On the remarkable structural diversity and kinetic lability of $Tp^{C*}CaX$ complexes (X = NSi_2Me_6 , OC_6H_4 -*p*-Me, Tp^{C*}) where $Tp^{C*} = tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate[†]$

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The preparation, structures and solution NMR properties of the title compounds are reported and, remarkably, the compounds $(Tp^{C*})_2M$, where M = Ca and Mg, exist as salts in the solid state and undergo facile Tp^{C*} ligand exchange in solution.

Ring-opening polymerization of cyclic esters derived from renewable resources can be brought about by both metal coordinate catalysis and organic catalysis leading to polyesters that find numerous commercial applications.¹ These polymers can be viewed as green polymers being both derived from renewable resources and biodegradable. In many instances they also are biocompatible and find uses in drug delivery, sutures, stints, pins and tissue matrices. Examples of these polymers include polylactide, PLA, polyglycolide (PG) and polycaprolactone (PC) along with their copolymers. Metal coordinate catalysis can lead to trace quantities of the metal residing in the polymer, as is the case for polyethylenes synthesized from chromium or titanium metal catalysts. Thus catalysts containing biologically benign metals are desirable for all polymers employed in medical applications, and in the storage of food and liquids for human consumption. In our studies aimed at single-site catalyst development with initiators of the form LMOR, we have found^{2,3} that the reactivity follows the order M = Ca > Mg > Zn, where R = alkyl and L = a sterically demanding ligand such as the β-diketoiminate CH(CMeN-2,6-Prⁱ₂-C₆H₄)₂, popularized by Coates and co-workers^{4,5} in connection with zinc, or the bulky tris(3-tert-butylpyrazolyl)hydroborate, commonly regarded as a "tetrahedral enforcer."⁶ Despite the high initial reactivity of the calcium complexes of the type LMOR toward the ROP of cyclic esters, their chemical persistence proved problematic and the kinetic lability of the metals, which also followed the order Ca > Mg > Zn, meant that deleterious side reactions, involving hydrolysis or ligand scrambling due to the Schlenk equilibrium, led to catalyst death.³ In an attempt to suppress these side reactions we have synthesized the Tp^C* ligand, $Tp^{C*} = tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]$ hydroborate, which, as shown in the drawing below, is similar to the tris(3-tert-butylpyrazolyl)hydroborate in its steric demand as a k³-N donor but has the advantage of behaving

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as a potential tetradentate, pentadentate or hexadentate ligand due to the ether appendages.^{7,8}



The ability of the Tp^{C*} ligand to act in this manner toward M^+ ions has been noted previously.^{7,8} Herein we describe its versatility as a ligand in calcium complexes of the form Tp^{C*}CaX, where $X = NSi_2Me_6$, OC_6H_{4-p} -Me and Tp^{C*}, together with a comparison with the related magnesium compound $(Tp^{C*})_2Mg$. The latter provides an interesting and rare comparison of the relative kinetic labilities of these M^{2+} ions in a common coordination environment.

In an attempt to prepare a calcium compound of the form $Tp^{C*}CaX$, where X = an amide or alkoxide, metathetic reactions were carried out involving Tp^C*CaI, which exists as a salt $[Tp^{C*}Ca]^+I^-$, and each of LiNMe₂, LiN(SiMe₃)₂, LiOBu^t, NaOBu^t, KOBu^t and KOSiMe₃ in toluene by employing standard procedures for the manipulation of airsensitive materials. In each case a reaction occurred but did not yield the desired product; the group 1 metal trispyrazolylhydroborate MTp^{C*} was formed. Similar kinetic lability was observed in ligand exchange reactions involving tris(trimethylsilyl)cyclopentadienyl calcium iodide by Hanusa and Harvey.⁹ The compound Tp^C*CaNSi₂Me₆ was, however, formed in the reaction between Ca(NSi₂Me₆)₂ and TITp^C* in hydrocarbon solvents, and when this reaction was carried out in pentane the compound Tp^C*CaNSi₂Me₆, I, was isolated in $\geq 80\%$ by its precipitation as a white microcrystalline solid. In aromatic hydrocarbons the similar solubilities of I and TlNSi₂Me₆ make their separation difficult and the preferential vacuum sublimation of Tl(NSi₂Me₆) leads to recovery of I in much lower yields.⁷

Compound I reacts with alcohols and phenols to give $Tp^{C*}CaX$ compounds, and where $X = p-CH_3C_6H_4O$ compound II is formed in >90% isolated yield. The latter compound and its related alkoxides are, indeed, good precursor complexes for the ring-opening polymerization of lactides, caprolactone and trimethylene carbonate and this topic is the subject of an ongoing study. Quite remarkably, compound II is chemically persistent in air for several hours as a white crystalline solid and is tolerant of undried hydrocarbon solvents. This contrasts with other LCaOR compounds of the type noted before.

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Compound I slowly reacts in hydrocarbon solvents at room temperature and more rapidly (<1 h) at 80 °C to give Ca[(NSi₂Me₆)₂]₂ and (Tp^{C*})₂Ca, III. The latter compound preferentially crystallizes from hydrocarbon solvents as a white crystalline solid.³ The seemingly straightforward synthesis of III from the metathetic reaction involving Tp^{C*}CaI and TlTp^{C*} in toluene was not successful. Initially a yellow material formed which was sparingly soluble in hydrocarbons but with time yellow TII (insoluble in hydrocarbons) was precipitated. Tentatively, we suggest that the initial compound is a salt, perhaps of the form [Tp^{C*}Ca]⁺[ITITp^{C*}]⁻, and that this metastability thwarts the straightforward, direct synthesis of (Tp^{C*})₂Ca.

Rather interestingly, reactions involving either MgMe₂ or MgBuⁿ₂ and TlTp^{C*} (2 equiv.) lead directly to the compound $(Tp^{C*})_2Mg$, **IV**, along with Tl(m) and when 1 equiv. of TlTp^{C*} is employed, compound **IV** and an equivalent of MgR₂ are formed (R = Me or Bu).⁴

The molecular structure of **I** in the solid state is shown in Fig. 1.‡ The Ca²⁺ ion is five-coordinate and, most interestingly, the Tp^{C*} ligand is ligated by only two of the pyrazolyl ligands. Undoubtedly the steric demands of the bulky NiSi₂Me₆ ligand impede the Tp^{C*} ligand from being hexadentate and it is interesting that the Ca²⁺ ion elects to employ the coordination of the two N,O-chelates in preference to say three N donors supplemented by one ether donor, *cf*. the molecular structure of TlTp^{C*}.⁸ By ¹H and ¹³C{¹H} NMR spectroscopy in toluene-d₈ all the arms of the Tp^{C*} ligand are equivalent even at -80 °C and NOE experiments confirm the time-averaged proximity of the SiMe₃ and OMe protons. We conclude that this molecule is fluxional on the NMR time-scale as was seen for a related Na[B(pz^{*})₄] compound, where pz^{*} = 3-(2-methoxyl-1,1-dimethylethylpyrazolyl).⁸

The molecular structure of compound **II** is shown in Fig. 2.‡ The Ca^{2+} is seven-coordinate with the Tp^{C*} being hexadentate, k^3-N_3,O_3 . The ¹H NMR spectrum is not surprisingly quite simple and as expected.

Compounds III and IV are structurally similar[‡] and reveal their salt-like nature $[Tp^{C*}M]^+[Tp^{C*}]^-$, where M = Ca and Mg. The molecular structure of III is shown in Fig. 3[‡] and a

Fig. 1 An ORTEP drawing of $Tp^{C*}CaN(SiMe_3)_2$, I, with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) to Ca: N(7) 2.310(1); N(2) 2.455(1); N(6) 2.461(1); O(1) 2.370(1); O(3) 2.376(1).



Fig. 2 An ORTEP drawing of $Tp^{C*}CaOC_6H_4$ -p-Me, **II**, with thermal ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) to Ca: N(2) 2.513(2); N(4) 2.526(2); N(6) 2.497(2); O(1) 2.526(1); O(2) 2.446(1); O(3) 2.498(1); O(4) 2.177(1).



Fig. 3 An ORTEP drawing of $[Tp^{C*}Ca]^+[Tp^{C*}]^-$ (III) with thermal ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity.

comparison of selected structural parameters for the $[Tp^{C*}M]^+$ cation is given in Table 1. The M–O distances are notably somewhat smaller than the M–N distances and this difference is greater for M = Ca than for M = Mg. We propose that this subtle difference is largely a result of the fact that the larger Ca²⁺ ion with an ionic radius of ~1.0 Å is more ideally suited for the Tp^{C*} ligand, as is the Na⁺ ion

Table 1 Selected bond distances (Å) and angles (°) for the $[Tp^{C*}M]^+$ ions in the $(Tp^{C*})_2M$ complexes (M = Mg and Ca)

		Distance/Å					Angle/ $^{\circ}$	
A	В	Mg	Ca	А	В	С	Mg	Ca
М	N2	2.219(3)	2.436(5)	N2	М	N6	87.3(1)	79.0(2)
М	N4	2.187(3)	2.423(5)	N2	Μ	01	76.9(1)	75.6(2)
Μ	N6	2.173(3)	2.434(5)	N2	Μ	O2	120.7(1)	126.5(2)
Μ	O1	2.157(3)	2.380(4)	N2	Μ	O3	150.5(1)	131.0(2)
Μ	O2	2.163(3)	2.369(4)	O1	Μ	N4	146.7(1)	131.9(2)
Μ	O3	2.150(3)	2.346(4)	O3	Μ	01	87.4(1)	90.9(2)

C6



Fig. 4 Stacked VT ${}^{13}C{}^{1}H$ -NMR spin saturation transfer spectra of compound IV in toluene-d₈. (See ESI† for details.)

relative to the Li⁺ ion in the related MTp^{C*} compounds.⁸ Given the similar ionic radii¹⁰ of Li⁺ and Mg²⁺ it is thus noteworthy that the Li–O distances are ~0.3 Å longer than their Mg–O counterparts. This can most reasonably be correlated with the greater effective charge on the Mg²⁺ ion and its greater oxophilicity.

The NMR spectra of compounds III and IV in toluene-d₈ are also of particular interest in comparing the coordination properties of the two elements as M²⁺ ions. The ¹H NMR spectrum for the magnesium compound $[Tp^{C*}Mg]^+[Tp^{C*}]^$ shows two distinct sets of Tp^C* resonances consistent with the bound and free ligands, whereas the calcium complex III shows only one set of Tp^{C*} signals, even at -80 °C. By spin magnetization transfer experiments, the ${}^{13}C{}^{1}H{}$ signals of the compound IV in toluene-d₈ show evidence of dynamic exchange of the coordinated and free Tp^{C*} ligands, see Fig. 4. We propose that both complexes, III and IV, exist as tight ion pairs in toluene-d₈ and that the dynamic exchange between free and coordinated Tp^{C*} is >100 times faster for the larger and softer Ca²⁺ ion relative to the smaller, harder M²⁺ ion for which exchange is $<10^{-1}$ s⁻¹. These are, at this time, "ball-park" estimates and are the subject of further study.

Although considerable recent attention has been given to the coordination chemistry of the heavier group 2 elements,^{11,12} an understanding of their reaction chemistry is in its infancy. What we believe, is abundantly apparent from the data reported in this communication, is the remarkable lability of the ligands bound to Ca^{2+} ions. One might thus question the ability of ever establishing single-site catalysis by a compound of the form LCaOR based on the facility of ligand exchange and side reactions such as hydrolysis. However, we believe that this really has more to do with the nature of L and the reaction under consideration and point to the recent success of Barrett and Hill in hydroamination and hydrophosphination catalysis

employing $HC(CMeNC_6H_4-Pr_2^i-2,6)_2Ca(NSi_2Me_6)$.^{13,14} We propose that it will, indeed, be possible to develop LCaOR catalysts for the ROP of polyoxygenates given the appropriate L and reaction conditions, and note the recent success reported by Darensbourg and co-workers.¹⁵

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Notes and references

‡ Crystal data for Tp^C*CaN(SiMe₃)₂, I, C₃₀H₅₈BCaN₇O₃Si₂, M = 671.90, monoclinic, a = 13.1496(5), b = 15.5703(8), c = 18.9206(8) Å, $\beta = 99.351(2)^{\circ}$, U = 3822.4(3) Å³, T = 95 K, space group $P2_1/c$ (no. 14), $z = 4, 42\,864$ reflections measured, 10864 unique ($R_{int} = 0.051$), which were used in all calculations. Final *R* values are $R_1 = 0.063$ and $wR_2 = 0.112$ (on all data).

Crystal data for $\text{Tp}^{C*}\text{Ca}(\text{OC}_6\text{H}_4\text{-}p\text{-Me})$, **II**, $\text{C}_{31}\text{H}_{47}\text{BCaN}_6\text{O}_4$, toluene, M = 710.77, monoclinic, a = 13.390(1), b = 15.831(1), c = 19.583(2) Å, $\beta = 109.058(3)^\circ$, U = 3923.6(6) Å³, T = 150 K, space group $P2_1/n$ (no. 14), z = 4, 63 707 reflections measured, 6918 unique ($R_{\text{int}} = 0.039$), which were used in all calculations. Final Rvalues are $R_1 = 0.055$ and $wR_2 = 0.103$ (on all data). Crystal data for $[\text{Tp}^{C*}\text{Ca}]\text{Tp}^{C*}$, **III**, $C_{48}\text{H}_{80}\text{B}_2\text{CaN}_{12}\text{O}_6$,

Crystal data for $[Tp^{C*}Ca]Tp^{C*}$, **III**, $C_{48}H_{80}B_2CaN_{12}O_6$, M = 982.94, monoclinic, a = 14.2546(2), b = 16.7217(3), c = 24.6146(5) Å, $\beta = 102.840(1)^\circ$, U = 5720.4(2) Å³, T = 230 K, space group $P2_1/c$ (no. 14), z = 4, 51 480 reflections measured, 7420 unique ($R_{int} = 0.085$), which were used in all calculations. Final *R* values are $R_1 = 0.150$ and $wR_2 = 0.259$ (on all data).

Crystal data for $[Tp^{C*}Mg]Tp^{C*}$, **W**, C48H80B2MgN12O6, M = 967.17, triclinic, a = 14.3126(1), b = 14.5131(2), c = 14.9368(2) Å, $\alpha = 97.536(1)^\circ$, $\beta = 115.884(1)^\circ$, $\gamma = 99.546(1)^\circ$, U = 2679.34(5) Å³, T = 150 K, space group $P\overline{1}$ (no. 2), z = 2, 47 258 reflections measured, 9449 unique ($R_{int} = 0.038$), which were used in all calculations. Final R values are $R_1 = 0.119$ and $wR_2 = 0.289$ (on all data).

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