Synthesis, Structures and Characterization of the Calcium Pyrrolates [Ca{(2-(dimethylaminomethyl)pyrrolyl}$_2$ donor$_n$] (donor = THF and pyridine, n = 2; DME and TMEDA, n = 1) as Potential Precursors for Solid-State Applications

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In memory of the late Ron Snaith

Keywords: Calcium / N ligands / Chemical vapor deposition / Transamination / Metallation / Intramolecular donation

The synthesis and characterization of novel alkaline earth metal pyrrolyl derivatives is described. The target molecules were synthesized using transamination and metallation protocols, involving either the treatment of calcium bis[bis(trimethylsilyl)]amide with two equivalents of 2-(dimethylaminomethyl)pyrrole (2-DMAMP) or the reaction of elemental calcium with two equivalents of 2-DMAMP. Different donors, namely THF, pyridine (py), DME (dimethoxyethane), and TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) were utilized to study their influence on the structural chemistry of the target compounds. In order to compare the influence of the metal coordination on the pyrrole ligand, we included the crystal structure of the free 2-DMAMP ligand. All new compounds were characterized using ^{1}H, ^{13}C NMR and IR spectroscopy in addition to X-ray crystallography**.** Crystal data with Mo-K_α radiation (λ = 0.71073 Å) are as follows: **1**: [Ca(2-DMAMP)$_2$(THF)$_2$], a = 15.440(2) Å, b = 14.992(2) Å, c = 10.175(1) Å, β = 94.9(3)°,V= 2346.6(6) Å^3, Z = 4, monoclinic, space group $P2_1/c$, $R1$(all data) = 0.0981; **2**: [Ca(2-DMAMP)$_2$(py)$_2$], a = 9.168(6) Å, b = 10.418(7) Å, c = 13.329(8) Å, α = 85.9(1)°, β = 72.9(1)°, γ = 86.2(1)°, V = 1212.2(1) Å^3, Z = 2, triclinic, space group $P\bar{1}$, $R1$ (all data) = 0.0711; **3**: [Ca(2-DMAMP)$_2$(DME)], a = 10.814(1) Å, b = 12.907(1) Å, c = 15.170(1) Å, V = 2117.3(3) Å^3, Z = 4, orthorhombic, space group $P2_12_12_1$, $R1$ (all data) = 0.0729; **4**: [Ca(2-DMAMP)$_2$(TMEDA)], a = 9.403(6) Å, b = 15.810(1) Å, c = 15.417(1) Å, V = 2292.0(3) Å^3, Z = 4, orthorhombic, space group $Pbcn$, $R1$ (all data) = 0.0997; **5**: 2-DMAMP, a = 10.8820(7) Å, b = 15.2186(10) Å, c = 9.7578(6) Å, β = 109.736(2)°,V = 1521.05(17) Å^3, Z = 2, monoclinic, space group Cc, $R1$ (all data) = 0.0382.

Introduction

Calcium-containing solid-state materials showing huge negative resistance or colossal magnetoresistance (CMR) have become prominent not only for fundamental physics but also for their possibilities in device applications.[1] Amongst these materials, the doped manganates $A_{1-x}Ca_xMnO_3$ (A = rare earth metals) are especially interesting for their potential employment in the development of magnetic recording heads.[2,3] The production of these materials by CVD procedures requires precursors with a high volatility. The well-established β diketonate[4] derivatives decompose cleanly, but their volatility is not sufficient for these applications. Conventional means to improve the volatility by -$SiMe_3$ or -CF_3 substitution are not applicable since small amounts of fluorine or silicon impurities are detrimental to electronic applications.[5]

Nitrogen-based precursors are ideally suited for the production of a wide array of solid-state materials. In addition, the structural flexibility of the ligand system, since two not one organic groups (as in oxygen-based precursors) are linked to a monoanionic, secondary amido ligand, significantly increases ligand design opportunities. The most intensively studied nitrogen-based calcium derivatives carry the sterically demanding hexamethyldisilazane ligand in conjunction with various mono and bidentate donors. A number of donor-containing monomers in addition to a donor-free dimer have been reported and recently summarized in an excellent review article.[6] However, the promise of the calcium bis[bis(trimethylsilyl)]amides as potential precursor materials has not been fulfilled due to the facile acid-promoted cleavage of the N−Si bonds[7] and consequent silicon contamination of the final products. Derivatives of the hexamethyldisilazane ligand replacing one trimethylsilyl group by a bulky aromatic substituent display a reduced

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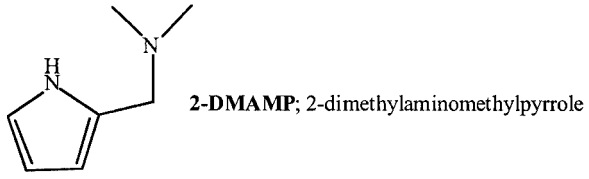
  DOI: 10.1002/ejic.200300311

tendency towards N−Si bond cleavage and have partially fulfilled the aim for volatile precursors.[8] Still, advanced amido-based precursors would avoid the presence of silyl groups altogether, but synthetic difficulties have so far precluded the preparation of these highly reactive materials.[9]

Volatile precursor materials will likely consist of monomeric compounds. However, heavy alkaline earth metal derivatives exhibit a pronounced tendency towards oligomerization due to their large ionic radii.[10] Multiple strategies exist to prevent the formation of oligomers, most prominently the use of sterically demanding ligands, and application of donors and intramolecularly coordinating ligands. Since the use of bulky ligands alone does not ensure the presence of monomeric molecules,[11] a combined approach of multiple strategies is advantageous. As an added incentive, intramolecular coordination is likely to increase the solubility of the target compounds in common organic solvent systems, thus facilitating the delivery of the target compounds in CVD applications.

Amongst the array of nitrogen ligands with intramolecular stabilization capabilities, we identified the monoanionic bidentate pyrrole derivative 2-(dimethylaminomethyl)pyrrole (2-DMAMP), as shown in Scheme 1, as being ideally suited for our purpose, with the $(CH_3)_2NCH_2$- linker providing the desired intramolecular stabilization to allow for the isolation of monomeric species.



2-DMAMP; 2-dimethylaminomethylpyrrole

Scheme 1. Schematic drawing of the 2-DMAMP ligand

Although first reported in the 1940′s,[12] 2-DMAMP has received little attention as a ligand system. In fact, well-characterized main group derivatives are limited to aluminum,[13] gallium and indium[14] in addition to some recently published mixed magnesium cyclopentadienide/amido derivatives.[15] Other metal complexes bearing DMAMP-type ligands include titanium,[16] tungsten,[16] zirconium,[17−19] vanadium,[19] thallium,[20] chromium,[19] molybdenum,[21] cobalt[19] and nickel.[19]

Pyrrolylcalcium and -strontium derivatives with two *tert*-butyl substituents have been reported.[22] This sterically demanding ligand disfavors the η^1-type bonding observed in the 2-DMAMP compounds; instead, π-bonding involving an η^5 arrangement is observed. A related metal geometry is also observed in a calcium porphyrinogen derivative. Here, four pyrrolyl rings are arranged in a macrocycle, each binding in an η^3 fashion to calcium.[23] If, instead, calcium is coordinated to a pyrollyl ring in a porphyrin system, η^1 binding is ensured by the planar nature of the macrocycle.[24] Studies focusing on the unsubstituted pyrrole ligand in conjunction with the heavier alkaline earth metals have been limited to the gas-phase synthesis of the monopyrrolylcalcium and -strontium free radicals.[25]

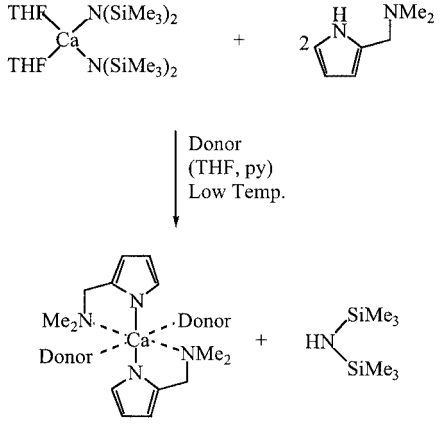
We report here on a group of monomeric pyrrolylcalcium derivatives carrying the 2-(dimethylaminomethyl)pyrrolyl ligand (2-DMAMP), in addition to mono- and bidentate donors, namely $[Ca(2\text{-DMAMP})_2(THF)_2]$ (**1**), $[Ca(2\text{-DMAMP})]_2(py)_2]$ (**2**), $[Ca(2\text{-DMAMP})]_2(DME)]$ (**3**), and $[Ca(2\text{-DMAMP})_2(TMEDA)]$ (**4**). The crystal structure of the free 2-DMAMP ligand **5** is also reported.

Results and Discussion

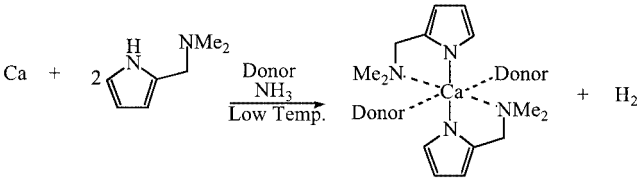
Synthetic Aspects and Reactivity

Multiple synthetic methods were probed to identify the most facile route that allows the production of the target compounds in a simple and efficient manner. The initial starting point was salt elimination, used successfully for the preparation of amidocalcium derivatives.[6,8] Following a similar procedure, we obtained an inseparable precipitate containing the pyrrolyl target compound and potassium iodide. A change in reaction conditions did not improve this result.

Two reaction schemes, transamination[26] (Scheme 2) and metallation[27] (Scheme 3) were identified as viable alternatives, since both have been used successfully to prepare a host of alkaline earth metal derivatives. Limitations of the transamination scheme are based on the required pK_a difference between the liberated amine and the reagent, and only substrates with a higher acidity than the secondary amine may be successfully utilized. If, on the other hand, the acidity would be too high, as for example observed in aromatic thiols, consumption of acid, with protonation of the liberated amine and formation of primary amine and silylated substrate, is observed.[7]



Scheme 2. The synthesis of calcium pyrrolates by transamination



Scheme 3. The synthesis of calcium pyrrolates by direct metallation

Compounds **1** and **2** were prepared using transamination (Scheme 2), although the purity of the resulting products was not consistently high. A common technique to obtain high quality products by transamination is the removal of $HN(SiMe_3)_2$ in vacuo to shift the equilibrium to the product side and assure the quantitative release of $HN(SiMe_3)_2$.[26c] Still, elimination of amine was occasionally incomplete as evidenced by ^1H NMR analysis. Attempts to remove the amine at elevated temperature and under vacuum resulted in the removal of the donor and consequent formation of insoluble precipitates. This was also observed if the acid and the amide were combined too rapidly, or donors were omitted, despite the use of very dilute solutions and low reaction temperatures.

Metallation, used successfully to prepare the target compounds in a facile, reproducible manner, requires the activation of calcium since the oxide layer in commercially available calcium effectively passivates the metal. Several methods are available to activate the metal. Westerhausen et al. successfully use the distillation of the metals for this purpose,[28] while recent collaborative work between the Deacon group and our group showed mercury activation, as used frequently for the rare earth metals, to be effective.[29] Alternatively, dissolving the metals in anhydrous, liquid ammonia followed by addition of acid, as shown with the preparation of a selection of alkaline earth metal derivatives, is also a viable method.[27] As an example, the preparation of the barium amide $[Ba\{N(SiMe_3)_2\}_2(THF)_2]$ by metallation in the presence of ammonia proceeds smoothly,[30] whereas no product is observed if ammonia is omitted. Since the reactivity of the alkaline earth metals increases upon descending the group, metallation is most efficient for barium, whereas no reaction, even after extended reflux in liquid ammonia (dry-ice condenser), is observed for calcium.

With these parameters in mind, we proceeded by dissolving calcium in anhydrous, condensed ammonia, followed by addition of the acid and extended reflux of the reaction mixture. Consistently, the reaction mixture turned dark, and intractable, insoluble solids were obtained. If, however, a small amount of ammonia is condensed onto the reaction mixture to dissolve the metal (as indicated by the formation of deep-blue solutions), followed by the evaporation of most of the ammonia and brief heating, the reaction proceeds smoothly, as evidenced by the vigorous evolution of gas. This method produces the target compounds in excellent yield and purity.

The initially surprising fact that compounds **1**−**4** may be prepared in good yields and purity, while the reaction of calcium metal with $HN(SiMe_3)_2$ does not yield the amide, may be explained by the lower pK_a of the pyrrole vs. the amine, its reduced steric demand and the pyrrole's capability for intramolecular stabilization yielding a thermodynamically favored five-membered ring.

Spectroscopic Studies

The ^1H NMR spectra of compounds **1**−**4** show a consistent change from the spectrum of the free 2-DMAMP ligand **5**. Due to limited solubility of the target compounds, all NMR spectra were recorded in $[D_8]$THF. The most prominent difference is observed for the proton in the 5-position, which shifts from δ = 6.57 ppm in the free ligand **5** to δ = 6.63−6.67 ppm in compounds **1**−**4**. The protons in the 3- and 4-positions in the free ligand lie very close together at δ = 5.90 and 5.85 ppm. In **1**−**4** these signals are shifted slightly upfield, moving even closer together; they are observed at δ = 5.79 and 5.78 ppm. In the free ligand the CH_2 and $N(Me)_2$ protons are observed as singlets at δ = 3.31 and 2.13 ppm, respectively. Upon deprotonation both signals experience a slight downfield shift to δ = 3.46 and

Table 1. Crystallographic data for compounds **1**−**5**

	1	**2**	**3**	**4**	**5**
Formula	$CaN_4O_2C_{22}H_{38}$	$CaN_6C_{24}H_{32}$	$CaN_4O_2C_{18}H_{32}$	$CaN_6C_{20}H_{38}$	$C_{14}H_{24}N_4$
Fw	430.64	444.64	376.56	402.64	99.35
a (Å)	15.440(2)	9.168(6)	10.814(1)	9.403(6)	10.8820(7)
b (Å)	14.992(2)	10.418(7)	12.907(1)	15.810(1)	15.2186(10)
c (Å)	10.175(1)	13.329(8)	15.170(1)	15.417(1)	9.7578(6)
α (deg)		85.9(1)	90	90	90
β (deg)	94.916(3)	72.9(1)	90	90	109.736(2)
γ (deg)		86.2(1)	90	90	90
V (Å^3)	2346.6(6)	1212.2(1)	2117.3(3)	2292.0(3)	1521.05(17)
Z	4	2	4	4	2
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	*Pbcn*	*Cc*
d_{calc} (g/cm^3)	1.219	1.218	1.181	1.167	1.085
Linear abs coeff (mm^{-1})	0.291	0.281	0.314	0.290	0.067
T (K)	93(2)	93(2)	87(2)	85(2)	96(2)
2θ range (deg)	3.80 −50.0	3.20−65.78	4.14−50.00	5.14−65.76	4.80- 65.64
Indep reflns	4048	8176	3712	4120	2979
No. of params	265	283	226	199	259
*R*1, *wR2* (all data)[a]	0.0981, 0.1730	0.0700, 0.1253	0.0729, 0.1096	0.0997, 0.0766	0.0382, 0.0770
*R*1, *wR*2 (>2σ)	0.0515, 0.1345	0.0505, 0.1253	0.0568, 0.1074	0.0401, 0.0674	0.0349, 0.0760

[a] $R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$; $wR2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

2.25 ppm. These values are in good agreement with literature data.[13−15]

Structural Aspects

Crystallographic information and data collection parameters for compounds **1**−**4** are summarized in Table 1 and the Exp. Sect. A compilation of selected geometrical parameters for the compounds is given in Table 2 and 3, while Figures 1−5 illustrate the structural principles displayed in compounds **1**−**5**. Compounds **1** and **2**, bearing the monodentate donors THF and pyridine, and **3** and **4**, carrying bidentate donors DME and TMEDA, display very similar structural features and will be described together.

Table 2. Selected bond lengths (Å) and angles (°) for **1**−**4**

	1[a]	**2**[a]	**3**	**4**
Ca−N*p*[b]	2.386(6)	2.394(2)	2.384(6)	2.404(1)
Ca−N*id*	2.523(6)	2.532(2)	2.523 (6)	2.584(1)
Ca−O*nd*	2.372(4)		2.378(4)	
Ca−N*nd*		2.524(2)		2.595(1)
N*p*1−Ca−N*p*2	180.0	180.0	112.26(1)	115.95(5)
N*id*1−Ca−N*id*2	180.0	180.0	166.75(1)	148.88(4)
N*p*1−Ca−N*id*1	75.22(2)	75.71(8)	73.16(2)	72.59(4)
N*p*1−Ca−O*nd*1	91.99(9)		156.51(1)	
N*p*1−Ca−N*nd*1		89.68(8)		87.47(4)
O*nd*1−Ca−O*nd*2	180.0		67.55(8)	
N*nd*1−Ca−N*nd*2		180.0		69.38(6)

[a] Independent molecules averages. [b] N*p* = pyrrolyl nitrogen; N*id* = intramolecular donor nitrogen; O*nd* = neutral donor oxygen; N*nd* = neutral donor nitrogen.

Table 3. Selected bond lengths (Å) and angles (°) for **5**

C1−N1	1.37(2)
C1−C2	1.37(3)
C2−C3	1.42(2)
C5−N2	1.47(2)
C6−N2	1.46(2)
C1−N1−C4	108.9(2)
C6−N2−C7	110.0(1)
N1−C1−C2	108.1(1)
C1−C2−C3	107.3(2)
N1−C1−C5	120.4(2)
N2−C5−C1	113.7(1)

[Ca(2-DMAMP)$_2$(THF)$_2$] (1) and [Ca(2-DMAMP)$_2$(py)$_2$] (2): Compounds **1** (Figure 1) and **2** (Figure 2) exhibit monomeric six-coordinate calcium centers. The two independent metal centers in compounds **1** and **2** are located on inversion centers, thus, two half molecules are located in each asymmetric unit, of which only one is shown. The coordination geometry around calcium is distorted octahedral with a center of symmetry requiring a linear geometry of the trans oriented ligands and donors. The distortion from octahedral geometry stems from the narrow bite angles within the intramolecularly coordinating ligand, with values of 75.22(2)° for **1** and 75.71(8)° for **2**. Ca−N(pyrrolate) and Ca−N(NMe$_2$) distances in **1** are 2.386(6) Å and 2.523(6) Å, respectively, with closely related values [2.394(2) Å and 2.532(2) Å] for **2**. The Ca−O(THF) distances in **1** are 2.372(4) Å, while the Ca−N(pyridine) distances in **2** are 2.524(2) Å.

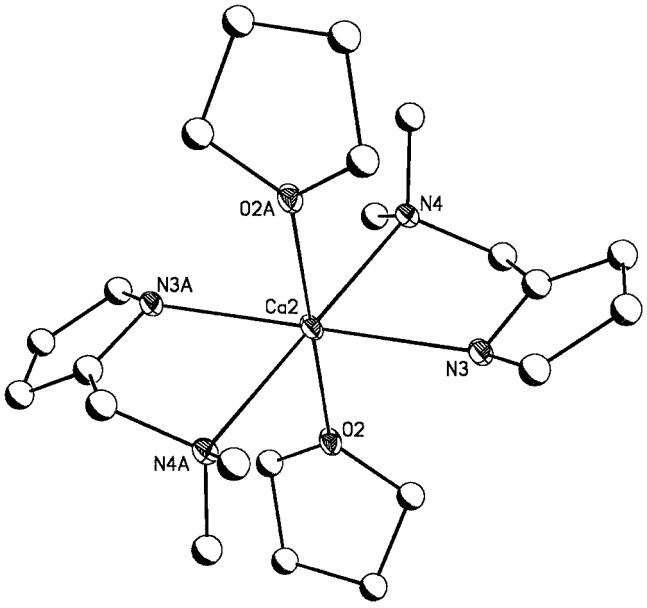


Figure 1. Computer-generated plot of **1** with anisotropic displacement parameters depicting 30% probability for all non-carbon atoms; the hydrogen atoms have been omitted for clarity

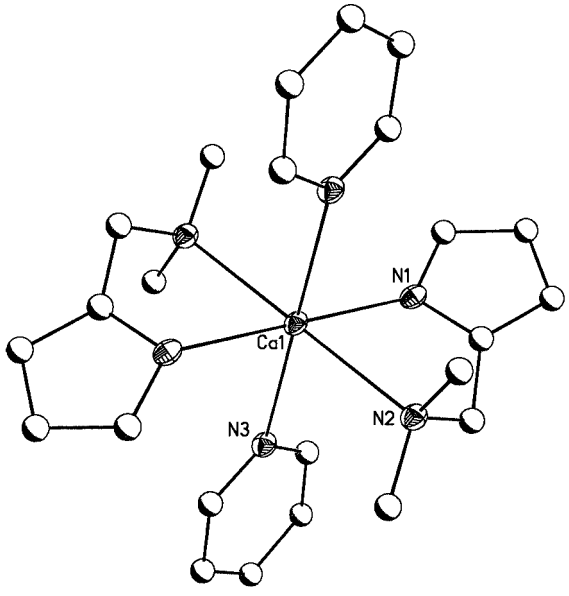


Figure 2. Computer-generated plot of **2** with anisotropic displacement parameters depicting 30% probability for all non-carbon atoms; the hydrogen atoms have been omitted for clarity

[Ca(2-DMAMP)$_2$(DME)] (3) and [Ca(2-DMAMP)$_2$-(TMEDA)] (4): Compounds **3** and **4,** represented in Figures 3 and 4, respectively, feature monomeric, six-coordinate metal centers with two 2-DMAMP ligands and one DME or TMEDA donor. In compound **4** the metal center is located on a twofold axis, generating the second half of the

molecule. In both **3** and **4** the 2-DMAMP ligands adopt a *cisoid* conformation to accommodate the bidentate donors, resulting in a significant distortion from ideal octahedral geometry, as reflected in N1−Ca1−N1A, N2−Ca1−N2A and O1−Ca1−O2 angles of 112.35(1)°, 166.65(1)° and 67.82(8)°, respectively, in **3**, and N1−Ca1−N3, N2−Ca1−N4 and N5−Ca1−N6 angles of 115.95(5)°, 142.23(5)° and 69.38(6)°, respectively, in **4**. The calcium center and the 2-DMAMP ligand form five-membered rings with N−Ca−N angles of 73.22(2)° in **3**, and 72.59(4)° in **4**, which are in part responsible for the distortion from octahedral geometry. The Ca−N(pyrrolate) and Ca−N(NMe_2) distances are 2.378(6) Å and 2.522(6) in **3** and 2.384(6) Å and 2.523(6) Å in **4**, respectively. The calcium-oxygen bond lengths in **3** average 2.378(4) Å, while Ca−N(TMEDA) contacts in **4** are 2.595(1) Å.

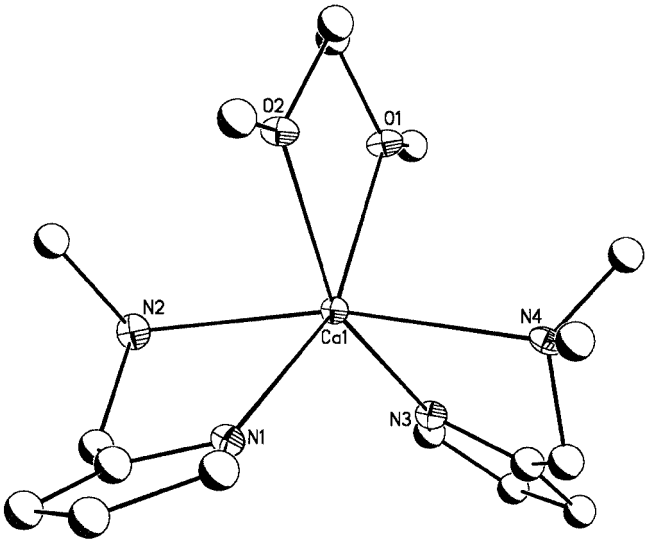


Figure 3. Computer-generated plot of **3** with anisotropic displacement parameters depicting 30% probability for all non-carbon atoms; the hydrogen atoms have been omitted for clarity

DMAMP-2 (5): The free ligand is depicted in Figure 5; pertinent bond lengths and angles are summarized in Table 3. Compound **5** crystallizes with two independent molecules per asymmetric unit which are connected through a hydrogen bond (2.024 Å) involving the pyrrole hydrogen atom on one molecule and the dimethylamine fragment on the second pyrrole. The geometrical parameters in the two independent molecules are very similar, therefore only one is described. Pyrrole nitrogen-carbon bond lengths are observed at 1.370(2) Å, the C−C bond lengths between carbons 2 and 3 and 4 and 5 are slightly shorter, at 1.356(3) and 1.361(2) Å, while the C−C bond between carbons 3 and 4 is the longest, at 1.422(2) Å. This is consistent with the location of the double bonds. The angle at nitrogen is 108.81(16)°. The (CH_2)NMe_2 linker is attached to carbon 2, with a C2−C6 bond length of 1.497(2) Å.

The observed calcium-pyrrolate binding mode in **1**−**4** is a sigma-type η^1-bond through the nitrogen atom on the pyrrole ring. η^5 Coordination, as observed for di-*tert*-butyl-substituted pyrrolates of calcium and strontium,[22] or calcium porphyrinogen,[23] is not observed. The differences in coordination mode can be explained by the steric bulk of the di-*tert*-butyl-substituted pyrrolate, or the arrangement of pyrrolyl groups in the macrocycle, which effectively block the σ-type Ca−N(pyrrolyl) bonding observed here. In addition, the formation of a thermodynamically favored five-membered ring utilizing the intramolecularly coordinating $(CH_3)_2NCH_2$- linker also favors the σ-type bonding observed in compounds **1**−**4**.

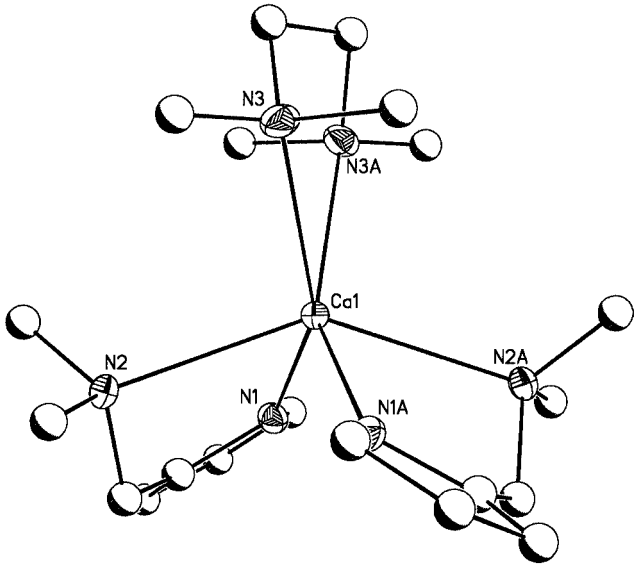


Figure 4. Computer-generated plot of **4** with anisotropic displacement parameters depicting 30% probability for all non-carbon atoms; the hydrogen atoms have been omitted for clarity

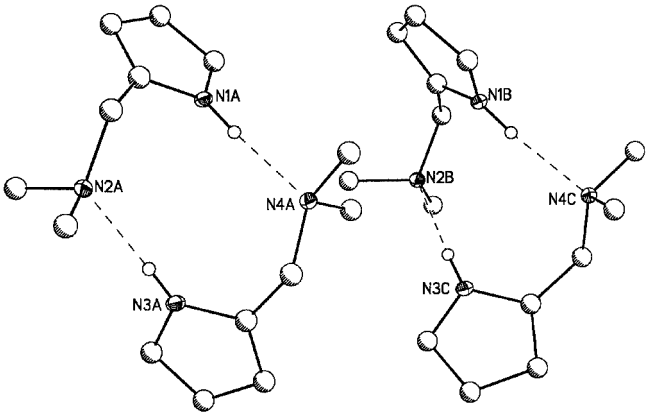


Figure 5. Computer-generated plot of **5** with anisotropic displacement parameters depicting 30% probability for all non-carbon atoms; the hydrogen atoms, except on the pyrrole nitrogen have been omitted for clarity

In compounds **1** and **2** the two 2-DMAMP ligands occupy the equatorial plane, with the two monodentate donors occupying the axial positions. In the case of the bidentate donors DME and TMEDA, this arrangement is no longer possible, since the donor bite angle prevents the coordination to both axial positions. Instead, a *cisoid* ligand arrangement is observed.

Calcium-pyrrolyl nitrogen bond lengths in **1**−**4** lie in a narrow range [2.378(6)−2.404(1) Å], as do the calcium-nitrogen [Ca−N(CH_3)$_2$] contacts involving the intramolecular linker [2.522(2)−2.584(1) Å]. As expected, the Ca−N bond lengths to the anionic pyrrolyl ligand are significantly shorter than to those to the neutral -N(CH_3)$_2$ donor. The Ca−N(pyrrolyl) values compare favorably with the four-coordinate calcium amides [Ca{N($SiMe_3$)$_2$}$_2$(THF)$_2$] [2.301(6) Å],[31] and [Ca{N($SiMe_3$)(2,6-*i*Pr$_2$$C_6H_3$)}$_2(THF)_2$] [2.326(8) Å],[8] despite the lower coordination number observed in these compounds. The only marginally longer Ca−N(pyrrolyl) bond lengths in compounds **1**−**4** are an expression of the larger steric demand of the amido ligands as compared to the pyrrolyl system. The ligand size is based on the narrow N(pyrrolyl)−Ca−N[N(CH_3)$_2$] bite angle [72.59(4) to 75.71(8)°], effectively reducing the steric bulk of the ligand. The Ca−N(pyrrolyl) bond lengths also compare favorably with the seven coordinate tris-pyridine solvated calcium porphyrin with Ca−N(pyrrolyl) distances of 2.382(4)−2.416(3) Å.[23]

Metal binding has only a negligible influence on the overall features of the pyrrolyl ring, and the structural parameters of **1**−**4** are within standard deviations compared to the free 2-DMAMP ligand **5**. Compounds **1**−**4** may be compared with a family of furfurylsilylamides, of which the magnesium compound is closest to the calcium species presented here.[32] In this ligand system, a furan ring is connected in the 2-position to a methyltrimethylsilylamine linker. This linker is deprotonated yielding an amido function with the opportunity for intramolecular furan coordination. In the presence of non-coordinating solvents, both the furan oxygen and the amido function are coordinated to the magnesium. If, however, donating solvents such as THF are utilized, only the amide coordinates to the metal. In the pyrrole system presented here, the intramolecular coordinating ability of the ligand is used in all cases, even in the presence of strong or multidentate donors such as pyridine, TMEDA or DME, with analogous results for a series of magnesium compounds.[33] Clearly then, without relying on silyl substitution, the 2-DMAMP ligand displays excellent capabilities to stabilize monomeric heavy alkaline earth metal derivatives, as needed for solid-state applications.

Solid-State Studies

Compounds **1**−**4** were analyzed for their capacity as CVD precursor molecules. To this effect, TGA and sublimation studies were conducted. Remarkably, the compounds involving nitrogen donation by either pyridine (compound **2**) or TMEDA (compound **4**) show a clean decomposition pattern in the TGA, whereas **1** and **3** display a complex decomposition behavior, with a significant amount of residue remaining at 450 °C. The TGA pattern for compound **4** is shown in Figure 6, indicating a clean decomposition process at low temperatures. To confirm the usefulness of the material as a CVD precursor, extended sublimation studies were conducted with the most promising material, the TMEDA adduct **4**. It was shown that compound **4** sublimes cleanly into a uniform calcium-containing solid-state species, demonstrating the potential of these compounds as precursor materials.

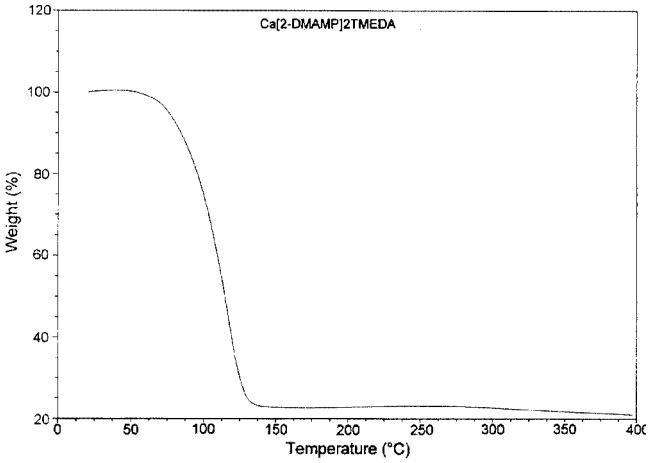


Figure 6. TGA profile for compound **4**

Conclusion

Four new calcium pyrrolates containing intramolecularly coordinating linkers were synthesized and characterized. The compounds exhibit monomeric structures in the solid state as shown by X-ray crystallography. Extended studies involving TGA and sublimation showed that compounds **2** and **4** show considerable promise as precursor materials for the production of calcium-containing solid-state materials. This result is especially important in the light of desirable silicon-free calcium source material.

We have probed salt-elimination, transamination, and metallation procedures and found that calcium pyrrolate derivatives are most conveniently accessible by metallation. This method also holds the greatest promise of a facile large-scale preparation.

Experimental Section

General Procedures: All reactions were performed using standard procedures using a purified nitrogen atmosphere by utilizing either modified Schlenk techniques and/or a Braun Labmaster 100 dry box. Pyridine, THF, DME, TMEDA, hexamethyldisilazane and pyrrole were distilled prior to use from CaH_2 or Na/K alloy. Ca[N($SiMe_3$)$_2$]$_2$$THF_2$ [31] and 2-DMAMP[12] were synthesized according to literature procedures. Formaldehyde and dimethylamine hydrochloride were obtained from commercial sources and used as received. Anhydrous ammonia was further dried by condensing over sodium metal. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 or -500 spectrometer. Spectra were recorded in deuterated THF and are referenced to residual solvent resonances. Use of C_6D_6 or $CD_3C_6D_5$ as NMR solvents did not allow for the dissolution of the target compounds, precluding the recording of quality spectra. Infrared spectra were recorded as Nujol mulls between NaBr plates on a Perkin−Elmer PE 1600 FI-IR spectrometer. Thermogravimetric analysis (TGA) was performed on

vacuum dried samples kept under inert conditions and loaded manually onto a Auto TGA2950HR thermogravimetric analyzer. The TGA experiments were performed under an N_2 atmosphere using a heating rate of 10 °C /min. Reliable elemental analyses could not be obtained, even when glove-box handling was attempted, due to the high moisture and oxygen sensitivity of all compounds reported. Repeated elemental analysis of high quality samples with clean ^{1}H NMR spectra and perfect integration afforded large deviations between duplicate runs, even when V_2O_5 was added as a combustion aid. This is a well-known problem in alkaline earth metal chemistry.[34]

Procedure A, Transamination: In a typical experiment, a Schlenk tube was charged with one equivalent of $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ (typically 3.6 mmol), dissolved in 40 mL of donor solvent (THF, pyridine or DME) and stirred at low temperature for half an hour. To this, a solution of two equivalents of 2-DMAMP in 20 mL of the same solvent was added dropwise with vigorous stirring. The resulting clear solution was stirred for three hours at low temperature, −78 °C (acetone/dry ice) for THF or DME, or −40 °C (acetonitrile/dry-ice) for the pyridine reactions, due to the higher melting point of pyridine. The clear, yellow solution was slowly warmed to room temperature before being filtered through a fine filter frit. The filtrate was reduced in volume to about 30 mL, followed by storage at −23 °C.

Procedure B, Metallation: In a typical experiment, a Schlenk tube was charged with calcium metal (typically 1 mmol) and two equivalents of 2-DMAMP. To this, about 60 mL of solvent (THF, pyridine or a toluene/TMEDA (10:1 v/v mixture) was added and stirred at −78 °C (THF, DME or toluene/TMEDA), or at −40 °C if pyridine was utilized. Into this mixture approximately 20 mL of ammonia was condensed. The solution was then removed from the cold bath and allowed to warm up to room temperature. After most of the ammonia had evaporated, the presence of ammoniates was indicated by a characteristic bronze color. Heat was applied briefly, initiating vigorous bubbling. The evolution of gas persisted for several minutes. After the formation of bubbles had ceased, the homogeneous clear solution was filtered through a fine filter frit. The volume of the filtrate was reduced to about 30 mL followed by storage at −23 °C (unless otherwise noted).

[Ca(2-DMAMP)$_2$(THF)$_2$] (1). Procedure A: $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ (1.89 g, 3.6 mmol) in 40 mL of THF and 2-DMAMP (0.93 g, 7.5 mmol) in 20 mL of THF stirred at −78 °C. Within a week colorless block-shaped crystals suitable for X-ray crystallography studies formed. Yield: 47% (0.73 g, 1.70 mmol).

Procedure B: Calcium metal (0.04 g, 1 mmol) and 2-DMAMP (0.25 g, 2 mmol), stirred at −78 °C. Within a day colorless block-shaped crystals suitable for X-ray crystallography studies formed. Yield: 65% (0.28 g, 0.65 mmol).

$C_{22}H_{38}CaN_4O_2$ (430.64): calcd. C 61.36, H 8.89, Ca 9.31, N 13.01; found C 54.88, H 8.24, Ca 10.34, N 18.41. M.p.: turns opaque at 80 °C (presumably loss of donor solvent), turns dark above 135 °C. ^{1}H NMR ([D]$_8$THF): δ = 1.80 (m, 4 H), 2.25 (s, 12 H), 3.46 (s, 4 H), 3.64 (m, 4 H), 5.79 (s, 4 H), 6.63 (s, 2 H) ppm. ^{13}C NMR ([D]$_8$THF): δ = 23.63 (THF), 45.70 (NMe_2), 57.63 (CH_3), 62.25 (CH_2), 68.28 (THF), 106.34 (CH), 107.77 (CH), 127.21 (CH) ppm. IR (Nujol): $\tilde{\nu}$ = 3084.4 cm^{-1}, 1353.3, 1294.5, 1261.8, 1160, 1136, 1086, 1037, 767.2, 623.5.

[Ca(2-DMAMP)$_2$(py)$_2$] (2). Procedure A: $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ (1.89 g, 3.6 mmol) in 40 mL of pyridine and 2-DMAMP (0.93 g, 7.5 mmol) in 20 mL of pyridine (−40 °C). The solution turned cloudy and was removed from the cold bath and warmed to room temperature upon which it turned clear. Within a week, colorless block-shaped crystals suitable for X-ray crystallography studies formed. Yield: 55% (0.88 g, 1.97 mmol).

Procedure B: Calcium metal (0.04 g, 1 mmol) and 2-DMAMP (0.25 g, 2 mmol). Stirred at −40 °C. Yield: 72% (0.32 g, 0.72 mmol).

$C_{24}H_{32}CaN_6$ (444.64): calcd. C 64.82, H 7.25, Ca 9.01, N 18.90; found C 55.20, H 7.63, Ca 9.88, N 18.00.. M. p.: turns opaque at 95 °C (presumably loss of donor solvent), turns dark above 120 °C, sublimes above 200 °C. ^{1}H NMR ([D]$_8$THF): δ = 2.25 (s, 12 H), 3.46 (s, 4 H), 5.79 (s, 4 H), 6.68 (s, 2 H), 7.25 (m, 4 H), 7.66 (t, 2 H), 8.53 (d, 4 H) ppm. ^{13}C NMR ([D]$_8$THF): δ = 45.82 (NMe_2), 62.36 (CH_2), 106.3 (CH), 106.4(CH), 124.5 (py), 127 (CH), 136.4 (py), 151 (py) ppm. IR (Nujol): $\tilde{\nu}$ = 2723.1 cm^{-1}, 1591.9, 1345.6, 1169.6, 1021, 947.8, 729.4, 627.9.

[Ca(2-DMAMP)$_2$(DME)] (3). Procedure A: $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ (1.89 g, 3.6 mmol) in 40 mL of DME and 2-DMAMP (0.93 g, 7.5 mmol) in 20 mL of dimethoxyethane stirred at −78 °C. The solution turned cloudy and was removed from the cold bath, first warmed up to room temperature and subsequently heated to reflux temperature. On reaching reflux temperature, the solution turned clear. Upon cooling to room temperature, colorless needle-shaped crystals suitable for X-ray crystallography studies formed. Yield: 44% (0.59 g, 1.56 mmol).

$C_{18}H_{32}CaN_4O_2$ (376.56): M.p.: turns opaque at 80 °C (presumably loss of donor solvent), turns dark above 155 °C. ^{1}H NMR ([D]$_8$THF): δ = 2.25 (s, 12 H), 3.27 (s, 6 H), 3.43 (s, 4 H), 3.60 (s, 4 H), 5.79 (s, 4 H), 6.68 (s, 2 H), 7.25 (m, 4 H) ppm. ^{13}C NMR ([D]$_8$THF): δ = 45.40 (NMe_2), 57.63 (CH_3), 59.00 (CH_2), 72.83 (OCH_2), 107.6 (CH), 107.8(CH), 127 (CH) ppm. IR (Nujol): $\tilde{\nu}$ = 1261.2 cm^{-1}, 1242.9, 1224, 1172.4, 11.38.2, 1100.8, 1069.6, 1025.9, 992.9, 827.9.

[Ca(2-DMAMP)$_2$(TMEDA)] 4. Procedure B: Calcium (0.04 g, 1 mmol) and 2-DMAMP (0.25 g) in 5 mL of TMEDA and 50 mL of toluene (−78 °C). Block-shaped crystals suitable for X-ray crystallography formed within 24 hours. Yield: 67% (0.17 g, 0.44 mmol).

$C_{20}H_{38}CaN_6$ (402.64): calcd. C 59.65, H 9.51, Ca 9.95, N 20.89; found C 51.82, H 8.30, Ca 12.35, N 21.24. M.p.: turns opaque at 85 °C (presumably loss of donor solvent), turns dark above 145 °C, sublimes above 200 °C. ^{1}H NMR ([D]$_8$THF): δ = 1.73 (s, 12 H), 3.27 (s, 6 H), 3.30 (s, 4 H), 3.45 (s, 4 H), 5.79 (s, 4 H), 6.68 (s, 2 H), 7.25 (m, 4 H), 7.66 (t, 2 H), 8.53 (d, 4 H) ppm. ^{13}C NMR ([D]$_8$THF): δ = 45.50 (TMEDA, NMe_2), 45.82 (NMe_2), 57.73 (TMEDA, CH_2), 62.03 (CH_2), 106.29 (CH), 106.45(CH), 127.4 (CH) ppm. IR (Nujol): $\tilde{\nu}$ = 3361.8 cm^{-1}, 1506.1, 1376.4, 1096.0, 1027.2, 947.8, 714.1.

X-ray Crystallographic Study: X-ray quality crystals for all compounds were grown as described in the Exp. Sect. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of viscous hydrocarbon oil (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.[35] The intensity data sets for all compounds were collected using a Siemens SMART system, complete with three-circle goniometer and CCD detector operating at −54 °C. Data for compounds **1** and **2** were collected at 93(2)K and for **3**, **4** and **5** at 87(2), 85(2) and 96(2) K, respectively, using a custom-built low temperature device from Professor H. Hope (UC Davis). In all cases graphite-monochromated Mo-K_α radiation (λ = 0.71073Å) was employed. The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three

sets of exposures, each with a different angle, and each exposure covering 0.3° in φ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections. In all cases, no decay was observed. An absorption correction was applied for all compounds utilizing the program SADABS.[36] The crystal structures of all compounds were solved by Direct Methods, as included in the SHELXTL-Plus program package.[37] Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of all compounds were refined by full-matrix least-squares refinement on F^2 (SHELX-93). Hydrogen atoms were placed geometrically and refined using a riding model, 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. The crystallographic programs used for structure refinement and solution were installed on a PC clone. Scattering factors were those provided with the SHELX program system. All non-hydrogen atoms were refined anisotropically.

CCDC-210044−210047 (**1**−**4**) and -217175 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internet.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We are grateful for support from the National Science Foundation (CHE-9702246 and CHE-0108098), SHARP Corporation of North America and Syracuse University. Purchase of the X-ray diffractometer was made possible with grants from NSF (CHE-9527898), the W. M. Keck Foundation and Syracuse University. We thank Professor W. Winter (SUNY ESF, Syracuse) for his help in obtaining TGA analyses.

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Received May 23, 2003

