individual magnesium–nitrogen distances is much larger, ranging from 209.6(2) to 219.0(2) pm. On the one hand this may be attributed to steric interactions of one methyl group of ^{Me}Tpmd (C24) with the phenyl ligand (cf. torsion angle N3-N4-Mg1-C100 4.7°). On the other hand, trigonal-bipyramidal (D_{3h}) structures ML$_5$ typically have longer axial M–L distances (3c–4e bonding) than equatorial M–L distances. This was also found, for instance, by Chisholm et al. for the analogous compound [Mg{HB(3-Phpz)$_3$}Et(thf)] (cf. d(Mg–N$_{eq}$) = 218.2 pm, d(Mg–N$_{ax}$) = 228.6 pm).[33b] Compared to the latter, the Mg–N distances in **6** are, however, much shorter. The Mg–C$_{Ph}$ bond length of 214.1(3) pm is in agreement with other magnesium–phenyl distances known from the literature.[47] The distortion of the phenyl ligand (e.g., an acute C-C-C angle of 113.3° at the *ispo*-carbon atom) is comparable to examples known from the literature in which an aryl ligand is bonded to an electropositive metal. The additionally coordinated thf molecule (d(Mg–O) = 220.5(2) pm) is located between the remaining two pyrazolyl groups at N2 and N6. The oxygen atom slightly deviates from the ideal axial position ($\measuredangle$(N4-Mg1-O1) = 164.97(7)°).

Although sandwich-type bis[tris(pyrazolyl)methane] (i.e., neutral Tpm ligand) complexes of Ca^{2+} and Sr^{2+} have been reported,[48] no magnesium analogue is known. Therefore, following the successful protonation of [Mg(^{Me}Tpmd)Cl] (**2**) to afford **4** we carried out a similar reaction of **5** with 2 equiv of trifluoromethanesulfonic acid (HOTf). This furnished dicationic complex [Mg{HC(Me$_2$pz)$_3$}$_2$](OTf)$_2$ (**7**; OTf$^-$ = [O$_3$SCF$_3$]$^-$) in 63 % yield of isolated product (Scheme 5). Unlike its zwitterionic precursor, **7** is stable in air for days without any signs of decomposition. Note that **7** is also formed by treating two equivalents of HC(Me$_2$pz)$_3$ with Mg(OTf)$_2$ at room temperature in acetone. However, ^{1}H NMR spectroscopic monitoring of this reaction showed the conversion to be quite low.



Scheme 5. Synthesis of [Mg{HC(Me$_2$pz)$_3$}$_2$](OTf)$_2$ (**7**)

The ^{1}H NMR spectrum of **7** in [D$_6$]acetone clearly showed a signal for the apical HC(Me$_2$pz)$_3$ proton at $\delta = 8.46$ ppm and sharp methyl singlets at $\delta = 1.75$ and 2.87 ppm. The apical carbon atom is observed in an usual region in the ^{13}C NMR spectrum at $\delta = 69.8$ ppm, and the IR spectrum (solid, ATR) shows the characteristic stretching frequencies of the pyrazolyl rings at 1566 cm^{-1}. PGSE NMR measurements and determination of the diffusion coefficient for **7** ($D = 10.08 \times 10^{-10}$ m^{2}s^{-1} in [D$_6$]acetone at room temperature) revealed the compound to be integral in solution. The hydrodynamic radius (r_H(**7**) = 6.44 Å) and volume (V_H(**7**) = 1118 Å^3) are again in excellent agreement with the volume of an individual [Mg{HC(Me$_2$pz)$_3$}$_2$](OTf)$_2$ complex obtained by X-ray crystallography ($V_{X\text{-ray}} = 1113$ Å^3, vide infra). Again, the Mg^{2+} ion is fixed within the octahedral N$_6$ donor environment in solution.

The molecular structure of **7** is shown in Figure 5 (space group $P2_1/n$).[31] Consistent with the analytical data for **7**, the magnesium dication is coordinated by two HC(Me$_2$pz)$_3$ ligands and the triflate counteranions are well separated from the cation (shortest Mg···O distance ca. 488 pm). This is in contrast to the situation for analogous sandwich complexes of calcium and barium with HC(pz)$_3$: in these structures additional interactions of the counteranions result in coordination numbers of up to nine.[48] Like the other complexes described here, the coordination sphere around magnesium is trigonally distorted (two principle average N-Mg-N angles of 83.68 and 96.34°). The average Mg–N distance of 216.8 pm in **7** is marginally shorter than those in the zwitterionic complex [Mg(^{Me}Tpmd)$_2$] (**5**, av 218.9 pm) and the tris(pyrazolyl)hydroborate complex [Mg{HB(Me$_2$pz)$_3$}$_2$] (av 218.6 pm),[41] whereas a longer average Mg–N distance might have been expected compared to the latter complexes which contain anionic N$_3$ ligands. The origin of the shorter Mg–N distances in **7** is unclear, but since the differences are relatively small it may arise from crystal packing effects.

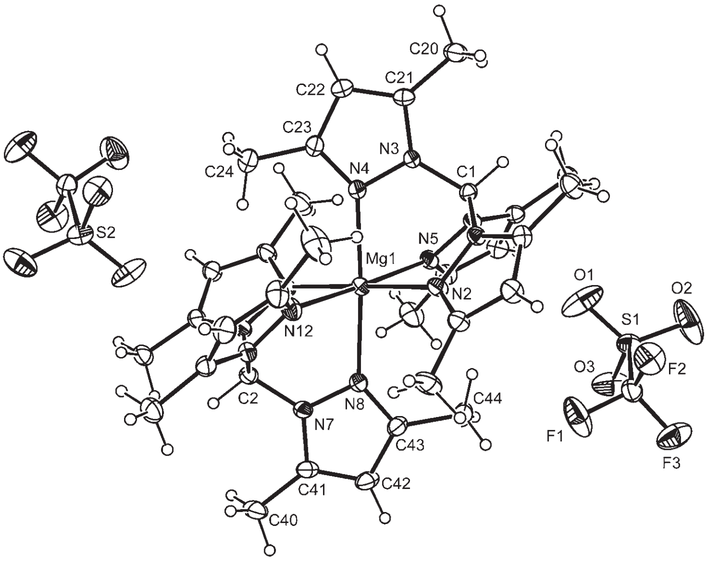
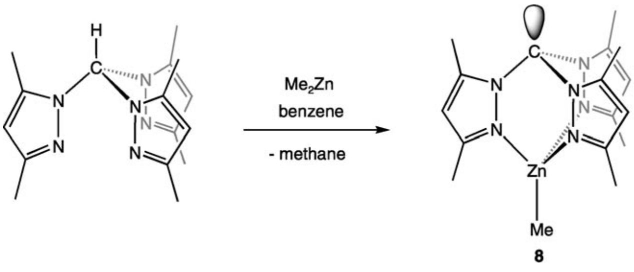


Figure 5. Molecular structure of [Mg{HC(Me$_2$pz)$_3$}$_2$](OTf)$_2$ (**7**). Displacement ellipsoids drawn at the 30 % probability level. Selected bond lengths [pm]: Mg1–N2 217.2(3), Mg1–N4 215.7(3), Mg1–N6 218.5(3), Mg1–N8 217.3(3), Mg1–N10 216.2(3), Mg1–N12 216.0(3), Mg1···C1 314.4, Mg1···C2 316.2.

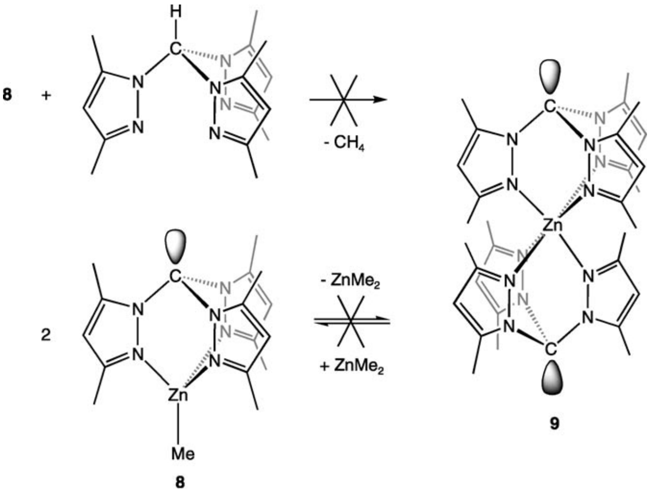
Reactions of HC(Me$_2$pz)$_3$ with dialkyl zinc reagents: To make comparisons with the magnesium chemistry discussed above and with the lithium compound [Li(^{Me}Tpmd)(thf)] (**1**), we performed analogous reactions of HC(Me$_2$pz)$_3$ with zinc alkyl and aryl reagents. Preliminary NMR-tube experiments with ZnMe$_2$ and HC(Me$_2$pz)$_3$ in C$_6$D$_6$ showed that this reaction was considerably slower than those between HC(Me$_2$pz)$_3$ and LiMe, MeMgX (X = Cl or Br) and MgR$_2$ (R = nBu or Ph) under analogous conditions. Nonetheless, treatment of HC(Me$_2$pz)$_3$ with a small excess of a toluene solution of $ZnMe_2$ in benzene and heating at 40 °C for six days gave $[Zn(^{Me}Tpmd)Me]$ (**8**) as an analytically pure powder in 45 % yield of isolated product (Scheme 6). Although we were not able to obtain single crystals of **8** the analytical, NMR and mass spectroscopic data are fully consistent with the half-sandwich structure depicted in Scheme 6.



Scheme 6. Synthesis of $[Zn(^{Me}Tpmd)Me]$ (**8**).

The EI mass spectrum showed no signals above the expected peaks for **8** at *m/z* 376 ($[M]^+$, 5 %) and *m/z* 361 ($[M{-}Me]^+$, 95 %) with the correct isotope distributions, and a bulk sample of **8** yielded a correct elemental analysis. The ^1H NMR spectrum of **8** showed resonances for a coordinated $^{Me}Tpmd$ ligand (presumably κ^3N) with no resonance for an apical CH moiety (C_6D_6, RT, $|\Delta\delta_{3,5}|=0.28$). The apical $C(Me_2pz)_3$ signal appeared at $\delta(^{13}C)=72.6$, and the methyl group attached to zinc gave a typical singlet at $\delta(^1H)=0.24$ ppm and quartet at $\delta(^{13}C)=-16.8$ ppm (non-decoupled ^{13}C). The $^1J_{CH}$ coupling constant of 118 Hz for the ZnMe group is identical to that reported for the tris(pyrazolyl)hydroborate complex $[Zn\{HB(Me_2pz)_3\}Me]$ by Parkin et al. (also in C_6D_6).[49] Since it is known that average $^1J_{CH}$ values of methyl groups are very sensitive probes of the effective electronegativity of the metal to which they are attached,[50] it can be concluded that the effective charge of the Zn atoms in these directly related zwitterionic complexes is the same and that the metal occupies more or less the same ligand environment in $[HB(Me_2pz)_3]^-$ and $[^{Me}Tpmd]^-$ complexes. This is also in line with our previous DFT calculations and experimental observations for other transition metal complexes, which suggest that $[HB(Me_2pz)_3]^-$ and $[^{Me}Tpmd]^-$ have similar bonding properties.[51]

Surprisingly, and in contrast to the zwitterionic magnesium compound $[Mg(^{Me}Tpmd)_2]$ (**5**), which can be readily prepared from both $Mg\textit{n}Bu_2$ and $MgPh_2$, or the highly reactive half-sandwich $[Mg(^{Me}Tpmd)Ph(thf)]$ (**6**), $ZnPh_2$ does not react with $HC(Me_2pz)_3$ even after extended periods of heating. This may be attributed to the stronger $Zn{-}C_{Ph}$ bond as compared to the organometallic magnesium counterpart, as investigated by DFT methods below. Similarly, monomethyl compound **8** does not react with a further equivalent of $HC(Me_2pz)_3$ to give a sandwich compound such as **9** (the Zn analogue of **5**). Furthermore, on heating solutions of **8** we found no NMR evidence for a ligand-redistribution process according to Scheme 7. This is also in sharp contrast to the behaviour observed for the magnesium compounds, which form highly reactive and hardly isolable half-sandwich compounds such as $[Mg(^{Me}Tpmd)Ph(thf)]$ (**6**) but instead readily form sandwich compounds (e.g., **5**, vide supra). Interestingly, and in contrast to our observations, Parkin et al. reported that ligand-exchange and -redistribution processes are facile for the tris(pyrazolyl)hydroborate analogue $[Zn\{HB(Me_2pz)_3\}Me]$.[52]



Scheme 7. Sandwich compound $[Zn(^{Me}Tpmd)_2]$ (**9**) is not experimentally accessible by reaction of **8** with $HC(Me_2pz)_3$ or by ligand redistribution.

Density functional calculations

As described above, the reactions of MgR_2 (R = *n*Bu, Ph) with $HC(Me_2pz)_3$ readily form the sandwich complex $[Mg(^{Me}Tpmd)_2]$ (**5**) or the reactive zwitterion $[Mg(^{Me}Tpmd)Ph(thf)]$ (**6**) in the case of $MgPh_2$. In contrast, $ZnMe_2$ forms only the half-sandwich complex $[Zn(^RTpmd)Me]$ (**8**), and no reaction was observed for $ZnPh_2$. Furthermore, in all instances only κ^3N-coordinated Tpmd ligands have been found. To gain further insight into the structures and reactivity patterns of the new sandwich and half-sandwich compounds and information on experimentally non-observable systems, we carried out a series of DFT calculations (RI-DFT/BP86/def2-TZVP)[53] using the TURBOMOLE program (see Supporting Information).[54]

Electronic structure of sandwich and half-sandwich compounds: Figure 6 shows the DFT computed geometries of $[Mg(^{Me}Tpmd)_2]$ (**5Q**, a model for the real compound **5**) and $[Mg(^{Me}Tpmd)Me]$ (**6Q**, a model for the half-sandwich compounds or intermediates $[Mg(^{Me}Tpmd)R]$ (R = *n*Bu or Ph) formed en route to **5**). Analogous geometries were computed for $[Zn(^{Me}Tpmd)_2]$ (**9Q**) and $[Zn(^{Me}Tpmd)Me]$ (**8Q**).

Table 1 lists relevant distances and angles for these model $^{Me}Tpmd$ compounds. We also carried out calculations on the corresponding H-substituted ^HTpmd systems ($^HTpmd = C(pz)_3$) $[M(^HTpmd)_2]$ [M = Mg (**5q**) or Zn (**9q**)) and $[M(^HTpmd)Me]$ (M = Mg (**6q**) or Zn (**8q**)], details of which

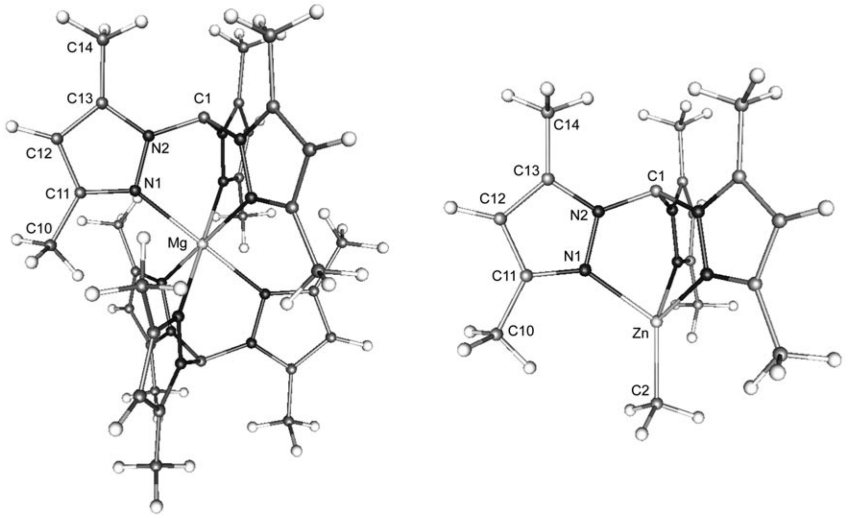


Figure 6. DFT computed structures of [Mg($^{\text{Me}}$Tpmd)$_2$] (**5Q**, left) and [Zn($^{\text{Me}}$Tpmd)Me] (**8Q**, right). The calculated structures of [Zn($^{\text{Me}}$Tpmd)$_2$] (**9Q**) and [Mg($^{\text{Me}}$Tpmd)Me] (**6Q**) are analogous.

Table 1. Selected DFT calculated bond lengths [pm] and angles [°] for the model sandwich and half-sandwich compounds [M($^{\text{Me}}$Tpmd)$_2$] [M = Mg (**5Q**) or Zn (**9Q**)] and [M($^{\text{Me}}$Tpmd)Me] [M = Mg (**6Q**) or Zn (**8Q**)].

Parameter	[M($^{\text{Me}}$Tpmd)$_2$]		[M($^{\text{Me}}$Tpmd)Me]	
	M = Zn (**9Q**)	M = Mg (**5Q**)[a]	M = Zn (**8Q**)	M = Mg (**6Q**)
M···C1	318.9	320.7 (319.8)	308.4	308.1
M−N1	221.0	225.5 (218.9)	210.6	214.0
C1−N2	144.1	144.2 (144.0)	144.5	144.5
M−C2	n.a.	n.a.	198.3	212.2
N2-C1-N2′	110.5	110.6 (108.9)	109.9	110.6
N1−N2	138.6	138.9 (138.1)	138.5	138.9

[a] Values in parentheses are distances and angles from the X-ray structure analyses of [Mg($^{\text{Me}}$Tpmd)$_2$] (**5**).

Table 2. DFT computed frontier orbital energies [eV] for various half-sandwich complexes [M($^{\text{R}}$Tpmd)Me] (R = H or Me; M = Mg or Zn).

Compound	Carbanion lone pair (HOMO)	M−Me bond orbital (HOMO−1)	$\Delta E_{\text{HOMO/HOMO−1}}$
[Mg($^{\text{H}}$Tpmd)Me] (**6q**)	−4.70	−4.95	0.25
[Zn($^{\text{H}}$Tpmd)Me] (**8q**)	−4.65	−5.74	1.09
[Mg($^{\text{Me}}$Tpmd)Me] (**6Q**)	−4.38	−4.81	0.43
[Zn($^{\text{Me}}$Tpmd)Me] (**8Q**)	−4.36	−5.55	1.19

are provided in Table S2 and Figure S1 in the Supporting Information. The structures and geometrical parameters for the pairs of homologous $^{\text{Me}}$Tpmd and $^{\text{H}}$Tpmd compounds [M($^{\text{R}}$Tpmd)$_2$] (and also [M($^{\text{R}}$Tpmd)Me]) complexes are effectively the same and independent of the nature of R and M, except that the Mg−N distances are slightly longer than those in the zinc analogues, as expected.[55]

Where experimental data are available (**5**) the agreement between computed and observed geometries is very good. The largest difference in interatomic distances between the Mg and Zn systems was found for the metal–methyl bond length, which is 14 pm shorter in [Zn($^{\text{Me}}$Tpmd)Me] (**8Q**) compared to the magnesium counterpart **6Q** (18 pm for [Zn($^{\text{H}}$Tpmd)Me] (**8Q**) compared to **6Q**). Similar results have been observed in X-ray structure analyses of structurally related [HB(Me$_2$pz)$_3$]$^-$ complexes of Mg and Zn.[55]

The half-sandwich compounds [M($^{\text{R}}$Tpmd)Me] are particularly interesting from a bonding and reactivity perspective. They feature a metal–methyl bond (formally an sp^3 CH$_3^-$ carbanion interacting with a cationic metal centre) and a uncoordinated sp^3-hybridised apical carbanion which shows no bonding interaction with the metal centre. The DFT calculations for [M($^{\text{R}}$Tpmd)Me] found in each case that the HOMO is localised on the apical carbanion, whereas the HOMO−1 is the σ(M−Me) bonding orbital. Table 2 summarises the HOMO and HOMO−1 energies for the four [M($^{\text{R}}$Tpmd)Me] compounds studied. In the previous DFT studies on the compounds [Li($^{\text{Me}}$Tpmd)(thf)] (**1**) and [Ti($^{\text{Me}}$Tpmd)(NR)Cl(thf)] the HOMO in each case was also the apical carbanionic lone pair.[17,18]

The energy of the carbanion-based HOMO is effectively independent of the nature of the metal for a given $^{\text{R}}$Tpmd ligand (cf. **8q**/**6q** and **8Q**/**6Q**), although some energy perturbations may occur due to symmetry-allowed mixing of HOMO and HOMO−1. The largest effect on the HOMO energy is in fact provided by the 3,5-methyl substituents of the pyrazolyl rings, presumably due to inductive effects. Therefore, although the carbanionic lone pair in the H-substituted [C(pz)$_3$]$^-$ anions is sterically more accessible, the Me-substituted [C(Me$_2$pz)$_3$]$^-$ anions are more nucleophilic.

The HOMO energy can serve as a kind of internal reference when comparing different metal complexes of a particular $^{\text{R}}$Tpmd ligand. The most significant difference between the Mg and Zn compounds is the energy difference (denoted $\Delta E_{\text{HOMO/HOMO−1}}$ in Table 2) between the carbanion HOMO and the metal–carbon bond HOMO−1. This may be attributed to the greater electronegativity of Zn ($\chi_{\text{P}} = 1.65$) versus Mg ($\chi_{\text{P}} = 1.31$) and higher effective nuclear charge of the metal valence s and p orbitals for Zn.[56] The well-recognised higher covalent character of the Zn−C bond compared to Mg−C leads to a much more energetically stabilised metal–carbon σ bond that is less polar (see below) and more covalent for Zn than Mg.[57]

κ^1*C* versus κ^3*N* coordination in [M($^{\text{Me}}$Tpmd)Me] systems: As mentioned, Au$^{\text{I}}$ $^{\text{R}}$Tpmd complexes exist as linear κ^1*C*-coordinated species $[Au(^{H}Tpmd)C_6F_5]^-$[25] or $[Au(^{Me}Tpmd)(PPh_3)]$,[19] whereas all other ^{R}Tpmd species so far described have κ^3*N*-coordinated ligands.[17,18,19] Diorgano zinc species ZnR_2 (R = alkyl or aryl) are often found as linear, two-coordinate complexes in the gaseous[58] and solid states,[59] especially for bulky ligands.[60] Although much less common, linear two-coordinate MgR_2 (R = alkyl, aryl) have also been structurally characterised for sterically demanding R groups.[43,61] It was therefore of interest to compare the relative energies of the κ^1*C*- and κ^3*N*-coordinated ^{Me}Tpmd isomers for Mg and Zn. The DFT computed structures for κ^1*C*-coordinated isomers [Mg(κ^1*C*-^{Me}Tpmd)Me] (**6Q′**) and [Zn(κ^1*C*-^{Me}Tpmd)Me] (**8Q′**) are shown in Figure 7; selected bond lengths and angles are compiled in Table 3. Although *C*-coordinated isomers featuring one κ^1*C*,κ^1*N*- or two κ^1*C*,κ^2*N*-coordinated pyrazolyl groups are also energetically viable, we focus exclusively on the κ^1*C*-coordinated systems in order to estimate the energetics arising solely from the metal–carbon bonds.

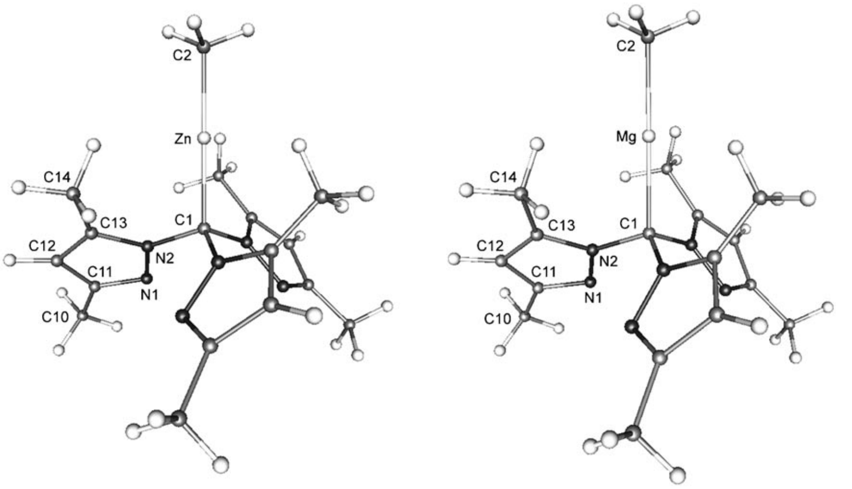


Figure 7. DFT computed structures of [Zn(κ^1*C*-^{Me}Tpmd)Me] (**8Q′**, left) and [Mg(κ^1*C*-^{Me}Tpmd)Me] (**6Q′**, right).

Table 3. Selected DFT computed bond lengths [pm] and angles [°] for the model κ^1*C*-coordinated complexes [Mg(κ^1*C*-^{Me}Tpmd)Me] [M = (**6Q′**) or Zn (**8Q′**)].

Parameter	[Mg(κ^1*C*-^{Me}Tpmd)Me] (**6Q′**)	[Zn(κ^1*C*-^{Me}Tpmd)Me] (**8Q′**)
M−C1	218.3	203.1
M−C2	209.4	194.9
C1-M-C2	179.6	179.8
C1−N2	109.5	109.4
N2-C1-N2′	146.5	146.7

In the κ^1*C*-^{Me}Tpmd complexes **6Q′** and **8Q′** the pyrazolyl substituents adopt a "propeller-like" arrangement. The geometries around the central Mg and Zn atoms are approximately linear, as is experimentally observed in the solid state and gas phase for dialkyl and diaryl complexes MR_2.[43,61] The $M{-}C(Me_2pz)_3$ distances are within bonding range (218.3 and 203.1 pm for **6Q′** and **8Q′**, respectively) but much longer than the M−Me distances (209.4 and 194.9 pm, respectively), as expected. The M−Me distances in **6Q′** and **8Q′** are shorter than in the κ^3*N*-coordinated isomers **6Q** (212.2 pm) and **8Q** (198.3 pm), and this reflects the higher coordination numbers in the latter. In all cases the Mg−C distances are longer than the Zn−C counterparts.

As a starting point for understanding the κ^1*C* versus κ^3*N* coordination preferences of the various [M(^{Me}Tpmd)Me] species, we computed the gas-phase reaction energies of forming CH_4 and [M(κ^1*C*-^{Me}Tpmd)Me] [M = Zn (**8Q′**) or Mg (**6Q′**)] from $HC(Me_2pz)_3$ and the dimethyl compounds MMe_2 [M = Zn or Mg; Eq. (3)].[62] In these calculations we used the $HC(Me_2pz)_3$ minimum structure featuring a "propeller-like" arrangement of the pyrazolyl groups with all nitrogen lone pairs oriented away from the apical C−H bond (analogous to the [M(κ^1*C*-^{Me}Tpmd)Me] species). A slightly different rotamer is found experimentally (one N lone pair "up" toward the CH group)[63] and DFT also finds this to be slightly favoured (by 16.5 kJ mol^{-1}). However, in order to exclude energetic contributions resulting from intramolecular rearrangement processes of the Me_2pz groups prior to reacting with MMe_2, and thus to account only for the energetics of the M−C bond, we performed the calculations with this "all lone pairs down" isomer.

$$HC(Me_2pz)_3 + MMe_2 \rightarrow [M(\kappa^1C\text{-}^{Me}Tpmd)Me] + CH_4 \qquad (3)$$

Overall we found that for Mg (**6Q′**) the reaction enthalpy was slightly favourable ($\Delta_rE = -15.4$ kJ mol^{-1}), whereas for Zn (**8Q′**) it was slightly unfavourable ($\Delta_rE = +6.1$ kJ mol^{-1}). We will return to a further discussion of these energetics of σ-bond metathesis later.

Whereas the κ^1*C*-coordinated isomers are not strongly favoured relative to the separated $HC(Me_2pz)_3$ and MMe_2 starting materials [Eq. (3)], the κ^3*N*-coordinated isomers are considerably more stable. According to the calculations [Zn(κ^3*N*-^{Me}Tpmd)Me] (**8Q**) is 129.8 kJ mol^{-1} more stable than [Zn(κ^1*C*-^{Me}Tpmd)Me] (**8Q′**), and [Mg(κ^3*N*-^{Me}Tpmd)Me] (**6Q**) is 233.0 kJ mol^{-1} more stable than [Mg(κ^1*C*-^{Me}Tpmd)Me] (**6Q′**) [Eq. (4)]. These differences for Mg and Zn highlight the importance of the nature of the metal on the deprotonation and coordination chemistry of $HC(Me_2pz)_3$ and ^{Me}Tpmd.

$$[M(\kappa^1C\text{-}^{Me}Tpmd)Me] \rightarrow [M(\kappa^3N\text{-}^{Me}Tpmd)Me] \qquad (4)$$

Based on these data, it is the overall change from κ^1C to κ^3N coordination that appears to provide the substantial driving force for the real reactions of $HC(Me_2pz)_3$ with organomagnesium and -zinc compounds. To gain a better understanding of the κ^1C to κ^3N rearrangement process we analysed the process in terms of three hypothetical steps using the thermodynamic cycle illustrated in Figure 8. We do not suggest that Figure 8 represents a true experimental mechanism. All geometries were fully optimised. Since the theoretical treatment of anionic species is often problematic, we used an appropriate "solvent-cage" approximation [conductor-like screening model[64] (COSMO) in Et_2O ($\varepsilon=4.27$)]. The energies for the individual steps in Figure 8 are compiled in Table 4. Note that some of the energies differ slightly from those discussed elsewhere in the text due to the use of the COSMO model.

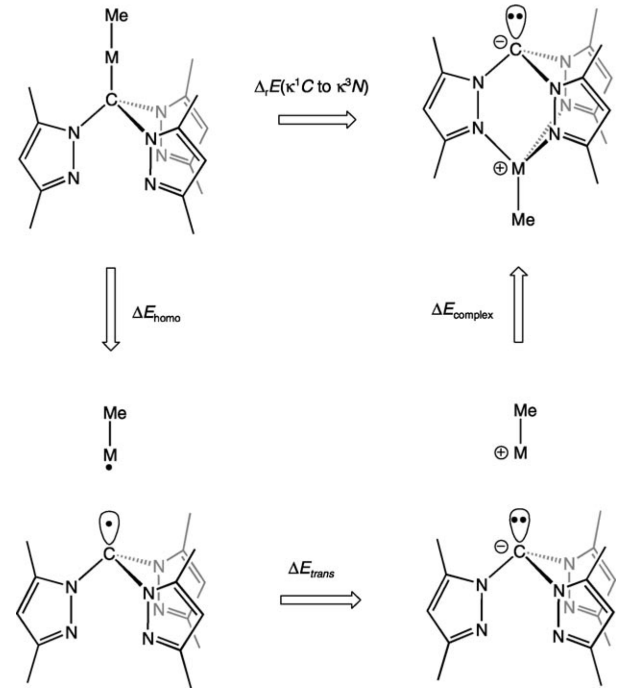


Figure 8. Hypothetical thermodynamic cycle for the κ^1C to κ^3N rearrangement of the [M(Tpmd)Me] complexes: M–C bond homolysis (ΔE_{homo}); electron transfer (ΔE_{trans}) from the $[MMe]^\bullet$ fragment (ionisation) to the $[^{Me}Tpm]^\bullet$ radical (electron gain); complexation of $[^{Me}Tpmd]^-$ to $[MMe]^+$ ($\Delta E_{complex}$). $\Delta_rE(\kappa^1C\rightarrow\kappa^3N)=\Delta E_{homo}+\Delta E_{trans}+\Delta E_{complex}$.

The M–C bond homolysis (ΔE_{homo}) is about 30 kJ mol^{-1} more unfavourable for Zn than for Mg. In contrast, the final complexation step of $[MMe]^+$ by $[^{Me}Tpmd]^-$ ($\Delta E_{complex}$) is considerably more favoured for Zn ($\Delta\Delta E_{complex}=$ 113.1 kJ mol^{-1}). Thus, in terms of metal–ligand bond energies alone the κ^1C to κ^3N rearrangement [($\Delta_rE(\kappa^1C\rightarrow\kappa^3N)$)] should be more favourable for Zn, which is not the case (Table 4). However, examination of the second step in Figure 8 (electron transfer from $[MMe]^\bullet$ to $[^{Me}Tpm]^\bullet$) shows a considerably more endothermic process for Zn than Mg ($\Delta\Delta E_{trans}=169.8$ kJ mol^{-1}), and it is this term which controls the overall $\Delta_rE(\kappa^1C\rightarrow\kappa^3N)$ value. This second step involves both the electron-gain process $[^{Me}Tpmd]^\bullet+e^-\rightarrow[^{Me}Tpmd]^-$ and the ionization process $[M^IMe]^\bullet\rightarrow[M^{II}Me]^++e^-$. Since the former is independent of Mg and Zn, the ionization of $[M^IMe]^\bullet$ is the only contribution dependent on the identity of the metal. The higher ΔE_{trans} term thus reflects the higher atomic ionisation energies for Zn ($I_{1,2}=906.4$, 1733.3 kJ mol^{-1}) than for Mg (737.1, 1450.7 kJ mol^{-1}).[65] From these calculations we conclude that the magnitude of Δ_rE for the κ^1C to κ^3N rearrangement of a general $[M(^{Me}Tpmd)X]$ system reflects both the bond-enthalpy changes on going from a κ^1C to κ^3N coordination mode, and also the energy required to move an electron from the [MX] fragment to a coordinated κ^3N-Tpmd moiety.

Table 4. Energetic contribution [kJ mol^{-1}] of the individual steps of the κ^1C to κ^3N rearrangement defined according to Figure 8.

	ΔE_{homo}	ΔE_{trans}	$\Delta E_{complex}$	$\Delta_rE(\kappa^1C\rightarrow\kappa^3N)$
M = Mg	136.4	88.7	−424.3	−199.2
M = Zn	167.6	258.5	−537.4	−111.3

Sandwich-complex formation: Mg versus Zn: As noted above, $HC(Me_2pz)_3$ reacts readily with MgR_2 (R = *n*Bu or Ph) to form the sandwich complex $[Mg(^{Me}Tpmd)_2]$ (**5**), whereas $ZnMe_2$ forms only the half-sandwich $[Zn(^{Me}Tpmd)Me]$ (**8**) even after prolonged reaction times. In contrast, the comparable half-sandwich compound $[Mg(^{Me}Tpmd)Ph(thf)]$ (**6**) was found to be highly reactive towards $HC(Me_2pz)_3$. To shed more light on the experimentally observed behaviour we calculated the electronic energies $\Delta_rE_{(R,M)}$ for the reaction of the methyl compounds $[M(^RTpmd)Me]$ with $HC(R_2pz)_3$ to afford the sandwich complexes $[M(^RTpmd)_2]$ and CH_4 [M = Mg or Zn; R = H or Me; Eq. (5)].

$$[M(^RTpmd)Me]+HC(R_2pz)_3\rightarrow[M(^RTpmd)_2]+CH_4 \qquad (5)$$

In addition to the gas-phase calculations, we also performed single-point calculations using the COSMO model[64] for Et_2O ($\varepsilon=4.27$) and benzene ($\varepsilon=2.28$)[65] and the gas-phase geometries. Entropy effects were not included and are assumed to be approximately equivalent in each case. However, the value of the $T\Delta_rS$ term is likely to be unfavourable in these reactions due to the higher ordering of the coordinated ^{R}Tpmd ligand in the products $[M(^RTpmd)_2]$ compared with the "free" $HC(R_2pz)_3$ ligand precursors. The results are summarised in Table 5.

Table 5 shows that in all cases the energy of formation of the $[M(^RTpmd)_2]$ systems ($\Delta_rE_{(R,M)}$) is considerably more thermodynamically favourable for M = Mg than for Zn by between −120 and −127 kJ mol^{-1}. This is in agreement with the experimental observations. The differences depend only to some extent on the R groups of the ^{R}Tpmd ligand and the calculation model. These differences are also comparable to that (124.7 kJ mol^{-1}) between the Δ_rE values for the formation of the κ^3N-coordinated $[M(^{Me}Tpmd)Me]$ com-

Table 5. Calculated reaction energies $\Delta_rE_{(R,M)}$[a] [kJ mol^{-1}] for Equation (5) in the gas phase (g) and in benzene ($\varepsilon=2.28$) or Et_2O ($\varepsilon=4.27$) "solution".

$\Delta_rE_{(R,M)}$	R=H (g)	R=H (benzene)	R=H (Et_2O)	R=Me (g)	R=Me (benzene)	R=Me (Et_2O)
M=Mg	−203.9	−182.2	−167.9	−174.0	−148.5	−134.6
M=Zn	−79.6	−59.4	−47.5	−46.9	−25.2	−13.2

[a] $\Delta_rE_{(R,M)}$ refers to the reaction energy for [M(^{R}Tpmd)Me] as a function of metal (M) and ^{R}Tpmd ligand substitutents R.

plexes from MMe_2 and $HC(Me_2pz)_3$ [Eqs. (3) and (4)] and presumably have analogous electronic origins (vide supra: a more unfavourable Zn−Me/H−C($R_2pz)_3$ σ-bond metathesis reaction and a more endothermic ionisation energy for Zn compared to Mg). Table 5 also predicts a destabilisation of between 30 and 34 kJ mol^{-1} on introducing the 3,5-dimethyl substituents in the [M(^{Me}Tpmd)$_2$] systems (R=H vs. Me). Although steric effects clearly may be important here, we note from Table 2 that the ring methyl substituents destabilise the carbanion lone pairs by about 30 kJ mol^{-1} and thus make a formal electron-transfer step from [M^I] to [^{Me}Tpmd]$^•$ less favourable.

Finally we note that the choice of reaction solvent might also contribute to the reaction energetics, since more polar solvents (benzene vs. Et_2O) substantially disfavour the formation of the sandwich compounds [M(^{Me}Tpmd)$_2$] according to the COSMO model. This effect is attributed to the larger dipole moment of the half-sandwich compounds [M(^{Me}Tpmd)Me], whereas the dipole moment of the sandwich compounds is essentially zero.

Thermodynamic aspects of the H−C/M−R exchange reactions of $HC(Me_2pz)_3$ with MR_2: Describing and understanding the relationships between M−R bond dissociation enthalpies ΔH(M−C) and the corresponding hydrocarbon R−H enthalpies ΔH(H−C) continues to attract much interest from both a DFT and experimental perspective.[28,29,58b,66] Density functional theory has been shown to reproduce experimental trends in bond enthalpy and has been applied to both transition metal and main group systems (notably zinc dialkyls) for both real systems and those for which experimental data do not exist. An important parameter when discussing relationships between M−C and H−C bond enthalpies is the gradient $\zeta^{M-C/H-C}$ of the best-fit line in plots of ΔH(M−C) versus ΔH(H−C).[28,29,58b] While the dissociation enthalpies of both M−C and H−C bonds increase in the general order tertiary < secondary < primary and sp^3-hybridised < sp^2 < sp, the former increase more rapidly and the values cover a wider range. The $\zeta^{M-C/H-C}$ values are therefore invariably greater than unity, although the actual gradients depend on the metal and method used.

Green, Downs and co-workers recently reported DFT correlations of the Zn−C and H−C bond enthalpies for dialkyls ZnR_2 (R = Me > CH_2SiMe_3 > CH_2CMe_2 > *n*Pr > Et > *i*Pr > *t*Bu), which furnished a $\zeta^{Zn-C/H-C}$ value of about 1.5.[58b] The calculated ΔH(Zn−C) values also correlated well with experimental Zn−C distances (longest Zn−C distances for the weakest Zn−C bonds) and the product −*Q*(Zn)*Q*(α-C), which was used as a measure of Zn−C bond polarity (*Q* is the net atomic charge based on Mulliken population analyses). Larger bond-polarity terms were associated with larger bond enthalpies.

With these observations in mind, it was surprising that the DFT calculations on the reaction of $HC(Me_2pz)_3$ with MMe_2 to form [M(κ^1*C*-^{Me}Tpmd)Me] and CH_4 [Eq. (3)] was in fact either only marginally disfavoured (M=Zn, Δ_rE = +6.1 kJ mol^{-1}) or slightly favoured (M=Mg, Δ_rE = −15.4 kJ mol^{-1}). These results suggested that the energy gain on replacing the tertiary apical CH group of $HC(Me_2pz)_3$ by a C−M bond (M=Zn, Mg) is significantly greater than would be expected based on the simple alkyls studied by Green et al.[58b]

To probe this apparently anomalous behaviour we evaluated the bond dissociation enthalpies of the M−R bonds in the model series of compounds M(R)Me (M=Mg or Zn; R=Ph, Me, Et, *n*Pr, *i*Pr, *t*Bu and C($Me_2pz)_3$). We compared the relative (with respect to R=C($Me_2pz)_3$) bond enthalpies ΔH(M−C)$_{rel}$ to those calculated for the alkanes HR (ΔH(H−C)$_{rel}$). The results are illustrated in Figure 9 for values obtained by using the BP86 functional (comparable results were obtained by using the B3PW91 functional). The geometries of the M(R)Me compounds correspond well to those obtained by others from DFT calculations[67,58] or which are known from structural determinations (κ^1*C*-^{Me}Tpmd complexes are not known for Zn or Mg).[42,43,59,60] Further parameters derived from the calculations are given in Tables S3 and S4 in the Supporting Information.

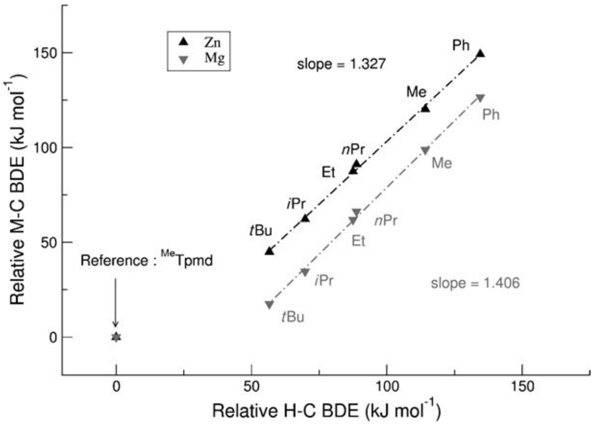


Figure 9. BP86 calculated ΔH(M−C)$_{rel}$ versus ΔH(C−H)$_{rel}$ bond dissociation enthalpies (BDE [kJ mol^{-1}]) for M(R)Me and RH. Values are given relative to R=^{Me}Tpmd. "Slope" refers to the quantity $\zeta^{M-C/H-C}$ (M=Zn or Mg) excluding the data point for R=TPM.

In agreement with previous work, Figure 9 shows an excellent correlation between ΔH(M−C)$_{rel}$ and ΔH(C−H)$_{rel}$ for the conventional alkyl groups and Ph (i.e., when the H−C($Me_2pz)_3$/M−C($Me_2pz)_3$ systems are excluded), with slopes of $\zeta^{M-C/H-C}$ = 1.327 (Zn) and 1.406 (Mg). The larger

$\zeta^{M-C/H-C}$ for Mg suggests a greater ionic contribution for Mg–C bonding relative to Zn–C cases.[58b,29] Consistent with this, the products $-Q(M)Q(\alpha\text{-CR})$ (natural population analyses,[68] see also Table S3 in the Supporting Information) are larger in magnitude for M = Mg for a given R group.

The data points for the H–C(Me$_2$pz)$_3$/M–C(Me$_2$pz)$_3$ systems are apparently anomalous. The calculated ΔH(H–C) for HC(Me$_2$pz)$_3$ is much lower than that of the other tertiary alkane *t*BuH.[69] The weakening of C–H bonds in positions alpha to N atoms has been noted previously.[70] In contrast, the ΔH(M–C) values are significantly larger than would be expected from extrapolation of the other values. The deviation of the calculated ΔH(Mg–C) from the extrapolated line is larger than that for ΔH(Zn–C) and points to an effect of the electronegativity of the metal. A similar plot to Figure 9 was obtained for both $\Delta H(\text{M–C})_{\text{rel}}$ versus calculated metal–carbon distances d(M–CR) or versus $-Q(M)Q(\alpha\text{-CR})$. Thus, the compounds M(R)Me with conventional alkyl groups gave an excellent correlation (as expected from the work of Green et al.),[58b] whereas the $\Delta H(\text{M–C})_{\text{rel}}$ values for [M(κ^1*C*-$^{\text{Me}}$Tpmd)Me] were consistently higher than expected, in particular for M = Mg.

The radical relaxation energies ($\Delta H_{\text{Relax}}(\text{R}^\bullet)$, see Table S3 in the Supporting Information) for the conventional alkyl groups after M–R bond homolysis are comparable [range −40 to −45 kJ mol^{-1} (M = Mg) and −36 to −42 kJ mol^{-1} (M = Zn)] so they do not significantly influence the $\zeta^{M-C/H-C}$ values (analogous results were reported by Green et al. for their homoleptic ZnR$_2$ systems). The corresponding values for the M(κ^1*C*-$^{\text{Me}}$Tpmd)Me systems are larger (−60.7 and −55.8 kJ mol^{-1} for Mg and Zn, respectively) and so would lead to a comparative lowering of ΔH(M–C),[71] not the apparent increase observed.

At this stage the origins of the higher than expected M–C bond enthalpies for M(κ^1*C*-$^{\text{Me}}$Tpmd)Me are not entirely clear, but we propose that they are associated with the ability of the pyrazolyl groups of $^{\text{Me}}$Tpmd to stabilise the negative charge which would otherwise accumulate on the carbon atom of the intrinsically polar M–C bond. This effect would be greater for the more electropositive Mg than Zn, in agreement with Figure 9 and the other correlation plots mentioned above.

For the "conventional" alkyl compounds Mg(R)Me, the metal charges Q(Mg) are broadly invariant and fall in the range +1.43 to +1.46 (+1.18 to +1.21 for Zn) while the $Q(\alpha\text{-CR})$ values vary from −1.39 (R = Me) to −0.52 (R = *t*Bu) (−1.29 to −0.46 for Zn). For M(κ^1*C*-$^{\text{Me}}$Tpmd)Me, the charges Q(M) are highest of all, namely +1.51 and +1.23, while the $Q(\alpha\text{-CR})$ values are almost zero (+0.09 and −0.02 for Mg and Zn, respectively). The $^{\text{Me}}$Tpmd ligand appears to delocalise the partial negative charge transferred from the MMe fragments on σ-bond formation, an effect that should be more important for the electropositive Mg in comparison with Zn (or H). To probe this idea further we evaluated electron-gain enthalpies $\Delta H_{\text{gain}}(\text{R})$ for the process $\text{R} + \text{e}^- \rightarrow \text{R}^-$ in the geometries found in the minimised M(R)Me species. The $\Delta H_{\text{gain}}(\text{R})$ values were significantly more favourable for R = $^{\text{Me}}$Tpmd (ca. −230 kJ mol^{-1}) than for the conventional alkyl groups (range ca. −84 to −178 kJ mol^{-1}).

The higher than expected ΔH(M–C) values for [M(κ^1*C*-$^{\text{Me}}$Tpmd)Me] and the differences for Mg and Zn potentially have important consequences for the reactions of main group metal alkyls (and related compounds) with HC(Me$_2$pz)$_3$. Using the values of $\Delta H(\text{M–C})_{\text{rel}}$ and $\Delta H(\text{C–H})_{\text{rel}}$ summarised in Figure 9, we calculated the enthalpies $\Delta_r E$ for a series of model reactions between M(R)Me and HC(Me$_2$pz)$_3$ [Eq. (6)]. Table 6 summarises the results.

$$\text{HC(Me}_2\text{pz)}_3 + \text{M(R)Me} \rightarrow [\text{M}(\kappa^1 C\text{-}^{\text{Me}}\text{Tpmd})\text{Me}] + \text{RH} \qquad (6)$$

Table 6. Calculated reaction enthalpies $\Delta_r E$ [kJ mol^{-1}] for Equation (6).

R	$\Delta_r E$ (M = Zn)	$\Delta_r E$ (M = Mg)
Ph	+14.7	−8.0
Me	+6.1	−15.4
*n*Pr	+2.4	−22.6
Et	−0.1	−25.6
*i*Pr	−7.6	−35.2
*t*Bu	−11.6	−39.1

Table 6 suggests that M–R/H–C(Me$_2$pz)$_3$ bond metathesis should be more favorable for Mg than Zn, and that within each series M(R)Me the reactions of the phenyl compounds would be the least thermodynamically favourable. These predictions are consistent with experimental observations (we are not able to comment on any kinetic limitations). Thus both MgR$_2$ (R = *n*Bu and Ph) compounds react rapidly with HC(Me$_2$pz)$_3$ to form sandwich derivatives. Only in the case of MgPh$_2$ can a half-sandwich compound be observed. For zinc only ZnMe$_2$ reacts at all (and only slowly). ZnPh$_2$ does not react with HC(Me$_2$pz)$_3$.

Conclusion

We have described an experimental and DFT study on the reactions of HC(Me$_2$pz)$_3$ with Grignard and diorgano magnesium and zinc reagents. The zwitterionic sandwich or half-sandwich complexes are the first such Mg and Zn species to feature "naked" pyramidal carbanion lone pairs. The lone pairs are the HOMOs of the compounds (as was also the case for previous $^{\text{Me}}$Tpmd complexes studied for M = Ti and Li) and are readily protonated. The sandwich structures are preserved in solution, as was shown by PGSE diffusion measurements. Density functional calculations showed that the pyrazolyl ring substituents destabilise the carbanion lone pair, whereas the nature of the metal (Zn or Mg) has little influence. The calculations also found that the preferred formation of κ^3*N*-coordinated complexes is driven by bond-enthalpy factors, but the formal transfer of an electron from the [MMe]$^\bullet$ metal fragment (ionisation) to the [$^{\text{Me}}$Tpm]$^\bullet$ radical (electron gain) is a significant factor. Another important feature of this chemistry is the weaker than anticipated H–

$C(Me_2pz)_3$ bond (according to DFT) and stronger M−C$(Me_2pz)_3$ bond, especially for more electropositive main group metals. It appears that the relative energetics of these two bonds in comparison with other H−C and M−C bonds control the course of metathesis reactions between $HC(Me_2pz)_3$ and dialkyls MR_2.

Experimental Section

Details of general synthetic techniques, NMR spectroscopic investigations, and X-ray crystal structure determinations, as well as computational details are compiled in the Supporting Information.

Synthesis of [Mg(^{Me}Tpmd)Cl] (2): A solution of MeMgCl in THF (3.0 M, 0.63 mL, 1.88 mmol) was added to a solution of $HC(Me_2pz)_3$ (0.56 g, 1.88 mmol) in benzene (40 mL). The mixture was stirred at room temperature for 24 h then filtered. The solid residue was washed with benzene (1×10 mL) and the washings combined with the filtrate. The solid was dried in vacuo to give a highly insoluble white solid which analysed as $[Mg(^{Me}Tpmd)Cl]_n$. Yield: 0.40 g (41%). IR (NaCl plates, Nujol mull): $\tilde{\nu}=3084$ (w), 1567 (s), 1551 (s), 1415 (s), 1305 (s), 1212 (w), 1157 (w), 1104 (m), 1040 (s), 980 (m), 906 (m), 860 (s), 810 (m), 729 (m), 708 (s), 688 (s), 633 cm^{-1} (m); EI-MS: *m/z*: 95 (48%, $[Me_2pz]^+$), 107 (20%, $[C(Me_2pz)]^+$), 202 (78%, $[C(Me_2pz)_2]^+$), 321 (20%, $[M-Cl]^+$); elemental analysis calcd (%) for $C_{16}H_{21}ClMgN_6$: C 53.8, H 5.9, N 23.4, Cl 9.6; found: C 53.8, H 5.9, N 23.5, Cl 9.9.

Dioxane (ca. 1 mL) was added to the combined filtrates and washings and the mixture stirred at room temperature for 3 h, whereupon a precipitate formed. The mixture was filtered and volatile substances were removed under reduced pressure from the filtrate. The resulting solid was dried in vacuo to give **5** as an analytically pure white powder. Yield: 0.21 g (18%).

Synthesis of [Mg(^{Me}Tpmd)Br] (3): A solution of MeMgBr in diethyl ether (3.0 M, 0.52 mL, 1.57 mmol) was added to a solution of $HC(Me_2pz)_3$ (0.47 g, 1.57 mmol) in benzene (15 mL). The mixture was stirred at room temperature for 30 min then filtered. The solid residue was washed with benzene (2×10 mL) then dried in vacuo to give a white solid. Yield: 0.30 g (47%). IR (NaCl plates, Nujol mull): $\tilde{\nu}=3058$ (m), 1569 (s), 1555 (s), 1306 (s), 1213 (w), 1174 (w), 1099 (m), 1038 (s), 982 (m), 906 (m), 870 (s), 859 (s), 802 (s), 780 (m), 729 (m), 709 (s), 633 cm^{-1} (w); EI-MS: *m/z*: 321 (20%, $[M-Br]^+$); EI-HRMS found (calcd for $[M-Br]^+$, $C_{16}H_{21}MgN_6$): 321.1686 (321.1678); elemental analysis calculated (%) for $C_{16}H_{21}BrMgN_6$: C 47.9, H 5.3, N 20.9, Br 19.7; found: C 47.9, H 5.3, N 20.9, Br 19.9.

Synthesis of [Mg{HC(Me$_2$pz)$_3$}Cl$_2$(thf)] (4): A solution of HCl in diethyl ether (1.0 M, 0.59 mL, 0.59 mmol) was added to a suspension of [Mg(^{Me}Tpmd)Cl] (**2**) in THF (0.21 g, 0.59 mmol), whereupon the appearance of the suspension immediately changed. The mixture was stirred at room temperature for 2 h then filtered to give an off-white solid, which was dried in vacuo. Yield: 0.08 g (29%). Diffraction-quality crystals were grown by contacting the solid with THF/hexane (1/1) at 4°C. IR (NaCl plates, Nujol mull): $\tilde{\nu}=3133$ (m), 3098 (m), 1567 (s), 1419 (s), 1391 (s), 1307 (s), 1165 (w), 1109 (m), 1044 (s), 987 (m), 904 (s), 860 (s), 837 (m), 708 (s), 633 cm^{-1} (m); elemental analysis calcd (%) for $C_{20}H_{30}Cl_2MgN_6O$: C 51.5, H 6.5, N 18.2, Cl 15.2; found: C 51.6, H 6.5, N 18.1, Cl 15.2.

Synthesis of [Mg(^{Me}Tpmd)$_2$] (5): A solution of nBu_2Mg in heptane (1 M, 2.00 mL, 2.00 mmol) was slowly added to a suspension of $HC(Me_2pz)_3$ (1.192 g, 4.00 mmol) in diethyl ether (30 mL). The mixture was stirred for 24 h at room temperature, over which time it became a yellow suspension. The remaining pale yellow solid was collected by filtration, washed with diethyl ether (2×15 mL) and dried in vacuo. Crystalline **5** can be obtained by recrystallisation from hot toluene. Yield: 760 mg (61%). M.p. 150°C (decomp). ^1H NMR (C_6D_6): $\delta=1.69$ (s, 9H, CH_3 (3)), 2.52 (s, 9H, CH_3 (5)), 5.62 ppm (s, 3H, CH_{pz} (4)); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 13.5 (s, CH_3 (5)), 13.7 (s, CH_3, (3)), 73.7 (s, $C_{anionic}$), 103.8 (s, CH_{pz}), 146.1 (s, C_{pz}), 148.6 ppm (s, C_{pz}); IR (KBr): $\tilde{\nu}=2923$ (m), 1551 (s) (ν(pyrazole ring), 1451 (s), 1421 (s), 1397 (s), 1364 (m), 1307 (w), 1216 (m), 1106 (m), 1024 (s), 978 (w), 875 (m), 785 (s), 730 (m), 661 (w), 496 (m), 475 cm^{-1} (m); EI-MS: *m/z*: 321 (100%, $[M-C(Me_2pz)_3]^+$), 428 (5%, $[M-2Me_2pz]^+$), 523 (5%, $[M-Me_2pz]^+$), 618 (10%, $[M]^+$); elemental analysis calcd (%) for $C_{32}N_{12}H_{42}Mg$: C 61.9, H 6.8, N 27.2, Cl 0.0; found: C 62.1, H 6.8, N 27.1, Cl 0.0.

Synthesis of [Mg(^{Me}Tpmd)Ph(thf)] (6): A solution of Ph_2Mg in toluene (14 mL, 1 M) was cooled to −40°C, and a solution of $HC(Me_2pz)_3$ (500 mg, 1.67 mmol) in THF (20 mL) was added slowly via a dropping funnel over 30 min. After warming to room temperature the reaction mixture was stirred for 24 h. The resulting yellow solution was concentrated in vacuo and cooled to −30°C. Considerable amounts of the byproduct **5** can be crystallised by repeated cooling/concentration of the mother liquors from toluene. Crystalline **6** containing impurities of Ph_2Mg can be obtained in the fifth crop from toluene. Due to the impurities no correct elemental analysis could be obtained. Only NMR spectroscopic data are given here. ^1H NMR (C_6D_6): $\delta=2.06$ (s, 9H, CH_3), 2.37 (s, 9H, CH_3), 5.42 ppm (s, 3H, CH_{pz}); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=13.2$ (s, CH_3), 14.4 (s, CH_3), 73.3 (s, $C_{anionic}$), 104.2 (s, CH_{pz}), 147.6 (s, C_{pz}), 149.2 ppm (s, C_{pz}). The ^1H and ^{13}C NMR resonances of the Ph group could not be assigned due to overlap with those of Ph_2Mg.

Synthesis of [Mg{HC(Me$_2$pz)$_3$}$_2$](OTf)$_2$ (7): A solution of CF_3SO_3H (0.11 mL, 1.3 mmol) in *n*-pentane (20 mL) was added dropwise to a suspension of [Mg(^{Me}Tpmd)$_2$] (**5**) (400 mg, 0.65 mmol) in cold (−96°C) *n*-pentane (20 mL). The reaction mixture was stirred at room temperature for three days. The resulting light brown precipitate was collected by filtration and dried in vacuo to afford **6**. Yield: 380 mg (64%). M.p. >210°C. ^1H NMR ([D$_6$]acetone): $\delta=1.75$ (s, 9H, CH_3 (3)), 2.87 (s, 9H, CH_3 (5)), 6.32 (s, 3H, CH_{pz} (4)), 8.46 ppm (s, 1H, CH); $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): $\delta=12.1$ (s, CH_3 (5)), 13.2 (s, CH_3 (3)), 69.8 (s, CH), 109.6 (s, CH_{pz}), 145.5 (s, C_{pz} (5)), 155.2 ppm (s, C_{pz} (3)); ^{19}F NMR ([D$_6$]acetone): $\delta=-78.8$ ppm; IR (KBr): $\tilde{\nu}=1566$ (w) (ν(pyrazole ring)), 1421 (w), 1255 (s), 1154 (m), 1031 (s), 858 (m), 707 (m), 637 (s), 517 (m), 483 cm^{-1} (m). Elemental analysis calcd (%) for $C_{37}H_{50}F_6MgN_{12}O_7S_2$ (**7**·Me_2CO): C 45.3, H 5.0, N 16.9; found: C 45.5, H 5.2, N 17.2.

Synthesis of [Zn(^{Me}Tpmd)Me] (8): A solution of $ZnMe_2$ in toluene (2.0 M, 0.94 mL, 1.88 mmol) was added to a solution of $HC(Me_2pz)_3$ (0.28 g, 0.94 mmol) in benzene (15 mL). The mixture was heated to 40°C for 6 days. The volatile meterials were removed under reduced pressure to leave an analytically pure white solid, which was dried in vacuo. Yield: 0.16 g (45%). ^1H NMR (C_6D_6, 293 K): $\delta=5.42$ (s, 3H, CH_{pz}), 2.37 (s, 9H, CH_3), 2.09 (s, 9H, CH_3), 0.24 ppm (s, 3H, ZnMe); ^{13}C NMR (C_6D_6, 293 K): $\delta=147.4$ (C_{pz}), 145.5 (C_{pz}), 103.0 (CH_{pz}), 72.6 ($C_{anionic}$), 13.2 (CH_3), 12.2 (CH_3), −16.8 ppm (q, $^1J_{CH}=118$ Hz, ZnMe); IR (NaCl plates, Nujol mull): $\tilde{\nu}=1556$ (m), 1409 (m), 1205 (w), 1197 (m), 1169 (w), 1109 (m), 1050 (s), 864 (m), 791 (s), 728 (m), 695 (w), 665 (m), 656 cm^{-1} (m); EI-MS *m/z*: 361 (95%, $[M-Me]^+$), 376 (10%, $[M]^+$); elemental analysis calcd (%) for $C_{17}H_{24}N_6Zn$: C 53.9, H 6.5, N 22.1; found: C 54.0, H 6.4, N 22.2.

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