A *tris*-pyrazolylborate ligand with hemilabile O-donor groups. Examples of η^3, η^5, η^6 and bridging modes of bonding to Li^+, Na^+, K^+, Tl^+ and Ca^{2+} ions†

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A *tris*-pyrazolylborate ligand bearing ether appendages is shown to be a potential hemilabile ligand based on NMR studies and structural characterization of its η^3, η^5, η^6, and μ-binding modes in coordination with Li^+, Na^+, K^+, Tl^+, and Ca^{2+} ions.

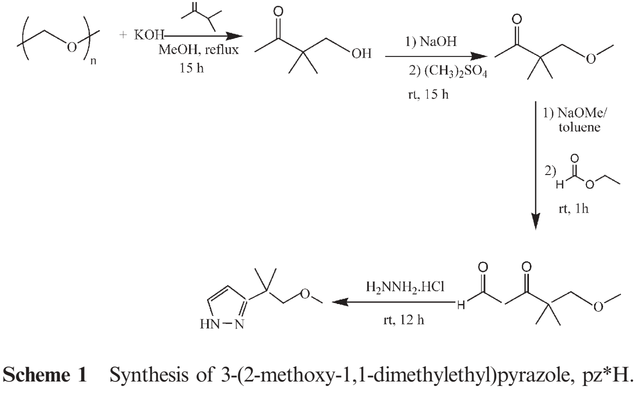
The development of single-site catalysts is one of the major success stories in the field of contemporary inorganic coordination chemistry. For any given reaction, the development process rests upon the delicate interplay between the metal ions' coordination appetite and the ligands' ability to satisfy this hunger. If the metal ion is completely satisfied, then it will show little affinity for substrate binding and activation. On the other hand, if the metal ions' requirements are too poorly satisfied, the kinetic lability of that specific ligand–metal combination will lead to deleterious side reactions such as ligand scrambling and thereby loss of single-site activity. Metal ions such as Mg^{2+} and Ca^{2+} are particularly labile, as evidenced by their rates of H_2O exchange in their M^{2+} aqua ions which are $\sim 10^5$ and 10^9 s^{-1}, respectively.[1] In order to suppress ligand scrambling, chelating ligands are desirable, but even the bulky β-diiminate ligand $CH(CMeN\text{-}C_6H_3\text{-}2,6\text{-}{}^iPr_2)_2$ which has enjoyed so much success in combination with Zn^{2+} ions for ring-opening polymerization of lactides[2] and related cyclic esters.[3] and in the copolymerization of 1,2-oxiranes and carbon dioxide,[4] failed to meet the requirements of Mg^{2+} and Ca^{2+}. These form dimeric products $[(\eta^2\text{-L})Mg(\mu\text{-OR})]_2$[5] or by ligand scrambling $(\eta^2\text{-L})_2Ca$.[6] The more bulky η^3 *tris*-pyrazolylborate, $HB(3\text{-Bu}^t pz)_3$ coordinates well to Mg^{2+} and Zn^{2+} to form discrete η^3-LMOR complexes, but for Zn^{2+} , the coordination of the ligand is too strong, leading to loss of substrate binding.[7] For the Ca^{2+} ion, however, even this bulky η^3-ligand is insufficient to secure kinetic persistence, and after initial rapid reaction, catalytic activity dies.[6] We reasoned that, for the larger ion Ca^{2+} and the extremely oxophilic Mg^{2+}, it could be useful to employ a *tris*-pyrazolylborate ligand bearing O-donor appendages which might stabilize the complex toward ligand scrambling, yet leave the metal center kinetically accessible to substrate binding. We describe here the synthesis of one such ligand and its coordination to the M^+ ions of Li, Na, K and Tl, together with Ca^{2+}. The results described herein reveal the remarkably flexible responsiveness of this new ligand towards the demands of the metal. We shall subsequently describe the use of this ligand in metal mediated catalysis.

The pyrazolyl group was first synthesized by the stepwise series of reactions shown in Scheme 1. Then, as in the synthesis of the *tris*-3-*tert*-butylpyrazolylborate ligand, the pyrazolyl was allowed to react with the group 1 metal borohydride at $\sim$180 °C and H_2 evolution was monitored with time with the intent of satisfying the stoichiometric reaction given in eqn. 1 (see Supporting Information).‡

$$\mathrm{MBH_4} + 3\mathrm{pz^*H} \xrightarrow{180\,^{\circ}\mathrm{C}} \mathrm{MTp^*} + 3\mathrm{H_2(g)} \qquad (1)$$

Although the reaction depicted by eqn. 1 can reasonably be understood to proceed in a stepwise manner, the kinetics of the reaction profile can lead to a mixture of products. Thus, while the complexes MTp* where Tp* = *tris*[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]borohydride and M = Li, Na and K, have been isolated from 1, so have some "over reaction" products. For example, in the reaction involving $LiBH_4$, when the temperature exceeds 180 °C, the four-coordinate η^3-N_3, η^1-N complex **1** shown in Fig. 1 was isolated. As can be seen, the B–H bond has somewhat mysteriously been replaced by a B–O bond and a methyl group has been lost. The η^3-Tp* ligand is further supported by a η^1-bound pz* ligand. The electrophilic Li^+ ion is clearly demonstrating its preference for nitrogen ligation, over the available O-donor of the ether. However, in the LiTp* complex whose structure has not yet been determined, we can reasonably assume that one or more ether oxygens are involved in ligation.

The structure of the complex NaTp* **2** is shown in Fig. 2. The Na^+ ion is completely encapsulated by the η^6-N_3,O_3-Tp* ligand



Scheme 1 Synthesis of 3-(2-methoxy-1,1-dimethylethyl)pyrazole, pz*H.

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† Electronic supplementary information (ESI) available: Selected preparative details, ^1H and $^{13}C\{^1H\}$-NMR data and crystallographic data. See DOI: 10.1039/b517640a

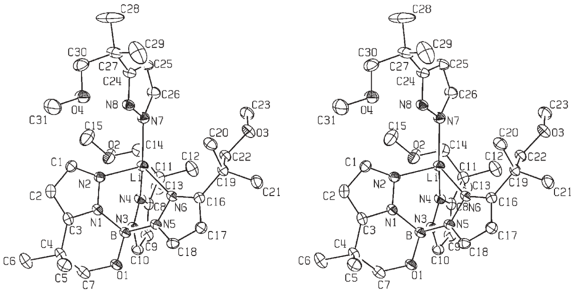

Fig. 1 A stereo drawing of the lithium complex **1**, with thermal ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths are Li–N(Tp*) = 2.06(2) Å (ave) and Li–N(pz*) = 2.042(3) Å.

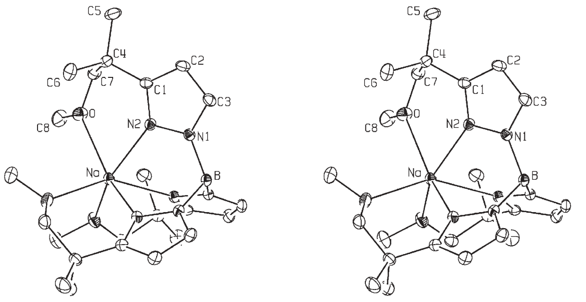

Fig. 2 A stereo drawing of **2**, with thermal ellipsoids drawn at the 30% probability level. The molecule contains a crystallographic C_3 axis with the Na and B atoms positioned on this axis. Hydrogen atoms are omitted for clarity. Selected bond lengths are Na–N 2.400(2) Å and Na–O 2.472(1) Å. The trans N–Na–O angles are 147.56(5)°.

which affords a *pseudo* facial octahedral geometry to the group 1 metal ion. A similar geometry is seen for the "over reaction" product $NaB(pz^*)_4$ **3** where the fourth B–H bond is substituted by a pz* group (see Supporting Information). The $B(pz^*)_4^-$ ligand is of potential interest as a bridging ligand, and the "dangling" pz* moiety could facilitate intermolecular exchange reactions of an otherwise kinetically inert η^6-N_3,O_3 sequestered metal ion.

The structure of the KTp* containing complex **4** is shown in Fig. 3. This is a most fascinating dinuclear structure: one potassium ion, K(1), is coordinated to three pyrazolyl nitrogens, one of which is bridging to K(2), one ether oxygen and is π-bonded, η^5- to another pyrazole ligand. The other potassium ion, K(2), is bound to only two nitrogen atoms (one of which is bridging as noted before), three ether oxygens and one π, η^5-pyrazolyl ligand. The bridging bonding modes seen in Fig. 3 are suggestive of the possible manner in which Tp* ligands are transferred between group 1 metal Tp* complexes and other metal centers in metathetic reactions of the type described below.

The reaction between **2** and CaI_2 in THF (slurry) leads to the formation of the compound Tp*CaI **5**. The structure of **5** consists of an η^6-Tp* ligand, as seen for Na^+, with the I^- ion well removed from and unligated to the Ca^{2+} center (see Fig. 4). The ionic radii for six-coordinate Na^+ and Ca^{2+} ions differ by only 0.02 Å, with that for Ca^{2+} being smaller.[8] Thus, in a comparison of the M–N and M–O distances for NaTp* and $[CaTp^*]^+$, it is interesting to note that the Δ(M–N) conforms to the expected, while the Δ(M–O) distances are significantly different, being ~0.1 Å shorter to Ca^{2+}. Evidently, the greater effective charge on the Ca^{2+} ion manifests itself more strongly with the weaker ligating ether oxygen donors.

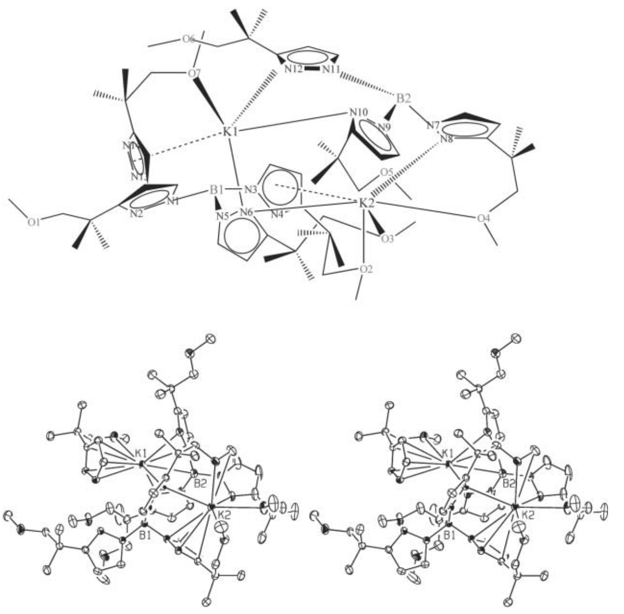

Fig. 3 A ChemDraw and a stereo drawing of the complex $K_2Tp^*_2.pz^*H$, **4**, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. The structure consists of two K^+ ions, two Tp* ligands and one additional pz*H ligand bonded to K(1). Selected bond lengths are given in the Supporting Information.

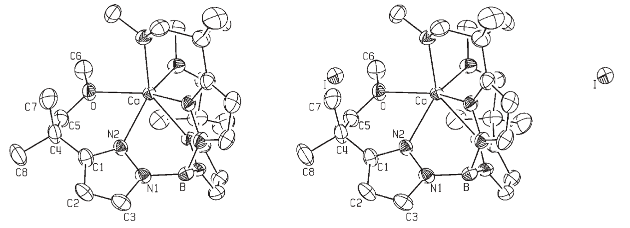

Fig. 4 A stereo drawing of **5**, with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity. The Ca complex contains a crystallographic C_3-axis. Selected bond lengths (Å) are Ca–N = 2.384(4), Ca–O = 2.380(3), and Ca···I = 6.865(2) Å. The trans N–Ca–O angle is 146.8(1)°.

A more efficient preparation of **5** involves the employment of the TlTp* complex **6** which contains kinetically more labile Tp* ligands. **6** is readily prepared from the reaction between **2** and TlOAc in dichloromethane, where the insoluble NaOAc is separated by filtration from the benzene-soluble **6**. The structure of TlTp* is shown in Fig. 5. Although the Tl^+ ion is larger than K^+ (1.4 *vs.* 1.2 Å), the Tp* ligand is η^5-bound, employing the three pyrazolyl nitrogens and two ether oxygens, O1 and O3 which are just within the bonding distance (~3 Å) and may be viewed as structural models for the hemilabile ether ligands.[9] In the reaction between **6** and CaI_2 in THF, the yellow insoluble TlI can be removed by filtration and **5** was recrystallized from hydrocarbon solvents (see Supporting Information). In the reaction between $Ca(N(SiMe_3)_2)_2$ and TlTp*, the complex $Tp^*CaN(SiMe_3)_2$ **7** is formed, along with $TlN(SiMe_3)_2$. The latter compound may be removed by sublimation under a vacuum allowing isolation of **7**.

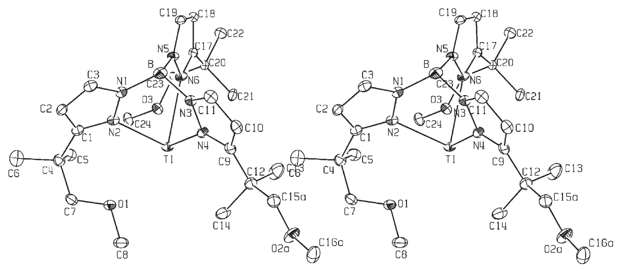

Fig. 5 A stereo drawing of **6**, with thermal ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) are Tl–N(2) = 2.600(3), Tl–N(4) = 2.703(3), Tl–N(6) = 2.597(3) Å, Tl···O(1) = 3.109(3), Tl···O(3) = 3.050(2), and Tl···O(2) = 6.258(2).

All of the aforementioned Tp* metal complexes are hydrocarbon-soluble and show molecular ions, M^+, in the mass spectrometer. With the exception of $Tp^*CaN(SiMe_3)_2$, the new Tp* metal complexes are air-stable. The ^1H NMR spectra recorded in benzene-d_6 for MTp* and Tp*CaI show only one type of pz* ligand, consistent with either η^6-ligation as seen in the solid state (M = Na, Ca) or implying a facile dynamic exchange of the hemilabile ether linkages.[8] The appearance of the same for the potassium complex, together with the molecular ion $Tp^*K_2^+$ in the mass spectrum, implies that the dinuclear structure having bridging Tp* ligands is readily broken up. The ^1H NMR spectrum of $Tp^*CaN(SiMe_3)_2$ in toluene-d_6 shows significant line broadening of the OMe, CMe_2 and $SiMe_3$ methyl signals at low temperature (in contrast to Tp*CaI), and this leads us to propose that the $N(SiMe_3)_2$ ligand is bound to the Ca^{2+} center, and one or more ether atoms is ligated in the ground state structure.

In conclusion, we have prepared a new *tris*-pyrazolylborate ligand bearing ether appendages and its coordination to M^+ ions (M = Li, Na, K, Tl) and Ca^{2+}, reveals a rich and varied coordination chemistry. Further studies of the coordination chemistry of this versatile ligand are in progress and the results of these studies, together with reactivity studies of its M^{2+} complexes in metal mediated catalysis, will be reported subsequently. We note, however, that compound **7** is active in the polymerization of lactides.

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Notes and references

‡ CCDC 290330–290335. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517640a

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