Heavy Alkaline Earth Metal Pyrazolates: Synthetic Pathways, Structural Trends, and Comparison with Divalent Lanthanoids

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Abstract: Two series of heavy alkaline earth metal pyrazolates, $[M(Ph_2pz)_2(thf)_4]$ **1a–c** (Ph_2pz = 3,5-diphenylpyrazolate, M = Ca, Sr, Ba; THF = tetrahydrofuran) and $[M(Ph_2pz)_2(dme)_n]$ (M = Ca, **2a**, Sr, **2b**, $n=2$; M = Ba, **2c**, $n=3$; DME = 1,2-dimethoxyethane) have been prepared by redox transmetallation/ligand exchange utilizing $Hg(C_6F_5)_2$. Compounds **1a** and **2b** were also obtained by redox transmetallation with $Tl(Ph_2pz)$. Alternatively, direct reaction of the alkaline earth metals with 3,5-diphenylpyrazole at elevated temperatures under solventless conditions yielded compounds **1a–c** and **2a–c** upon extraction with THF or DME. By contrast, $[M(Me_2pz)_2(Me_2pzH)_4]$ **3a–c** (M = Ca, Sr, Ba; Me_2pzH = 3,5-dimethylpyrazole) were prepared by protolysis of $[M\{N(SiMe_3)_2\}_2(thf)_2]$ (M = Ca, Sr, Ba) with Me_2pzH in THF and by direct metallation with Me_2pzH in liquid NH_3/THF. Compounds **1a–c** and **2a–c** display η^2-bonded pyrazolate ligands, while **3a,b** exhibit η^1-coordination. Complexes **1a–c** have *transoid* Ph_2pz ligands and an overall coordination number of eight with a switch from mutually coplanar Ph_2pz ligands in **1a,b** to perpendicular in **1c**. In eight coordinate **2a,b** the pyrazolate ligands are *cisoid,* whilst **2c** has an additional DME ligand and a metal coordination number of ten. By contrast, **3a,b** have octahedral geometry with four η^1-Me_2pzH donors, which are hydrogen-bonded to the uncoordinated nitrogen atoms of the two *trans* Me_2pz ligands. The application of synthetic routes initially developed for the preparation of lanthanoid pyrazolates provides detailed insight into the similarities and differences between the two groups of metals and structures of their complexes.

Keywords: alkaline earth metals · coordination modes · lanthanides · N ligands · structure elucidation · synthetic methods

Introduction

The chemistry of calcium, strontium, and barium can be compared with that of the divalent rare earth metals, due to close similarities in the size/charge ratio for Eu^{2+}, Sm^{2+}/Sr^{2+} and Yb^{2+}/Ca^{2+}.[1] Indeed, the size relationship between Sr^{2+} and Eu^{2+} results in the frequent presence of europium in Group 2 minerals.[2] Despite the charge difference, Ca^{2+} can be replaced in some biological functions by Ln^{3+}, a factor of importance in biochemistry,[3] but Ln^{II} compounds are unstable under biological conditions.

This analogy has been little pursued and, apart from the well-developed cyclopentadienide chemistry,[4] few other molecular compounds have been prepared with identical ligand and donor sets to allow the direct comparison of their synthetic and structural chemistry.[5] However, Ca, Sr, and Ba have been shown to react with 2,6-diphenylphenol (HOdpp) at elevated temperatures yielding $[M(Odpp)_2]_2$,[6a] analogous to the syntheses of their divalent Yb and Eu counterparts.[6b] Similar structural motifs were observed for the calcium and ytterbium derivatives and for the strontium and europium species, though there were differences in the coordination modes of the pendant phenyl groups.[6]

Pyrazolates, intensively investigated for the rare earth metals,[7–13] allow a direct comparison between the two groups of metals, both in terms of synthetic methods and structural features. The steric bulk of the pyrazolate ligand can be varied by ring substitution, thus providing a set of ligands in which steric demand and electronic properties can be easily modulated.[7–13] This variation has important implications on solubility and association, with critical conse-

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quences for volatility and potential application in MOCVD.[14]

Alkaline earth metal pyrazolates have so far been limited to a handful of magnesium[15,16] and calcium[17] derivatives, as well as $[\{Ba(Me_2pz)_2\}_n]$,[18a] $[Ba\{(Me_2pz)_3Ge\}_2]\cdot0.5$ dioxane,[18a] and $[Ba_6(thf)_6(Me_2pz)_8\{(OSiMe_3)_2O\}_2]$.[18b] The calcium and magnesium compounds have played a pivotal role in establishing that η^2-coordination,[19] for many years restricted to f-block elements,[7,20] can be observed for both main group[16,17,18b,21] and d-block elements.[22]

The main synthetic route to the target compounds has been metathesis from the Group 2 halides (Mg, Ca) and potassium pyrazolates (Table 1, Method 1).[17] However, the need to prepare the air-sensitive potassium pyrazolate, combined with the low solubility and high cost of anhydrous $CaBr_2$ prompted us to investigate syntheses from the free metals, as developed for rare earth elements.[23] Some support for the viability of this approach has been provided by the preparation of $[Ba(Me_2pz)_2]$ and $[Ba_6(thf)_6(Me_2pz)_8\{(OSiMe_3)_2O\}_2]$ by prolonged reactions of Ba metal with 3,5-dimethylpyrazole in refluxing THF.[18]

We now report multiple synthetic approaches towards heavy Group 2 3,5-diphenyl- and 3,5-dimethylpyrazolates with particular emphasis on metal-based reactions, transamination, and direct metallation with ammonia-activated metals. The last two have previously been used in alkaline earth chemistry.[24] Of particular interest in the structures of the products is the variation resulting from different metal sizes and donors, providing insight into the preferred metal coordination.

Results and Discussion

Synthetic chemistry: Five routes to heavy alkaline earth metal pyrazolates have been devised (Methods 2–6, Table 1).

Heavy alkaline earth metals react smoothly with 3,5-diphenylpyrazole in THF or DME at room temperature if the organomercurial $Hg(C_6F_5)_2$ is added (Method 2, Table 1) affording compounds $[M(Ph_2pz)_2(thf)_4]$ (M = Ca, Sr, Ba) **1a**–**c** and $[M(Ph_2pz)_2(dme)_n]$ ($n=2$, M = Ca, Sr; $n=3$, Ba) **2a**–**c** in good yield and purity. The organomercurial is considered to initially react with the alkaline earth metal to form the organometallic derivative [redox transmetallation, M = Ca, Sr, Ba; Eq. (1)], which then reacts with the weakly acidic[25] pyrazole through ligand exchange [Eq. (2)]. Related chemistry with ytterbium has established the intermediate formation of $Yb(C_6F_5)_2$.[23]

$$M + Hg(C_6F_5)_2 \rightarrow M(C_6F_5)_2 + Hg \qquad (1)$$

$$M(C_6F_5)_2 + 2\,Ph_2pzH \rightarrow M(Ph_2pz)_2 + 2\,HC_6F_5 \qquad (2)$$

The presence of the organomercurial is crucial, since barium, the most reactive alkaline earth metal, reacted only incompletely under the same reaction conditions with 3,5-diphenylpyrazole if the mercurial was absent.

Direct metallation can be achieved under solventless conditions (Method 3, Table 1) if the reactants are heated to 250–300 °C. Added mercury is not needed, but is required to afford a smooth reaction with the lanthanoids.[11] This observation is consistent with the greater electropositive character of the alkaline earth metals. Extraction of the reaction products with the appropriate donor solvent afforded compounds **1a**–**c** and **2a**–**c**.

A further route to the representative pyrazolate target compounds **1a**, **2b**, namely, redox transmetallation between thallium 3,5-diphenylpyrazolate[12,26] and Ca or Sr (Method 4, Table 1) was successful and parallels the analogous preparation of divalent rare earth derivatives.[12,13]

Ammonia activation of the alkaline earth metals[27] allows their direct reaction with the weakly acidic 3,5-dimethylpyrazole, affording compounds $[M(Me_2pz)_2(Me_2pzH)_4]$ (M = Ca, Sr, Ba) **3a**–**c** in good yield and purity (Method 5, Table 1). Consistent with the relative reactivity of the metals, barium reacts very rapidly whilst calcium is slower. However, the reproducibly obtained colorless crystals of the barium compound **3c** decomposed immediately upon removal of the mother liquor, preventing detailed characterization. A ^1H NMR spectrum of the powdered product suggests that the composition is $[Ba(Me_2pz)_2(Me_2pzH)_4]$ **3c**, analogous to **3a** and **3b**, as do IR spectral similarities.

Transamination (Method 6, Table 1), entailing the reaction of 3,5-dimethylpyrazole with alkaline earth metal bis[bis(trimethylsilyl)]amides yielded compounds **3a**–**c** in good purity

Table 1. Synthetic routes towards alkaline earth metal pyrazolates.

Method	Synthetic route	Products
1[a]	$CaBr_2 + 2\,KtBu_2pz \xrightarrow{THF} [Ca(tBu_2pz)_2(thf)_2]$ (**4a**) $+ 2\,KBr \xrightarrow[-2\,THF]{n\,L,\ hexane} [Ca(tBu_2pz)_2L_n]$	**4a**–**f**[17]
2[b]	$M + Hg(C_6F_5)_2 + 2\,Ph_2pzH \xrightarrow[RT]{donor\ solvent} [M(Ph_2pz)_2(donor)_n] + Hg + 2\,C_6F_5H$	**1a**–**c**, **2a**–**c**[e]
3[b]	$M + 2\,Ph_2pzH \xrightarrow[2)\ donor\ solvent]{1)\ 250-300\,^oC} [M(Ph_2pz)_2(donor)_n] + H_2$	**1a**–**c**, **2a**–**c**[e]
4[c]	$M + 2\,[Tl(Ph_2pz)] \xrightarrow[1)\ \Delta,\ 2)\ RT]{donor\ solvent} [M(Ph_2pz)_2(donor)_n] + 2\,Tl$	**1a**, **2b**[e]
5[d]	$M + 6\,MepzH \xrightarrow[RT]{THF, NH_3(l)} [M(Me_2pz)_2(Me_2pzH)_4] + H_2$	**3a**–**c**[e]
6[d]	$[M\{N(SiMe_3)_2\}_2(thf)_2] + 6\,Me_2pzH \xrightarrow[RT]{THF} [M(Me_2pz)_2(Me_2pzH)_4] + 2\,HN(SiMe_3)_2$	**3a**–**c**[e]

[a] L = pyridine, $n=3$ **4b**; TMEDA, $n=1$ **4c**; PMDTA, $n=1$ **4d**; triglyme, $n=1$ **4e**; tetraglyme, $n=1$ **4f**. [b] M = Ca, Sr, Ba; donor solvent = THF, DME. [c] M = Ca, Sr; donor solvent = THF, DME. [d] M = Ca, Sr, Ba. [e] This work.

but low yield. Curiously, compounds **3a**–**c** are best obtained from a reactant ratio 2.5:1, explaining the low yields. Increasing the ratio led to the precipitation of free pyrazole and impure products.

Isolation of crystallographically characterized [M(Ph_2pz)$_2$(thf)$_4$] **1a**–**c** contrasts the inability to crystallize [Ca($t$$Bu_2pz$)$_2(thf)_2$] **4a**,[17] the THF complexes of [M(Me_2pz)$_2$] (M = Ca,[17] Ba[18a]), and the corresponding THF complexes of Ln^{II} diphenylpyrazolates,[12,13] possibly owing to facile desolvation. Nevertheless, some loss of coordinated donors occurred for most of the present complexes: compounds **1a**–**c**, **3c** desolvate at room temperature, compounds **2a**–**c** on heating, and **3a,b** showed loss of Me_2pzH upon heating under vacuum. Thus, the THF adduct **1a** partly desolvates upon removal of the solvent, affording [Ca(Ph_2pz)$_2$(thf)$_{3.5}$] (**1a***) as indicated by microanalysis and metal analysis. Evaporation of THF solutions of **1c** affords [Ba(Ph_2pz)$_2$(thf)$_3$] (**1c**$^{\#}$) as indicated by metal analysis soon after isolation. The compound completely desolvates into [Ba(Ph_2pz)$_2$] (**1c**†) on further standing as revealed by subsequent microanalysis.

As complexes **1a**–**c** are only sparingly soluble in benzene, NMR data were obtained from solutions of the complexes in [D_8]THF, negating determination of the THF/Ph_2pz ratio, but suitable solubilities enabled confirmation of the donor/Ph_2pz or Me_2pz ratio for **2a**–**c** and **3a**,**b**. As the spectra of **2a**–**c** are simpler than expected if the solid state structures were maintained in solution, some dynamic processes for example, rapid reversible dissociation of DME, are likely. The IR spectra of the bulk samples showed the expected absorptions for the ligands and coordinated donors,[28] and verified that no 3,5-diphenylpyrazole was present as an impurity in **1a**–**c** and **2a**–**c**. On the other hand, a ν(N–H) absorption attributable to coordinated Me_2pzH was observed near 3200 cm^{-1} for **3a**–**c**. It is not possible to compare the NMR spectra of **2a**–**c** with those of *cis*-[Ln(Ph_2pz)$_2$(dme)$_2$] (Ln = Yb[12] or Sm[13]), because of the solubility-driven solvent mismatch and Sm paramagnetism. However, the spectrum of the Yb complex in C_4D_8O, in which presumably [Yb(Ph_2pz)$_2$(C_4D_8O)$_4$] is formed, shows Ph_2pz resonances comparable with those of **1a**–**c**.

Comparison with syntheses of lanthanoid(II) pyrazolates: Successful syntheses of alkaline earth pyrazolates by metal-based reactions (Methods 2–4, Table 1) previously used for lanthanoid pyrazolates support the concept of close analogies in their chemistry, but there are differences in the details. Thus redox transmetallation/ligand exchange between a Ln metal, Hg(C_6F_5)$_2$, and a pyrazole, widely used to prepare lanthanoid(III) pyrazolates,[7–11,29] is applicable and effective for the alkaline earth metal derivatives (**1a**–**c**, **2a**–**c**; Method 2). However, this method cannot be utilized to prepare lanthanoid(II) 3,5-diphenylpyrazolates, which require the use of the less oxidizing $HgPh_2$.[12,13] The direct metal/pyrazole reaction, successfully used for a variety of homoleptic lanthanoid pyrazolates,[10a,11,30] yielded products **1a**–**c**, **2a**–**c** in good yields (Method 3) after an extraction with THF or DME. Redox transmetallation with thallium pyrazolates developed specifically for lanthanoid(II) pyrazolates[12,13] was found equally applicable for **1a**, **2b** (Method 4). Overall there is good evidence that Ca, Sr, Ba react more readily with pyrazoles than the rare earth metals.

Compounds **3a**–**c** were prepared using methods commonly used for the alkaline earth metals (Method 5 and 6 Table 1).[24] The successful use of liquid ammonia to prepare compounds **3a**–**c** (Method 5), prompted attempts to prepare divalent lanthanoid pyrazolates,[31] as also indicated by the previous preparation of Eu^{II} and Yb^{II} cyclopentadienides and phenolates.[32] Protolysis of silylamides as used for **3a**–**c** (Method 6, Table 1) provided the synthetically evasive [Sm(Ph_2pz)$_2$(dme)$_2$],[13] and is a standard route to lanthanoid organoamides, alkoxides and aryloxides.[33]

Structural aspects: Low-temperature single-crystal X-ray structure determinations have been carried out for **1a**–**c**, **2a**–**c**, **3a**,**b**. Details of the crystallographic data are provided in the Experimental Section. Representative examples of the crystallographically different structures are shown in Figures 1–5 and selected bond lengths and angles are presented in Tables 2–4. All compounds are monomeric and

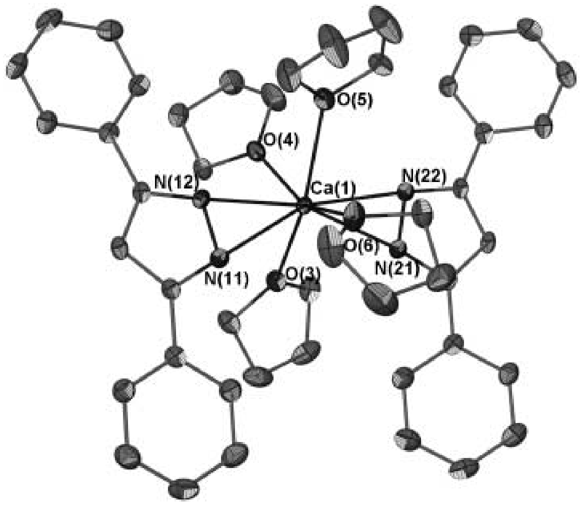

Figure 1. Computer-generated plot of **1a** with anisotropic displacement parameters depicting 50 % probability. The hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] of THF adducts **1a**–**c**.

	1a	1b	1c
M–N(11)	2.470(2)	2.539(3)	2.795(5)
M–N(12)	2.430(2)	2.639(3)	2.736(5)
M–N(21)	2.393(2)	2.587(3)	2.813(5)
M–N(22)	2.532(2)	2.573(3)	2.749(5)
M–O(3)	2.494(2)	2.613(3)	2.744(4)
M–O(4)	2.460(2)	2.614(3)	2.756(4)
M–O(5)	2.479(2)	2.591(3)	2.734(4)
M–O(6)	2.502(2)	2.578(3)	2.710(4)
N(11)-M-N(12)	32.43(6)	30.69(9)	28.5(2)
N(21)-M-N(22)	32.18(6)	30.73(9)	28.6(2)
N(11)-M-N(21)	125.72(7)	126.54(9)	162.2(2)
N(12)-M-N(22)	169.58(7)	171.75(9)	156.4(2)
O(3)-M-O(4)	74.87(6)	75.74(9)	93.8(1)
O(4)-M-O(5)	80.59(6)	131.38(9)	84.4(1)
O(5)-M-O(6)	74.56(7)	74.25(9)	87.5(1)
O(6)-M-O(3)	130.51(6)	79.36(9)	94.2(1)

display one crystallographic independent molecule with the exception of **2c**, in which three independent molecules have been observed. The THF adducts **1a** and **1b** are isomorphous, whereas compounds **2a** and **2b**, and **3a** and **3b** are isostructural.

The monomeric, eight coordinate THF adducts **1a–c** show a *transoid* orientation of two η^2-3,5-diphenylpyrazolate ligands with four THF donors in equatorial positions (Figure 1, Table 2). For compounds **1a,b** the metal sits in a plane generated by the pyrazolate rings, and the phenyl groups are almost coplanar with the pyrazolate ring (maximum torsion angle Ph–pz 18°). One ligand binds almost symmetrically (Δ(M−N) 0.014–0.040 Å, Table 2), while the second is more asymmetrical (Δ(M−N) 0.100–0.139 Å), resulting in a slight twist of the pyrazolate ligands towards each other. The O-M-O angles between adjacent THF donors range from 74.25(9)° to 131.38(9)°. If each pyrazolate ligand is considered attached through the center of the N−N bond (bite angles 30.69(8)–32.46(6)°), the coordination environment can be described as distorted octahedral with a *trans* angle (cen(N-N)-M-cen(N-N)) of 158.30° (**1a**), 157.44° (**1b**). The M−O(thf) distances (Table 2) are in the expected range,[17,24a] for example, **1a** 2.460(2)–2.502(2) Å, and display very similar values relative to the eight-coordinate [Ca(tBu$_2$pz)$_2$(triglyme)] **4e** (2.470(3)–2.544(2) Å).[17] The M−O(N) bond lengths differ by an amount similar to the differences between the ionic radii for eight-coordinate Ca^{2+} and Sr^{2+}.[1]

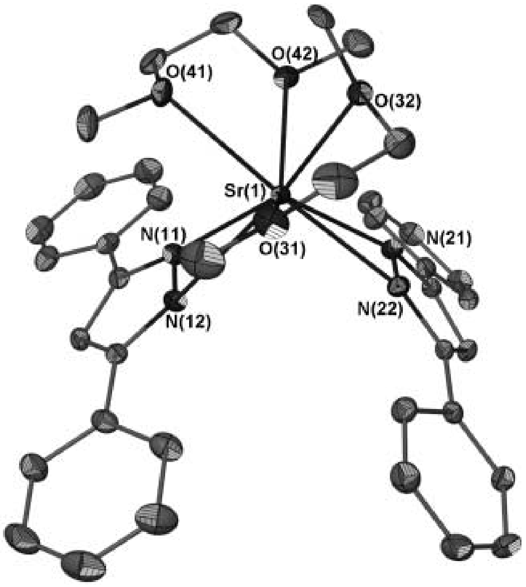

Figure 2. Computer-generated plot of **2b** with anisotropic displacement parameters depicting 50 % probability. The hydrogen atoms have been omitted for clarity.

In contrast, the DME complexes **2a** and **2b** display a *cisoid* orientation of the pyrazolate ligands with capping DME molecules (Figure 2, Table 3). Again, the phenyl rings are almost coplanar with the pyrazolate rings with a maximum twist out of plane of 23.7°. The average M−N distances in **2a** (2.398(8) Å) and **2b** (2.55(1) Å) are shorter than in **1a** (2.456(8) Å) and **1b** (2.59(1) Å), reflecting the reduced steric demand of two DME ligands as compared to four THF donors.[34] Both complexes show quite symmetrical chelation (Δ(M−N) 0.003–0.086 Å) and a (cen(N-N)-M-cen(N-N)) angle of 100.92° (**2a**) and 101.81°(**2b**) reflecting the *cisoid* ligand geometry. The chelation of the DME donors is quite symmetrical with Δ(M−O) distances of 0.051–0.060 Å. The bond length differences between **2a** and **2b** resemble the difference in corresponding ionic radii.

Table 3. Selected bond lengths [Å] and angles [°] of DME adducts **2a–c**.

	2a	**2b**	**2c**
M−N(11)	2.384(2)	2.547(3)	2.755(3)
M−N(12)	2.396(2)	2.566(3)	2.774(4)
M−N(21)	2.448(2)	2.542(3)	2.796(4)
M−N(22)	2.362(2)	2.539(3)	2.735(4)
M−O(31)	2.447(2)	2.633(3)	2.935(4)
M−O(32)	2.507(2)	2.579(3)	2.811(3)
M−O(41)	2.506(2)	2.651(3)	3.019(3)
M−O(42)	2.449(2)	2.600(3)	2.852(3)
M−O(51)			3.073(3)
M−O(52)			2.856(3)
N(11)-M-N(12)	33.40(6)	31.33(9)	28.74(9)
N(21)-M-N(22)	33.13(6)	31.31(9)	28.60(10)
N(11)-M-N(21)	98.35(7)	97.13(9)	126.43(11)
N(12)-M-N(22)	99.41(7)	96.34(9)	88.21(11)
O(31)-M-O(32)	66.93(6)	64.05(9)	55.36(11)
O(41)-M-O(42)	67.13(5)	63.11(9)	55.69(10)
O(51)-M-O(52)			54.33(8)
O(31)-M-O(41)	75.66(5)	89.69(9)	66.30(10)
O(32)-M-O(42)	75.95(6)	79.26(9)	118.46(11)
O(31)-M-O(51)			114.57(9)
O(32)-M-O(52)			149.39(10)
O(41)-M-O(51)			61.65(9)
O(42)-M-O(52)			73.29(11)

Whilst the barium derivative **1c** is eight coordinate, **2c** is ten coordinate with one more DME ligand than **2a,b**. The higher coordination number can be accommodated by the larger size of Ba^{2+} than Sr^{2+} (Δ = 0.16 Å). In **1c** and **2c** the relative dispositions of the η^2-pyrazolate ligands (Figures 3

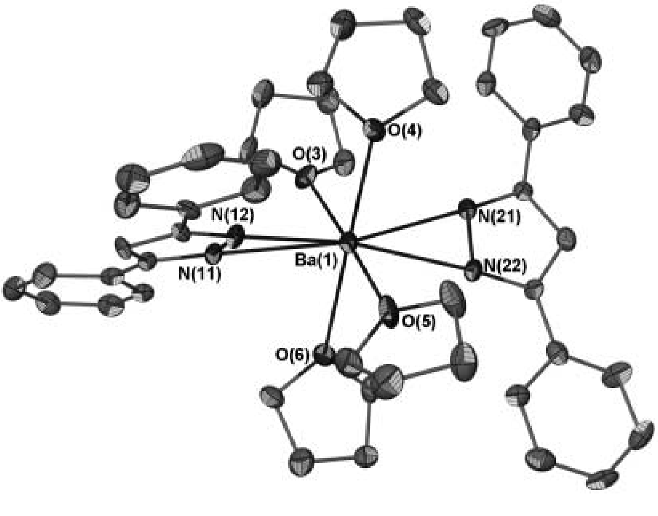

Figure 3. Computer-generated plot of **1c** with anisotropic displacement parameters depicting 50 % probability. The hydrogen atoms have been omitted for clarity.

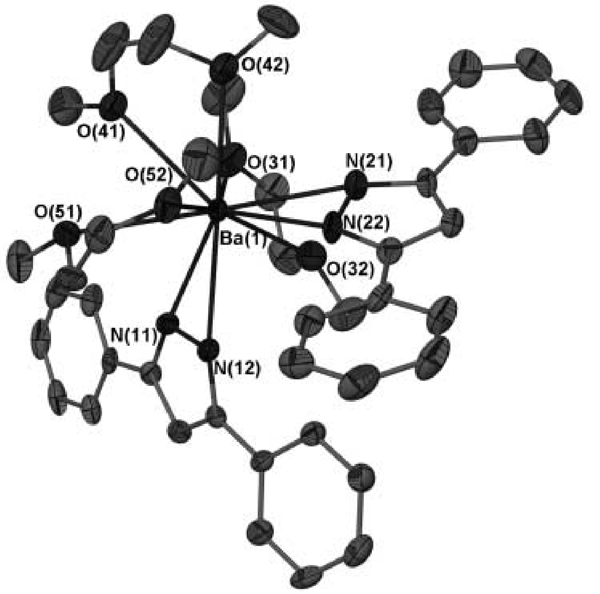

Figure 4. Computer-generated plot of **2c** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

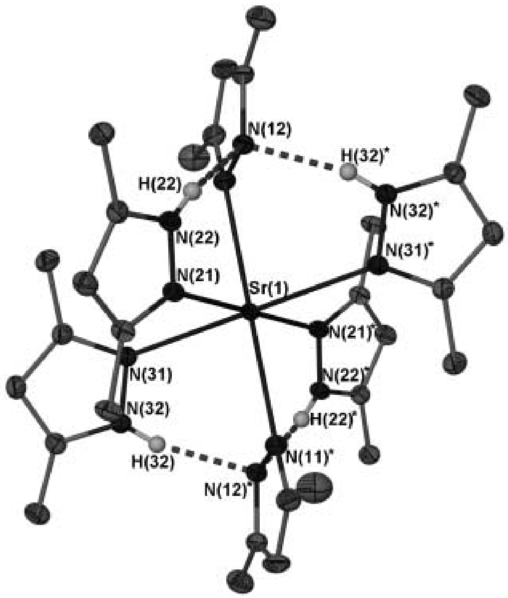

Figure 5. Computer-generated plot of **3b** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms not involved in hydrogen-bonding have been omitted for clarity.

and 4) are changed from **1a,b 2a,b** (Figures 1 and 2) and are now mutually perpendicular. In **1c**, there is a *trans* cen(N-N)-Ba-cen(N-N) angle of 176.97° (cf. 157–159° for **1a,b**) and near octahedral $BaO_4(cen)_2$ geometry. The four THF molecules are near square planar (90° ± 5° between adjacent oxygen atoms) with very similar M–O bond lengths (2.73 ± 0.02 Å). The reduced steric demand of the perpendicular ligand orientation allows the phenyl rings to be closer to coplanarity with the pyrazolate ring (maximum torsion angle 11° **1c**, 15° **2c**) than in **1a** and **2a**. This feature is associated with quite symmetrical η^2-Ph_2pz coordination with ⟨Ba–N⟩ of 2.77 ± 0.04 Å in **1c** and 2.77 ± 0.03 Å in **2c**, despite the difference of two in coordination number. In *cisoid* **2c**, the perpendicular orientation of the Ph_2pz ligands leaves a gap for coordination of an additional DME. The other two DME donors are *cisoid,* forming the base of a distorted square antiprism, with the third DME and the centers of the N–N bonds of the pyrazolate ligands occupying the top face. The M–O bond lengths of the basal *cis* DME donors are more asymmetric (2.95 ± 0.12 Å) than observed for the third DME between the *cis*-pyrazolates (2.91 ± 0.03 Å). Thus the Ba–O distances increase markedly (ca. 0.2 Å) from **1c** to **2c**, more than expected (ca. 0.1 Å) from the increase in coordination number, perhaps as compensation for the unexpected similarity in Ba–N bond lengths between the compounds.

Table 4. Selected bond lengths [Å] and angles [°] of pyrazole adducts **3a,b**.[a]

	3a	**3b**
M–N(11) and #1	2.447(2)	2.622(2)
M–N(21)	2.505(1)	2.652(2)
M–N(31)		2.675(1)
N(22)-H(22)···N(12)#1	2.01(2)	2.02(2)
N(32)-H(32)···N(12)#1		2.06(3)
N(11)-M-N(11)#1	180.0(0)	180.0(0)
N(21)-M-N(21)#1	180.0(0)	180.0(0)
N(11)-M-N(21)	97.06(4)	83.85(5)
N(11)-M-N(31)		96.14(5)
N(11)-M-N(21)#1	82.94(4)	96.15(5)
N(21)-M-N(31)		78.84(4)
N(21)-M-N(31)#		101.16(4)
N(21)#1-M-N(21)#2	83.32(6)	
N(21)#1-M-N(21)#3	96.68(6)	
N(22)-H(22)···N(12)#1	156(2)	
N(22)-H(22)···N(12)		161(2)
N(32)-H(32)···N(12)#1		161(2)

[a]: # symmetry generated atoms: **3a:** #1: $-x$, $-y+1$, $-z+1$; #2: $y-1/2$, $x+1/2$, $-z+1$; #3 $-y+1/2$, $-x+1/2$, z; **3b:** #1: $-x+1$, $-y+1$, $-z+1$.

In complexes **3a** and **3b** the 3,5-dimethylpyrazolates are arranged in a symmetry required *trans* orientation (Figure 5, Table 4). The dimethylpyrazole donors are located in the equatorial plane with N-Ca-N angles of 83.32–96.68°. In **3a**, the calcium atom is in a position of 2/*m* symmetry. Accordingly, only one pyrazole is symmetry independent with a single Ca–N distance of 2.505(1) Å. The apical η^1-binding pyrazolates have a significantly shorter Ca–N(11) bond (2.447(1) Å), reflecting the effect of charge. The nonbonding Ca···N(12) distance of the pyrazolate ligand is 0.89 Å longer, a difference similar to the bonding and nonbonding nitrogen atoms of the η^1-Me_2pz ligand in $[Nd(\eta^2\text{-}Me_2pz)_2(\eta^1\text{-}Me_2pz)(Me_2pzH)_2(py)]$ (0.83 Å)[10a] and the η^1-$t$$Bu_2pz$ ligand in $[Mg(\eta^1\text{-}tBu_2pz)_2(tBu_2pzH)_2]$ (**5a**; 0.70 Å).[15] Thus, η^1-binding of the Me_2pz ligand is clearly indicated. The Me_2pzH donors form intramolecular hydrogen bonds to the uncoordinated N(12) of the pyrazolates, stabilizing the η^1-binding mode and thereby preventing η^2-coordination. There is a close contact (N(22)–H(22)···N(12)#1 2.01(2) Å, 156(2)°) of two pyrazole rings to each pyrazolate, so that the non-coordinated pyrazolate nitrogen atom (N(12)) is held in a hydrogen-bonding embrace analogous to $[Nd(\eta^2\text{-}Me_2pz)_2(\eta^1\text{-}Me_2pz)$-

$(Me_2pzH)_2(py)]$.[10a] While the apical pyrazolates have a symmetry required 180° N-Ca-N angle, the pyrazole rings describe a dihedral angle of 50.5° with the equatorial plane enabling the hydrogen-bonding of pairs of pyrazole rings to N(12).

A similar arrangement is observed in **3b** with the strontium metal located on an inversion center and the η^1-Ph_2pz ligands in a symmetry enforced 180° *trans* orientation. The four pyrazole donors are symmetry related in pairs with 78.84(4)° and 101.16(4)° angles in the equatorial plane and Sr–N distances of 2.652(1) and 2.675(1) Å, compared with the shorter Sr–N(Me_2pz) distance 2.622(2) Å. In this case, the difference between the Sr–N(11) bond length and the non-bonding Sr···N(12) separation (0.84 Å), clearly indicates η^1-pyrazolate coordination. The differences between the corresponding Ca–N and Sr–N bond lengths (0.155–0.170 Å) closely approach the difference ($\Delta = 0.18$ Å) between the ionic radii of six-coordinate metal centers. Again, there is evidence for hydrogen-bonding: N(22)–H(22)···N(12) 2.02(2) Å, 161(2)° and N(32)–H(32)···N(12)#1 2.06(3) Å, 161(2)°. The pyrazole rings are again tilted away from the equatorial plane in a 54.6(1)° dihedral angle to allow for the chelation of the N–H(22), N–H(32) bonds to N(12) of the pyrazolate. Conceivably the instability of compound **3c** arises from less effective hydrogen-bonding, owing to longer metal-nitrogen bonds.

Structural overview and comparison with lanthanoid(II) pyrazolates: Even though the structures of **1a–c** have currently no lanthanoid(II) counterparts, it is plausible that the as yet uncrystallized Ln = Yb, Eu analogues will have similar structures as the isomorphous **1a,b**. Comparison of the structural features of **2a–c** and the $[Ln(Ph_2pz)_2(dme)_2]$ series reveals both similarities and surprises. For M = Ca **2a**, Sr **2b**, and Ln = Yb **5a**, the complexes all have *cisoid* eight-coordinate metal environments; however, **2b**, and not the expected **2a**, is isomorphous with the Yb complex. In contrast, for Ln = Eu eight-coordinate *transoid* geometry is observed despite the similar Eu^{2+} and Sr^{2+} ionic radii,[1] but **2b** is isostructural with $[Sm(Ph_2pz)_2(dme)_2]$ **5b**[13,35] (Sm^{2+} is 0.02 Å larger than Eu^{2+}). After allowance for the difference in ionic radii[1] the M–N bond lengths in **2a,b** and the $[Ln(Ph_2pz)_2(dme)_2]$ (Ln = Yb, Eu, Sm) analogues are almost identical, but with significantly increased Ln–O values (0.03 Å).

The ionic radii of eight and ten coordinate Ba^{2+} ions are 1.42 and 1.52 Å, respectively,[1] approximately 0.07 Å larger than corresponding radii of La^{2+} (estimated from extrapolation of Shannons data[1]), the largest possible divalent lanthanoid. Thus, the value of the barium structures as a guide to predict structures in theoretical La^{2+}, Ce^{2+}, and Pr^{2+} compounds is limited.

At first sight the difference in coordination number between **1c** (CN = 8) and **2c** (CN = 10) seems surprising. The sum of the steric coordination numbers[34] (StCN) of the ligands is 8.2 for **1c** and 8.8 for **2c.** The last is comparable with 8.7 observed for the nine-coordinate $[Nd(Ph_2pz)_3(thf)_3]$, though the appropriate Nd^{3+}/Ba^{2+} radii differ by 0.36 Å (Ph_2pz^- is estimated to have a steric coordination number of 1.7 from cone angle data for the ligand).[36] A nine-coordinate $[Ba(Ph_2pz)_2(thf)_5]$ would have a less sustainable ΣStCN of 9.4. Conversely, removal of one DME from **2c** gives ΣStCN of 7.0 (as for **2a,b**), resulting in reduced steric saturation for the large Ba^{2+}. For **3a,b**, the sum of the steric coordination numbers of the ligands is 8.2, if the value for Me_2pzH is considered similar to that of η^1-3,5-dimethylpyrazolate (1.37).[25b] However the somewhat larger M–N(Me_2pzH) than M–N(Me_2pz) bond length could suggest a slightly lower value (1.30) for η^1-Me_2pzH leading to a ΣStCN of 7.9. These values are similar to 8.2 for **1a–c**, but are much higher than for **2a,b** (7.0). If the Me_2pz ligands were η^2-bonded, ΣStCN would increase by about 0.3, resulting in a less favorable arrangement. In any case, η^2-bonding is prevented by the hydrogen-bonding of the uncoordinated nitrogen.

Compounds **3a,b** can be compared with $[Mg(tBu_2pz)_2(tBu_2pzH)_2]$ **5a**,[15] in which intramolecular hydrogen bonds between the NH of the pyrazole ligands and unbound pyrazolate nitrogens, prevents the expected η^2-coordination of the ligand as seen in other magnesium pyrazolates.[16] The much smaller size of four coordinate Mg^{2+} than Ca^{2+} in addition to the higher steric demand of the tBu_2pz than Me_2pz[34,25b] results in tetrahedral coordination of magnesium compared with the octahedral **3a,b**.

Conclusion

This work demonstrates that free-metal syntheses as developed for the rare earth metals can be applied to the heavy alkaline earth metals. Direct metal/pyrazole reactions demonstrate enhanced reactivity for the latter, underscoring the increased electropositive character and reactivity of the alkaline earth metals. With a range of syntheses now available for Ca–, Sr–, and Ba–pyrazolates, exploration of their potential as precursors for solid-state applications is now possible. Structural analogies between alkaline earth and rare earth metals based on size occur but have limitations. They provide a basis for suggesting that *trans*-$[Ln(Ph_2pz)(thf)_4]$ (Ln = Yb, Eu) complexes may be isolable despite past difficulties.[12,13]

Experimental Section

General Procedures: The compounds described above are extremely air and moisture sensitive requiring all manipulations to be carried out in an inert atmosphere (purified nitrogen) by using Schlenk-line and glove box techniques. THF and hexane were distilled from sodium/potassium alloy and degassed in two freeze-pump-thaw cycles; other handling methods and solvent purification have been reported previously.[37]

IR data (4000–650 cm^{-1}) were obtained for Nujol mulls sandwiched between NaCl plates with a Perkin–Elmer 1600 or Perkin–Elmer Paragon FTIR spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance spectrometers (300 MHz, 25 °C). The chemical shifts were referenced to the residual solvent signals. [D_6]benzene and [D_8]THF were dried over sodium/potassium alloy, and were then vacuum-transferred and stored under purified nitrogen. Alkaline earth metal analyses were performed by direct EDTA titration with Eriochrome Black T indicator[38] (in the presence of Mg–EDTA) of solutions prepared by digestion of accurately weighted samples in concentrated HNO_3 or aqua regia followed by dilution with water and adjusting the pH with NH_4OH/NH_4Cl buffer to pH 11. Microanalyses for samples sealed in glass ampoules under nitrogen were determined by the Campbell Microanalytical Service, University of Otago, New Zealand. Melting points were obtained in capillaries sealed under nitrogen and are uncalibrated. Alkaline earth metals were standard commercial turnings or granules (99 %), Sr, Ba being under oil. Ammonia was dried by treatment with sodium, and was then condensed into the reaction vessel. 3,5-Dimethylpyrazole was obtained commercially, 3,5-diphenylpyrazole,[39] bis(pentafluorophenyl)mercury(II),[40] thallium-3,5-diphenylpyrazolate,[12] calcium,[41] strontium,[41] and barium[41] bis[bis(trimethylsilyl)]amide[bis(tetrahydrofuran)] complexes were prepared according to literature procedures.

General procedure for syntheses of compounds 1a–c, 2a–c by Method 2 (Table 1): 3,5-Diphenylpyrazole (0.88 g, 4.0 mmol), bis(pentafluorophenyl)mercury(II) (1.07 g, 2.0 mmol) and excess alkaline earth metal (Ca, Sr, Ba; 0.41 g, 0.88 g, 1.37 g; 10 mmol) were stirred in THF or DME (40 mL) for 1–2 days at room temperature. The gray suspension was allowed to stand for several hours until the metal powder settled out. The reaction mixture was then filtered by using a filter cannula, concentrated, layered with hexane, and stored at −20 °C. Colorless crystals suitable for X-ray diffraction formed within a few days. The formation of C_6F_5H in a representative reaction was demonstrated by ^{19}F NMR spectroscopy.

General procedure for syntheses of compounds 1a–c, 2a–c by Method 3, (Table 1): 3,5-Diphenylpyrazole (0.11 g, 0.50 mmol, **1a–c**; 0.88 g, 4.0 mmol, **2a–c**), and an excess of alkaline earth metal (Ca, Sr, Ba; 0.08 g, 0.18 g, 0.27 g; 2.0 mmol, **1a–c**; 0.41 g, 0.88 g, 1.37 g; 10 mmol, **2a–c**) were placed into a Carius tube and sealed under vacuum (10^{-3} Torr). After heating at 250–300 °C for 48 h the resulting white solid was dissolved in a donor solvent (THF or DME; 30 mL), filtered, concentrated and layered with hexane. Crystals suitable for X-ray diffraction were grown at −20 °C.

General procedure for syntheses of compounds 1a, 2b by Method 4, (Table 1): Thallium 3,5-diphenylpyrazolate (0.22 g, 0.50 mmol for **1a**; 0.85, 2.0 mmol for **2b**) and excess alkaline earth metal (Ca, 0.08 g, 2.0 mmol; Sr, 0.44 g, 4.0 mmol) were stirred in THF or DME (30 mL) at room temperature overnight after initial heating. After the metal powder settled out, the solution was filtered through a filter cannula, concentrated, layered with hexane and stored at −20 °C. Crystals suitable for X-ray diffraction formed within days.

General procedure for syntheses of compounds 3a–c by Method 5, (Table 1): Anhydrous liquid ammonia was condensed into a solution of 3,5-dimethylpyrazole (0.38 g, 4.0 mmol, **3a,c**; 0.57 g, 6.0 mmol, **3b**) in THF (30 mL **3a,c**) or toluene (50 mL **3b**) with suspended alkaline earth metal (Ca, 0.04 g, 1.0 mmol, **3a**; Sr, 0.09 g, 1.0 mmol, **3b**; Ba, 0.14 g, 1.0 mmol, **3c**) and stirred until the metal dissolved. For **3a** after stirring for 1 h, all THF was removed in vacuo. Warm hexane was added to the remaining solid and cooling to room temperature yielded needle shaped crystals; for **3b** evaporation to 30 mL and storage at −13 °C yielded plate shaped crystals. Both were suitable for X-ray diffraction. For **3c** a white precipitate formed in the reaction solution. Proton NMR and IR spectra were obtained after removing most of the solvent in vacuo. Complete removal caused the powdered product to decompose immediately.

General procedure for syntheses of compounds 3a–c by Method 6, (Table 1): $[M(N[SiMe_3]_2)_2(thf)_2]$ (M = Ca: 0.20 g, 0.40 mmol; Sr: 0.28 g, 0.50 mmol; Ba: 0.30 g, 0.50 mmol) and 3,5-dimethylpyrazole (0.10 g, 1.0 mmol for **3a,b**; 0.29 g, 3.0 mmol for **3c**) were dissolved in THF (50 mL). The dilute solution of pyrazole was slowly added to the amide at −78 °C with stirring overnight and subsequent warming to room temperature. For **3a,b** the solvent was removed in vacuo leaving a white powder, which dissolved in hexane (20 mL) (and THF (1 mL) for **3b**) upon slight heating. Slow cooling to room temperature yielded needle shaped crystals, suitable for X-ray diffraction. For **3c** a white precipitate deposited from the reaction solution and was identified as **3c** by NMR and IR spectroscopy after removal of most of the solvent.

Several compounds were prepared using multiple routes. In all cases the products had spectra identical with those of the analytically pure material.

$[Ca(Ph_2pz)_2(thf)_4]$ (1a): Yield: 0.84 g (54 %; Method 2), 0.22 g (57 %; Method 3), 0.32 g (85 %; Method 5) of colorless thin needles; m.p. 87–90 °C; ^1H NMR (300 MHz, $[D_8]$THF, 25 °C): $\delta = 7.89$ (d, ^3J(H,H) = 7.1 Hz, 8 H; *o*-H(Ph)), 7.23 (t, ^3J(H,H) = 7.0 Hz, 8 H; *m*-H(Ph)), 7.08 (t, ^3J(H,H) = 7.0 Hz, 4 H; *p*-H(Ph)), 6.94 ppm (s, 2 H; H4-pz); ^{13}C NMR: $\delta =$ 151.4 (*C*(pz)-Ph), 137.1 (*ipso-C*(Ph)), 129.1 (*o-C*(Ph)), 126.4 (*p-C*(Ph)), 125.8 (*m-C*(Ph)), 100.8 ppm (*C*H(pz)); IR (Nujol): $\tilde{\nu} = 3033$ (m), 1956 (w), 1886 (w), 1817 (w), 1761 (w), 1669 (w), 1596 (s), 1511 (m), 1382 (s), 1337 (w), 1292 (w), 1251 (m), 1220 (m), 1179 (m), 1151 (w), 1044 (s), 965 (s), 897 (s), 760 (s), 684 cm^{-1} (s); elemental analysis calcd. (%) for $C_{46}H_{54}CaN_4O_4$ (767.01): C 72.03, H 7.10, N 7.30, Ca 5.23; elemental analysis calcd (%) for $[Ca(Ph_2pz)_2(thf)_{3.5}]$ $C_{44}H_{50}CaN_4O_{3.5}$ (730.97): C 72.29, H 6.89, N 7.66, Ca 5.48; found: C 70.95, H 6.83, N 8.03, Ca 5.45.

$[Sr(Ph_2pz)_2(thf)_4]$ (1b): Yield: 0.88 g (49 %; Method 2), 0.24 g (59 %; Method 3) of clear thin needles; m.p. 83–86 °C partial melting then solidifies to a white solid, slow decomposition > 305 °C; ^1H NMR (300 MHz, $[D_8]$THF, 25 °C): $\delta = 7.89$, (d, ^3J(H,H) = 7.0 Hz, 8 H; *o*-H(Ph)), 7.25 (t, ^3J(H,H) = 7.4 Hz, 8 H; *m*-H(Ph)), 7.06 (t, ^3J(H,H) = 7.0 Hz, 4 H; *p*-H(Ph)), 6.92 ppm (s, 2 H; H4-pz); ^{13}C NMR: $\delta = 151.1$ (*C*(pz)-Ph), 137.7 (*ipso-C*(Ph)), 128.9 (*o-C*(Ph)), 126.0 (*p-C*(Ph)), 125.7 (*m-C*(Ph)), 100.3 ppm (*C*H(pz)); IR (Nujol): $\tilde{\nu} = 3051$ (m), 3022 (m), 1941 (w), 1828 (w), 1813 (w), 1749 (w), 1668 (w), 1597 (s), 1514 (m), 1336 (w), 1291 (w), 1212 (w), 1218 (w), 1178 (w), 1042 (s), 964 (m), 905 (s), 796 (w), 758 (s), 692 cm^{-1} (s); elemental analysis calcd. (%) for $C_{46}H_{54}N_4O_4Sr$ (814.55): C 67.83, H 6.68, N 6.88, Sr 10.76; found: C 67.59, H 6.45, N 7.50, Sr 11.02.

$[Ba(Ph_2pz)_2(thf)_4]$ (1c): Yield: 1.42 g (82 %; Method 2), 0.27 g (62 %; Method 3) of clear, small blocks; m.p. > 350 °C; ^1H NMR (300 MHz, $[D_8]$THF, 25 °C): $\delta = 7.86$, (d, ^3J(H,H) = 7.1 Hz, 8 H; *o*-H(Ph)), 7.24 (t, ^3J(H,H) = 7.5 Hz, 8 H; *m*-H(Ph)), 7.06 (t, ^3J(H,H) = 7.4 Hz, 4 H; *p*-H(Ph)), 6.94 ppm (s, 2 H; H4-pz); ^{13}C NMR: $\delta = 150.5$ (*C*(pz)-Ph), 137.2 (*ipso-C*(Ph)), 128.9 (*o-C*(Ph)), 126.2 (*p-C*(Ph)), 125.7 (*m-C*(Ph)), 100.3 ppm (*C*H(pz)); IR (Nujol): $\tilde{\nu} = 3098$ (m), 3059 (m), 3034 (m), 1946 (w), 1889 (w), 1823 (w), 1751 (w), 1671 (w), 1560 (s), 1525 (w), 1512 (w), 1338 (w), 1291 (w), 1242 (w), 1217 (m), 1176 (w), 1155 (w), 1061 (m), 1041 (s), 997 (w), 967 (m), 909 (m), 885 (m), 840 (w), 798 (w), 780 (w), 754 (s), 698 (s), 681 cm^{-1} (m); elemental analysis calcd (%) for $C_{42}H_{46}BaN_4O_3$ (792.17): C 63.68, H 5.85, N 7.07, Ba 17.34; found: Ba 16.97 for $[Ba(Ph_2pz)_2(thf)_3]$; elemental analysis calcd (%) for $[Ba(Ph_2pz)_2]$ $C_{30}H_{22}BaN_4$ (575.85): C 62.57, H 3.84, N 9.73; found: C 62.76, H 3.75, N 9.82.

$[Ca(Ph_2pz)_2(dme)_2]$ (2a): Yield: 1.02 g (77 %; Method 2), 0.52 g (39.5 %; Method 3) of white, thin needles; m.p. > 350 °C; ^1H NMR (300 MHz, $[D_6]$benzene, 25 °C): $\delta = 7.90$ (d, ^3J(H,H) = 6.6 Hz, 8 H; *o*-H(Ph)), 7.21 (t, ^3J(H,H) = 7.6 Hz, 8 H; *m*-H(Ph)), 7.08 (t, ^3J(H,H) = 7.3 Hz, 4 H; *p*-H(Ph)), 6.96 (s, 2 H; H4-pz), 2.99 ppm (s, 20 H; DME); ^{13}C NMR: $\delta =$ 151.2 (*C*(pz)-Ph), 135.0 (*ipso-C*(Ph)), 129.2 (*o-C*(Ph)), 127.4 (*p-C*(Ph)), 126.3 (*m-C*(Ph)), 101.4 (*C*H(pz)), 71.6 ppm (CH_3OCH_2(DME)), 59.6 ppm (CH_3OCH_2(DME)); IR (Nujol): $\tilde{\nu} = 3060$ (m), 3027 (m), 1941 (w), 1873 (w), 1812 (w), 1748 (w), 1660 (w), 1599 (m), 1507 (w), 1295 (w), 1246 (m), 1192 (m), 1152 (w), 1116 (m), 1078 (s), 1023 (m), 966 (m), 912 (w), 856 (m), 789 (w), 758 (s), 694 cm^{-1} (s); elemental analysis calcd (%) for $C_{38}H_{42}CaN_4O_4$ (658.84): C 69.27, H 6.43, N 8.50, Ca 6.08; found: C 68.61, H 6.32, N 8.75, Ca 6.30.

$[Sr(Ph_2pz)_2(dme)_2]$ (2b): Yield: 1.19 g (84 %; Method 2), 1.02 g (77 %; Method 3), 1.10 g (83 %; Method 5) of clear, small plates; m.p. 171–175 °C partial melting turning into a white solid at 190 °C, no further solvent loss, m.p. > 350 °C; ^1H NMR (300 MHz, $[D_6]$benzene, 25 °C): $\delta =$ 8.13 (d, ^3J(H,H) = 6.6 Hz, 8 H; *o*-H(Ph)), 7.33 (t, ^3J(H,H) = 7.6 Hz, 8 H; *m*-H(Ph)), 7.24 (s, 2 H; H4-pz), 7.16 (t, ^3J(H,H) = 7.3 Hz, 4 H; *p*-H(Ph)), 2.91 (s, 12 H; (CH_3OCH_2(DME)), 2.83 ppm (s, 8 H; (CH_3OCH_2(DME)); ^{13}C NMR: $\delta = 152.3$ (*C*(pz)-Ph), 137.2 (*ipso*-C(Ph)), 129.2 (*o-C*(Ph)), 126.4 (*p-C*(Ph)), 125.9 (*m-C*(Ph)), 101.4 (*C*H(pz)), 71.3 (CH_3OCH_2(DME)), 59.5 ppm (CH_3OCH_2(DME)); IR (Nujol): $\tilde{\nu} = 3059$ (m), 3032 (m), 1944 (w), 1875 (w), 1806(w), 1747(w), 1663 (w), 1596 (m), 1519 (w), 1332 (w), 1297 (m), 1247 (w), 1210 (m), 1192 (m), 1098 (m), 1062 (s), 1010 (m), 963 (m), 911 (m), 854 (m), 756 (s), 691 cm^{-1} (s); elemental analysis calcd (%) for $C_{38}H_{42}N_4O_4Sr$ (706.38): C 64.61, H 5.99, N 7.93, Sr 12.40; found: C 64.71, H 6.08, N 7.75, Sr 12.42.

$[Ba(Ph_2pz)_2(dme)_3]$ (2c): : Yield: 0.85 g (51 %; Method 2), 1.28 g (76 %; Method 3) of clear, big blocks; m.p. > 350 °C; ^1H NMR (300 MHz, [D$_6$]benzene/[D$_8$]THF, 25 °C): $\delta = 7.96$ (d, ^3J(H,H) = 6.9 Hz, 8H; *o*-H(Ph)), 7.27 (t, ^3J(H,H) = 7.5 Hz, 8H; *m*-H(Ph)), 7.08 (d, ^3J(H,H) = 7.5 Hz, 4H; *p*-H(Ph)), 7.01 (s, 2H; H4-pz), 3.39 (s, 12H; (CH$_3$OC*H*$_2$(DME)), 2.98 ppm (s, 18H; (C*H*$_3$OCH$_2$(DME)); ^{13}C NMR: $\delta = 150.9$ (*C*(pz)-Ph), 138.3 (*ipso*-*C*(Ph)), 128.8 (*o*-*C*(Ph)), 125.6 (*p,m*-*C*(Ph)), 100.4 (*C*H(pz)), 72.8 (CH$_3$O*C*H$_2$(DME)), 59.1 ppm (*C*H$_3$OCH$_2$(DME)); IR (Nujol): $\tilde{\nu} = 3058$ (m), 1945 (w), 1880 (w), 1813(w), 1753(w), 1671 (w), 1592 (m), 1512 (m), 1289 (w), 1245 (w), 1198 (m), 1134 (m), 1070 (s), 1021 (m), 965 (m), 913 (w), 851 (m), 750(s), 689 cm^{-1} (s); elemental analysis calcd (%) for $C_{42}H_{52}N_4O_6Ba$ (846.23): C 59.61, H 6.19, N 6.62, Ba 16.23; found: C 59.67, H 6.49, N 6.90, Ba 16.31.

[Ca(Me$_2$pz)$_2$(Me$_2$pzH)$_4$] (3a): Yield: 0.03 g (30 %; Method 6) and (0.21 g; 50 %; Method 4) of colorless needles; m.p. 160–165 °C; ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): $\delta = 11.01$ (broad s, 4H, N-H), 5.69 (s, 6H; C-H), 1.99 ppm (s, 36H,CH$_3$); ^{13}C NMR: $\delta = 146.1$ (C(pz)-Me), 104.3 (CH(pz)), 12.6 ppm (pz-C(Me)); IR (Nujol): $\tilde{\nu} = 3178$ (m), 3126 (w), 3089 (m), 2716 (m), 2598 (m), 2360 (m), 1412 (s), 1085 (w), 1045 (w), 1019 (s), 860 (m), 799 (m), 755 (s) cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{46}CaN_{12}$ (614.87): C 58.61, H 7.54, N 27.33, Ca 6.52; found: C 58.86, H 7.87, N 27.84, Ca 6.30.

[Sr(Me$_2$pz)$_2$(Me$_2$pzH)$_4$] (3b): Yield: 0.04 g (30 %; Method 6) and 0.49 g (74 %; Method 4) of colorless thin needles; m.p. 130–131 °C; ^{1}H NMR (300 MHz, [D8]THF, 25 °C): $\delta = 12.58$, (s, 4H; N-H), 5.73 (s, 6H), 2.05 ppm (s, 36H); ^{13}C NMR: $\delta = 153.3$ (C(pz)-Me), 105.3 (CH(pz)), 12.2 ppm (pz-C(Me)); IR (Nujol): $\tilde{\nu} = 3197$ (w), 3098 (m), 2725 (w), 1512 (s), 1410 (s), 1072 (w), 1041 (m), 1014 (m), 965 (w), 901 (w), 765 cm^{-1} (w) ; elemental analysis calcd (%) for $C_{30}H_{46}N_{12}Sr$ (662.41): C 54.40, H 7.00, N 25.38, Sr 13.23; found: C 54.76, H 7.24, N 25.38, Sr 12.90.

[Ba(Me$_2$pz)$_2$(Me$_2$pzH)$_4$(thf)$_n$] (3c): ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): $\delta = 9.03$ (s, 4H; N-H), 5.68 (s, 6H), 1.99 (s, 36H), 3.57, 1.42 ppm (THF). Complete removal of THF caused the resulting powder to decompose, therefore a proton NMR was obtained after removing most of the solvent in vacuo. IR (Nujol): $\tilde{\nu} = 3103$ (w), 2722 (w), 1510 (s), 1406 (s), 1315 (w), 1017 (m), 962 (w), 871 (w), 788 (m), 747 cm^{-1} (w) .

X-ray crystallographic studies: The crystals obtained as described above were removed from the Schlenk tube in a nitrogen filled glove box or under a stream of N$_2$ and immediately covered with a layer of viscous hydrocarbon oil (Immersion Oil Type NVH, ProSciTech; Infineum). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature N$_2$ stream of the diffractometer.[42]

Structure determinations: For all compounds a hemisphere of low-temperature data was collected (monochromatic Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) using an Enraf-Nonius CCD area-detector instrument or a Bruker SMART system, complete with three-circle goniometer and CCD detector. A total of N unique reflections (N_0 [$I > 2\sigma(I)$] "observed") were used in least squares refinement (anisotropic U for non-hydrogen atoms, (x, y, z, U_{iso})$_\mathrm{H}$ constrained) after structure solution by Direct Methods as included in the XSEED[43] or SHELXTL-Plus program package.[44] Absorption corrections were performed using the programs maXus[45] (**1a**–**c**, **2a**–**c**) and SADABS (**3a,b**).[46] Hydrogen atoms were placed geometrically and refined, including free rotation about C–C bonds for methyl groups with U_{iso} constrained at 1.2 for non-methyl groups, and 1.5 for methyl groups times U_{eq} of the carrier C atom. A THF solvent molecule in **3a** was "squeezed out" by using Platon,[47] due to heavy disorder and consequent inability to locate and refine the positions adequately. The electron density of the void corresponds to one THF molecule.

Data for [Ca(3,5-Ph$_2$pz)$_2$(thf)$_4$] (1a): $C_{45}H_{55}CaN_4O_4$, $M_r = 767.01$, monoclinic, space group $P2_1/c$ (No. 14), $T = 123(2)$ K; $a = 24.581(5)$, $b = 9.141(2)$, $c = 19.704(4)$ Å, $\beta = 113.11(3)°$, $V = 4070.3$ Å^3; $\rho_{\mathrm{calcd}} = 1.251$ g cm^{-3}, $Z = 4$; $\mu_{\mathrm{Mo}} = 20.2$ cm^{-1}; crystal size: $0.13 \times 0.10 \times 0.05$ mm; transmission (min/max) = 0.9742/0.9899. $N_t = 41403$, $N = 7144$ ($R_{\mathrm{int}} = 0.0735$), $N_o = 5070$; $R = 0.0493$, $R_w = 0.1002$ [$I > 2\sigma(I)$]; $R = 0.0844$, $R_w = 0.1130$ (all data); $|\Delta\rho_{\max}| = 0.885$ e Å^{-3}.

[Sr(3,5-Ph$_2$pz)$_2$(thf)$_4$] (1b): $C_{45}H_{55}N_4O_4Sr$, $M_r = 814.55$, monoclinic, space group $P2_1/c$ (No. 14), $T = 123(2)$ K; $a = 24.697(5)$, $b = 9.247(2)$, $c = 19.737(4)$ Å, $\beta = 113.43(3)°$, $V = 4135.4$ Å^3; $\rho_{\mathrm{calcd}} = 1.308$ g cm^{-3}, $Z = 4$; $\mu_{\mathrm{Mo}} = 13.51$ cm^{-1}; crystal size: $0.18 \times 0.10 \times 0.03$ mm; transmission (min/max) = 0.9420/0.9891; $N_t = 33992$, $N = 6967$ ($R_{\mathrm{int}} = 0.1249$), $N_o = 4353$; $R = 0.0537$, $R_w = 0.0911$ [$I > 2\sigma(I)$]; $R = 0.1142$, $R_w = 0.1068$ (all data); $|\Delta\rho_{\max}| = 0.631$ e Å^{-3}.

[Ba(3,5-Ph$_2$pz)$_2$(thf)$_4$] (1c): $C_{45}H_{55}BaN_4O_4$, $M_r = 864.27$, monoclinic, space group $P2_1/c$ (No. 14), $T = 123(2)$ K; $a = 16.125(3)$, $b = 20.151(4)$, $c = 13.229(3)$ Å, $\beta = 98.98(3)°$, $V = 4246.0$ Å^3; $\rho_{\mathrm{calcd}} = 1.352$ g cm^{-3}, $Z = 4$; $\mu_{\mathrm{Mo}} = 9.82$ cm^{-1}; crystal size: $0.10 \times 0.10 \times 0.10$ mm; transmission (min/max) = 0.942/0.9891; $N_t = 39095$, $N = 7431$ ($R_{\mathrm{int}} = 0.1289$), $N_o = 4368$; $R = 0.0591$, $R_w = 0.1286$ [$I > 2\sigma(I)$]; $R = 0.1268$, $R_w = 0.1491$ (all data); $|\Delta\rho_{\max}| = 2.389$ e Å^{-3}.

[Ca(3,5-Ph$_2$pz)$_2$(dme)$_2$] (2a): $C_{38}H_{42}CaN_4O_4$, $M_r = 658.84$, monoclinic, space group $P2_1/n$ (No. 14); $T = 123(2)$ K; $a = 10.435(2)$, $b = 23.800(5)$, $c = 15.200(3)$ Å, $\beta = 109.12(3)°$, $V = 3566.7$ Å^3; $\rho_{\mathrm{calcd}} = 1.227$ g cm^{-3}, $Z = 4$; $\mu_{\mathrm{Mo}} = 2.20$ cm^{-1}; crystal size: $0.28 \times 0.08 \times 0.05$ mm; transmission (min/max) = 0.9420/0.9891; $N_t = 30481$, $N = 6275$ ($R_{\mathrm{int}} = 0.1109$), $N_o = 3359$; $R = 0.0458$, $R_w = 0.0703$ [$I > 2\sigma(I)$]; $R = 0.1287$, $R_w = 0.0873$ (all data); $|\Delta\rho_{\max}| = 0.289$ e Å^{-3}.

[Sr(3,5-Ph$_2$pz)$_2$(dme)$_2$] (2b): $C_{38}H_{42}N_4O_4Sr$, $M_r = 706.38$, monoclinic, space group $P2_1/c$ (No. 140), $T = 123(2)$ K; $a = 23.961(5)$, $b = 18.913(4)$, $c = 7.873(2)$ Å, $\beta = 91.20(3)°$, $V = 3567.1(1)$ Å^3; $\rho_{\mathrm{calcd}} = 1.315$ g cm^{-3}, $Z = 4$; $\mu_{\mathrm{Mo}} = 15.56$ cm^{-1}; crystal size: $0.30 \times 0.10 \times 0.10$ mm; transmission (min/max) = 0.7009/0.8679; $N_t = 32470$, $N = 6237$ ($R_{\mathrm{int}} = 0.0691$), $N_o = 5406$; $R = 0.0495$, $R_w = 0.1135$ [$I > 2\sigma(I)$]; $R = 0.0601$, $R_w = 0.1171$ (all data); $|\Delta\rho_{\max}| = 1.295$ e Å^{-3}.

[Ba(3,5-Ph$_2$pz)$_2$(dme)$_3$] (2c): $C_{42}H_{52}BaN_4O_6$, $M_r = 846.22$, monoclinic, space group $P2_1/c$ (No. 14), $T = 123(2)$ K; $a = 28.078(6)$, $b = 21.004(4)$, $c = 22.215(4)$ Å, $\beta = 105.46(3)°$, $V = 12627(4)$ Å^3; $\rho_{\mathrm{calcd}} = 1.335$ g cm^{-3}, $Z = 12$; $\mu_{\mathrm{Mo}} = 9.92$ cm^{-1}; crystal size: $0.20 \times 0.10 \times 0.10$ mm; transmission (min/max) = 0.8263/0.9073; $N_t = 69021$, $N = 21406$ ($R_{\mathrm{int}} = 0.0747$), $N_o = 13208$; $R = 0.0469$, $R_w = 0.08875$ [$I > 2\sigma(I)$]; $R = 0.1015$, $R_w = 0.1054$ (all data); $|\Delta\rho_{\max}| = 1.170$ e Å^{-3}.

[Ca(3,5-Me$_2$pz)$_2$(3,5-Me$_2$pzH)$_4$] (3a): $C_{30}H_{46}CaN_{12}$, $M_r = 614.87$, tetragonal, space group $P4_2/ncm$ (No. 138), $T = 90(2)$ K; $a = 21.3617(9)$, $b = 21.3617(9)$, $c = 8.1697(5)$ Å, $V = 3728.0$ Å^3; $\rho_{\mathrm{calcd}} = 1.096$ g cm^{-3}, $Z = 4$; $\mu_{\mathrm{Mo}} = 2.04$ cm^{-1}; crystal size: $0.78 \times 0.40 \times 0.38$ mm; transmission (min/max) = 0.8573/0.9266; $N_t = 28466$, $N = 1709$ ($R_{\mathrm{int}} = 0.0548$), $N_o = 29466$; $R = 0.0476$, $R_w = 0.1056$ [$I > 2\sigma(I)$]; $R = 0.0414$, $R_w = 0.1056$ (all data); $|\Delta\rho_{\max}| = 0.291$ e Å^{-3}.

[Sr(3,5-Me$_2$pz)$_2$(3,5-Me$_2$pzH)$_4$] (3b): $C_{30}H_{46}N_{12}Sr$, $M_r = 662.41$, triclinic, space group $P\bar{1}$ (No. 2), $T = 86(2)$ K; $a = 9.1899(8)$, $b = 10.0266(8)$, $c = 11.0350(9)$ Å, $\alpha = 95.404(2)$, $\beta = 105.046(2)$, $\gamma = 113.7250°$, $V = 875.98$ Å^3; $\rho_{\mathrm{calcd}} = 1.256$ g cm^{-3}, $Z = 1$; $\mu_{\mathrm{Mo}} = 15.76$ cm^{-1}; crystal size: $0.10 \times 0.30 \times 0.78$ mm; transmission (min/max) = 0.3727/0.8583, $N_t = 11368$, $N = 5841$ ($R_{\mathrm{int}} = 0.0450$), $N_o = 11368$; $R = 0.0397$, $R_w = 0.0907$ [$I > 2\sigma(I)$]; $R = 0.0469$, $R_w = 0.0927$ (all data); $|\Delta\rho_{\max}| = 1.292$ e Å^{-3}.

CCDC-207201–207206 (**1a–c, 2a–c**), CCDC-218224 (**3a**), and CCDC-218225 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

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