Synthesis and Characterization of Calcium Complexes Containing η^2-Pyrazolato Ligands

Dirk Pfeiffer, Mary Jane Heeg, and Charles H. Winter*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received August 31, 1999

Treatment of calcium bromide with 3,5-di-*tert*-butylpyrazolatopotassium (2 equiv) in tetrahydrofuran afforded $Ca(tBu_2pz)_2(THF)_2$ (69%). The reaction of this compound with pyridine (3 equiv), tetramethylethylenediamine (TMEDA, 1 equiv), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 1 equiv), triglyme (1 equiv), and tetraglyme (1 equiv) yielded $Ca(tBu_2pz)_2(py)_3$ (51%), $Ca(tBu_2pz)_2$(TMEDA) (74%), $Ca(tBu_2pz)_2$(PMDETA) (50%), $Ca(tBu_2pz)_2$(triglyme) (73%), and $Ca(tBu_2pz)_2$(tetraglyme) (57%), respectively. Treatment of the tetrahydrofuran adduct of $Ca(Me_2pz)_2$, generated in situ, with PMDETA (1 equiv), triglyme (1 equiv), and tetraglyme (1 equiv) afforded $Ca(Me_2pz)_2$(PMDETA) (65%), $Ca(Me_2pz)_2$(triglyme) (54%), and $Ca(Me_2pz)_2$(tetraglyme) (40%), respectively. The X-ray crystal structures of $Ca(tBu_2pz)_2(py)_3$, $Ca(tBu_2pz)_2$(TMEDA), $Ca(tBu_2pz)_2$(PMDETA), $Ca(tBu_2pz)_2$(triglyme), and $Ca(Me_2pz)_2$(PMDETA) revealed six-, seven-, or eight-coordinate calcium centers with η^2-pyrazolato ligands. $Ca(tBu_2pz)_2$(triglyme) sublimes at 160 °C (0.1 mmHg). The potential utility of these complexes as source compounds for chemical vapor deposition processes is discussed.

Introduction

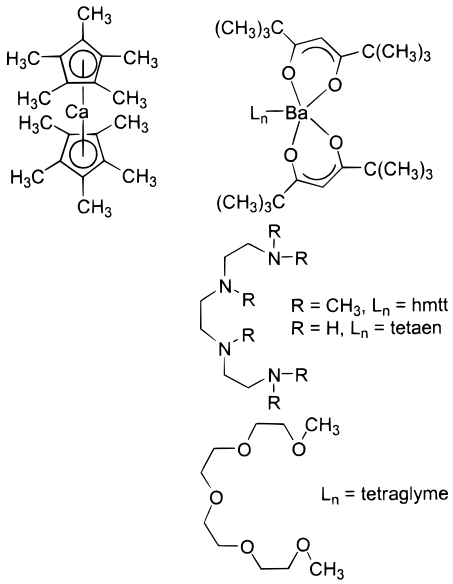
1,3-Diketonate complexes of the heavier group 2 metals are commonly used as source compounds in chemical vapor deposition (CVD) processes for the deposition of oxide materials.[1−10] However, the presence of metal−oxygen bonds makes diketonate-based source compounds inappropriate for the deposition of non-oxide materials. Furthermore, many group 2 complexes bearing 1,3-diketonate ligands have low vapor pressures (typically <1 Torr at >200 °C),[1] which leads to low film deposition rates and potentially erratic vapor transport due to the high bubbler temperatures required to achieve reasonable gas-phase concentrations.

Recent studies have indicated that the calcium ion should be a very useful dopant for the fabrication of p-type group 13 nitride semiconductor films.[11−15] The only volatile calcium compounds that do not contain calcium−oxygen bonds and lack potential dopant elements for semiconductor matrices (e.g., Si, B) are the calcocenes; for example, decamethylcalcocene sublimes at 80 °C at low pressure.[1,16] However, this class of compounds has only been recently used as precursors in film depositions.[17] Carbon−hydrogen defects are incorporated into GaN films under CVD growth conditions with moderate to heavy doping using bis(cyclopentadienyl)magnesium, suggesting that the cyclopentadienyl ligands are the carbon source.[18,19] Accordingly, precursors containing calcium−carbon bonds may give unacceptably high carbon incorporation in film depositions of non-oxide materials. An ideal precursor for the introduction of calcium into group 13 nitride films would possess only calcium−nitrogen bonds and would contain only calcium, nitrogen, carbon, and hydrogen. A glimpse of what might be possible with nitrogen ligands is illustrated by $Ba(tmhd)_2$(hmtt) (tmhd = tetramethylheptanedionate; hmtt = 1,1,4,7,10,10-hexamethyltriethylenetetramine), which binds hmtt selectively over tetraglyme and exhibits enhanced vapor transport relative to $Ba(tmhd)_2$(tetraglyme).[20] The compound $Ba(tmhd)_2(tetraen)_2$ (tetraen = triethylenetetramine) has been evaluated as a precursor to YBCO films and is claimed to be substantially more volatile and thermally stable than related $Ba(tmhd)_2$ sources.[21] Accordingly, exploration of group 2 compounds containing exclusively nitrogen donor ligand sets might lead to new classes of source compounds for CVD applications that are superior to currently available compounds.

With these considerations in mind, we report the synthesis, structure, and properties of calcium complexes bearing bis-η^2-pyrazolato ligand sets and neutral donors to cap the coordination sphere. These complexes are rare examples of main group metal compounds with η^2-pyrazolato ligands[22] and substantiate the idea that there is a significant analogy between 1,3-diketonate

(1) Wojtczak, W. A.; Fleig, P. F.; Hampden-Smith, M. J. *Adv. Organomet. Chem.* **1996**, *40*, 215.
(2) Wessels, B. W. *Annu. Rev. Mater. Sci.* **1995**, *25*, 525.
(3) Marks, T. J. *Pure Appl. Chem.* **1995**, *67*, 313.
(4) Schulz, D. L.; Marks, T. J. *Adv. Mater.* **1994**, *6*, 719.
(5) Winter, C. H. *Strem Chem.* **1994**, *15*, 1.
(6) Barron, A. R.; Rees, W. S., Jr. *Adv. Mater. Opt. Electron.* **1993**, *2*, 271.
(7) Schieber, M. *J. Cryst. Growth* **1991**, *109*, 401.
(8) Tiitta, M.; Niinisto, L. *Adv. Mater. CVD* **1997**, *3*, 167.
(9) Neumayer, D. A.; Studebaker, D. B.; Hinds, B. J.; Stern, C. L.; Marks, T. J. *Chem. Mater.* **1994**, *6*, 878.
(10) Belot, J. A.; Neumayer, D. A.; Reedy, C. J.; Studebaker, D. B.; Hinds, B. J.; Stern, C. L.; Marks, T. J. *Chem. Mater.* **1997**, *9*, 1638.
(11) Strite, S. *Jpn. J. Appl. Phys.* **1994**, *33*, L699.
(12) Boguslawski, P.; Briggs, E. L.; Bernhold, J. *Appl. Phys. Lett.* **1996**, *69*, 233.
(13) Zolper, J. C.; Wilson, R. G.; Pearton, S. J.; Stall, R. A. *Appl. Phys. Lett.* **1996**, *68*, 1945.
(14) Lee, J. W.; Pearton, S. J.; Zolper, J. C.; Stall, R. A. *Appl. Phys. Lett.* **1996**, *68*, 2102.
(15) Mensching, B.; Liu, C.; Rauschenbach, B.; Kornitzer, K.; Ritter, W. *Mater. Sci. Eng. B* **1997**, *50*, 105.
(16) For an overview of the area, see the following. Hanusa, T. P. *Chem. Rev.* **1993**, *93*, 1023.
(17) Vehkamaki, M.; Hatanpaa, T.; Hanninen, T.; Ritala, M.; Leskela, M. *Electrochem. Solid-State Lett.* **1999**, *2*, 504.
(18) Yi, G.-C.; Wessels, B. W. *Appl. Phys. Lett.* **1997**, *70*, 357.
(19) For a related study, see the following. Redwing, J. M.; Kuech, T. F.; Gordon, D. C.; Vaarstra, B. A.; Lau, S. S. *J. Appl. Phys.* **1994**, *76*, 1585.
(20) Gardiner, R. A.; Gordon, D. C.; Stauf, G. T.; Vaarstra, B. A.; Ostrander, R. L.; Rheingold, A. L. *Chem. Mater.* **1994**, *6*, 1967.
(21) Zama, H.; Morishita, T. *Jpn. J. Appl. Phys.* **1996**, *35* (Part 2), L770.

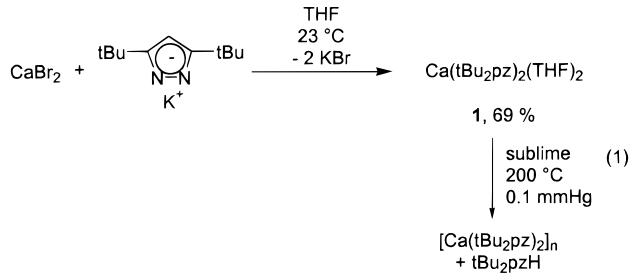
10.1021/ic991049c CCC: $19.00
Published on Web 05/04/2000



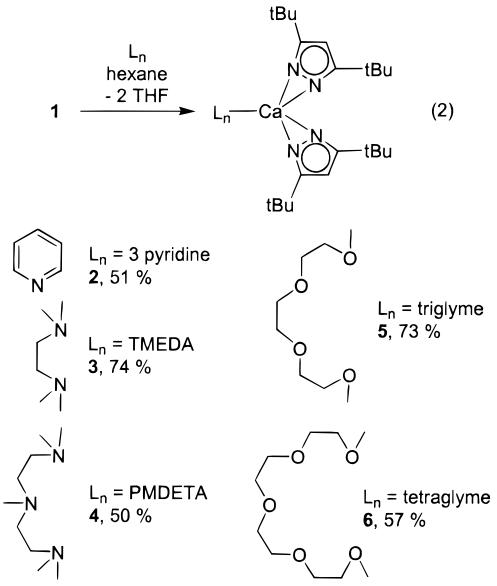
and η^2-pyrazolato ligands.[23−27] Finally, one of the compounds, bis(3,5-di-*tert*-butylpyrazolato)(triglyme)calcium, sublimes at 160 °C (0.1 mmHg) and provides structural insight into the factors that contribute to volatility in group 2 pyrazolato complexes.

Results

Syntheses of Calcium Complexes with 3,5-Disubstituted Pyrazolato Ligands. Our initial goal was to identify thermally stable, volatile pyrazolatocalcium complexes that might be used as source compounds in CVD. We recently reported that dimeric bis(bis(3,5-di-*tert*-butylpyrazolato)magnesium) possesses η^1- and η^2-pyrazolato ligands and sublimes at 150 °C (0.1 mmHg).[22] Since the calcium ion is larger than a magnesium ion (1.00 Å for a six-coordinate calcium ion versus 0.72 Å for a six-coordinate magnesium ion),[28] it is possible that the larger calcium ion would be able to support a bis(η^2-pyrazolato) ligand set. In addition, the presence of neutral donor ligands should promote the formation of monomeric complexes, and such complexes might be volatile. To probe this point, anhydrous calcium bromide was treated with 3,5-di-*tert*-butylpyrazolato-potassium[29] (2 equiv) as described in the Experimental Section to afford bis(3,5-di-*tert*-butylpyrazolato)bis(tetrahydrofuran)-calcium **(1**, 69%) as a white powder after workup (eq 1). The presence of two tetrahydrofuran ligands in **1** was evident from the spectroscopic and analytical data. However, **1** decomposed slowly after isolation by loss of tetrahydrofuran, as indicated by NMR spectroscopy. Since **1** was thermally unstable, single crystals suitable for X-ray structure determination could not be obtained. The attempted sublimation of **1** (200 °C, 0.1 mmHg) yielded a small amount of a white solid. Characterization of this solid by NMR spectroscopy showed it to be a 1.5:1 mixture of 3,5-di-*tert*-butylpyrazole and a complex with 3,5-di-*tert*-butylpyrazolato ligands that did not contain tetrahydrofuran. Accordingly, extensive decomposition occurred during the vapor transport.



To obtain pyrazolato complexes with increased thermal stability, replacement of the tetrahydrofuran ligands by other neutral donors was examined. It is well-known that polydentate ether or amine ligands stabilize monomeric group 2 complexes toward oligomerization.[1−10] Furthermore, we have reported that tris(pyrazolato)lanthanide(III) complexes bearing two neutral nitrogen donor ligands exhibit substantially increased thermal stability compared to analogous complexes bearing two tetrahydrofuran ligands.[30] In an initial reaction, treatment of **1** with pyridine (3 equiv) in hexane afforded bis(3,5-di-*tert*-butylpyrazolato)tris(pyridine)calcium (**2**, 51%; eq 2) as a colorless



crystalline solid. The structural assignment of **2** was based on spectral and analytical data. In addition, an X-ray crystal structure determination of **2** confirmed a monomeric formulation. Unlike **1**, which decomposed at ambient temperature with loss of tetrahydrofuran, **2** showed no evidence for loss of pyridine at ambient temperature over at least 6 months. However, **2** did not sublime at temperatures below 200 °C but instead decomposed at ca. 200 °C to afford an intractable white, sticky solid. In a fashion similar to **2**, treatment of **1** with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), triglyme, or tetraglyme afforded the complexes bis(3,5-di-*tert*-butylpyrazolato)-(TMEDA)calcium (**3**, 74%), bis(3,5-di-*tert*-butylpyrazolato)-(PMDETA)calcium (**4**, 50%), bis(3,5-di-*tert*-butylpyrazolato)-(triglyme)calcium (**5**, 73%), or bis(3,5-di-*tert*-butylpyrazolato)-

(22) Pfeiffer, D.; Heeg, M. J.; Winter, C. H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2517.
(23) Guzei, I. A.; Baboul, A. G.; Yap, G. P. A.; Rheingold, A. L.; Schlegel, H. B.; Winter, C. H. *J. Am. Chem. Soc.* **1997**, *119*, 3387.
(24) Guzei, I. A.; Yap, G. P. A.; Winter, C. H. *Inorg. Chem.* **1997**, *36*, 1738.
(25) Guzei, I. A.; Winter, C. H. *Inorg. Chem.* **1997**, *36*, 4415.
(26) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **1999**, *38*, 1871.
(27) Cosgriff, J. E.; Deacon, G. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 286.
(28) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: Oxford, 1997; p 111.
(29) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **1998**, *37*, 3892.
(30) Pfeiffer, D.; Ximba, B. J.; Liable-Sands, L. M.; Rheingold, A. L.; Heeg, M. J.; Coleman, D. M.; Schlegel, H. B.; Kuech, T. F.; Winter, C. H. *Inorg. Chem.* **1999**, *38*, 4539.

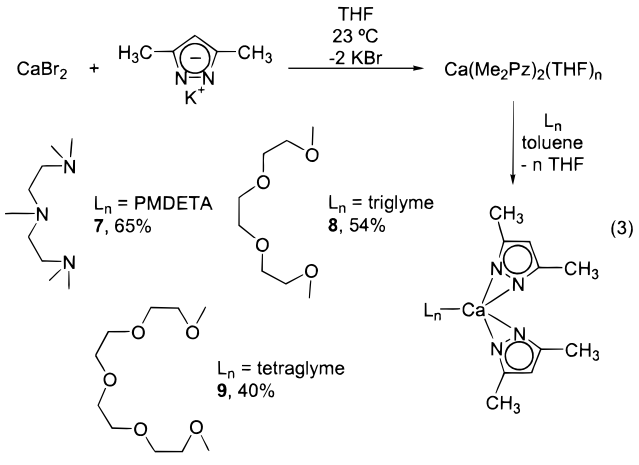
Table 1. Crystal Data and Data Collection Parameters for **2**−**5** and **7**

	2	**3**	**4**	**5**	**7**
empirical formula	$C_{37}H_{53}CaN_7$	$C_{28}H_{54}CaN_6$	$C_{31}H_{61}CaN_7$	$C_{30}H_{56}CaN_4O_4$	$C_{19}H_{37}CaN_7$
fw	635.94	514.85	571.94	576.87	403.64
space group	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	15.3230(4)	28.4089(10)	10.5291(3)	10.6413(3)	10.4958(4)
b (Å)	15.7527(4)	15.4992(4)	19.0050(4)	11.0950(2)	17.0670(6)
c (Å)	17.5494(5)	19.1660(6)	18.0605(4)	30.3077(8)	13.8618(6)
β (deg)	109.6570(10)	127.4000(10)	98.8850(10)	92.7790(10)	105.3240(10)
V (Å^3)	3990.3(2)	6704.1(4)	3570.6(2)	3574.1(2)	2394.8(2)
Z	4	4	4	4	4
temp (K)	295(2)	295(2)	295(2)	295(2)	295(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
calcd (g cm^{-3})	1.059	1.020	1.064	1.072	1.120
μ (mm^{-1})	0.189	0.210	0.204	0.210	0.279
$R(F)^a$ (%)	7.12	7.36	5.84	6.02	6.68
$R_w(F)^b$ (%)	18.70	15.56	15.03	14.74	13.29

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F)^2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

(tetraglyme)calcium (**6**, 57%), respectively, as colorless crystalline solids. The structural assignments for **3**−**6** were based on the spectral and analytical data. In addition, the X-ray crystal structures of **3**−**5** were determined. Compound **6** was difficult to purify presumably because of the presence of trace amounts of free tetraglyme.

Treatment of calcium bromide with 3,5-dimethylpyrazolatopotassium (prepared in situ from 3,5-di-*tert*-butylpyrazole and KH[29]) in tetrahydrofuran at ambient temperature for 18 h afforded a tetrahydrofuran adduct of bis(3,5-dimethylpyrazolato)calcium. This compound decomposed rapidly through tetrahydrofuran loss upon isolation to give an intractable white solid. However, the crude solid obtained after removal of the tetrahydrofuran solvent was soluble in toluene, and the resultant toluene solution could be treated with donor ligands to prepare tractable compounds. In this way, addition of the neutral donor ligands PMDETA, triglyme, and tetraglyme afforded bis(3,5-dimethylpyrazolato)(PMDETA)calcium (**7**, 65%), bis(3,5-dimethylpyrazolato)(triglyme)calcium (**8**, 54%), and bis(3,5-dimethylpyrazolato)(tetraglyme)calcium (**9**, 40%), respectively, as colorless crystalline solids after workup (eq 3). Complexes



7−**9** were characterized by spectral and analytical techniques. In addition, the solid-state structure of **7** was determined by X-ray crystallography. Like **6**, **9** was difficult to purify because of the presence of a small amount of free tetraglyme.

Volatility Evaluation. To assess their initial viability as precursors for CVD applications, **2**−**9** were evaluated for their ability to sublime. Complexes **2**−**4** and **6**−**9** did not sublime intact below 250 °C but rather liberated the neutral donor ligands between 160 and 200 °C. Upon extended heating at 200 °C,

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**

Ca(1)−N(1)	2.379(3)	Ca(1)−N(5)	2.526(3)
Ca(1)−N(2)	2.390(3)	Ca(1)−N(6)	2.548(3)
Ca(1)−N(3)	2.414(3)	Ca(1)−N(7)	2.564(3)
Ca(1)−N(4)	2.377(3)		
N(5)−Ca(1)−N(6)	174.86(10)	N(3)−Ca(1)−N(5)	92.29(10)
N(3)−Ca(1)−N(6)	87.53(10)	N(1)−Ca(1)−N(5)	97.32(10)
N(1)−Ca(1)−N(6)	92.82(10)	N(2)−Ca(1)−N(4)	113.53(10)
N(1)−Ca(1)−N(7)	88.59(10)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3**

Ca(1)−N(1)	2.336(3)	Ca(1)−N(3)	2.535(3)
Ca(1)−N(2)	2.331(3)	Ca(1)−N(3′)	2.535(3)
Ca(1)−N(1′)	2.336(3)		
Ca(1)−N(2′)	2.331(3)		
N(2)−Ca(1)−N(2′)	132.55(13)	N(1′)−Ca(1)−N(3′)	90.42(10)
N(1)−Ca(1)−N(2′)	113.62(9)	N(2)−Ca(1)−N(3)	98.23(10)
N(1′)−Ca(1)−N(2)	113.62(9)	N(2′)−Ca(1)−N(3)	120.98(10)
N(1)−Ca(1)−N(1′)	116.87(13)	N(1)−Ca(1)−N(3)	90.42(10)
N(2)−Ca(1)−N(3′)	120.98(10)	N(1′)−Ca(1)−N(3)	148.07(11)
N(2′)−Ca(1)−N(3′)	98.23(10)	N(3)−Ca(1)−N(3′)	70.3(2)
N(1)−Ca(1)−N(3′)	148.07(10)		

small amounts of a white solid were observed in the cold portion of the sublimation tube. However, the white solid was sparingly soluble in common NMR solvents and could not be obtained in sufficient quantity to allow more detailed characterization. Unlike the others, **5** sublimed at 160 °C (0.1 mmHg). In a preparative sublimation (ca. 0.5 g), a 39% sublimed yield of **5** was obtained. In addition, free triglyme was observed in the sublimation tube. Hence, **5** is volatile, but it also undergoes competitive decomposition during the sublimation process through loss of triglyme. The structurally related complex Ca(hfac)$_2$(triglyme) (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) sublimes without decomposition at 100 °C (0.02 mmHg).[31]

Crystal Structures of 2−5 and 7. The X-ray structures of **2**−**5** and **7** were determined in order to establish their molecular geometries. Experimental crystallographic data are summarized in Table 1. Selected bond lengths and angles are given in Tables 2−6, while perspective views are presented in Figures 1−5.

Compound **2** exists as a seven-coordinate, monomeric complex with three pyridine molecules and two pyrazolato ligands bound by their nitrogen atoms in a η^2-fashion. The coordination geometry about the calcium can be described as distorted trigonal bipyramidal if the centers of the nitrogen−

(31) Timmer, K.; Spee, K. I. M. A.; Mackor, A.; Meinema, H. A.; Spek, A. L.; van der Sluis, P. *Inorg. Chim. Acta* **1991**, *190*, 109.

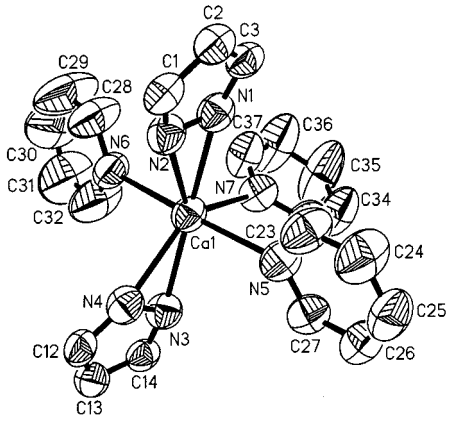


Figure 1. Perspective view of bis(3,5-di-*tert*-butylpyrazolato)tris(pyridine)calcium (**2**) with thermal ellipsoids at the 50% probability level. The *tert*-butyl groups have been removed for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **4**

Ca(1)−N(1)	2.354(3)	Ca(1)−N(5)	2.539(3)
Ca(1)−N(2)	2.434(3)	Ca(1)−N(6)	2.666(3)
Ca(1)−N(3)	2.529(3)	Ca(1)−N(7)	2.581(3)
Ca(1)−N(4)	2.311(3)		
N(1)−Ca(1)−N(4)	101.42(7)	N(2)−Ca(1)−N(7)	132.40(8)
N(2)−Ca(1)−N(4)	102.06(7)	N(3)−Ca(1)−N(7)	86.22(7)
N(1)−Ca(1)−N(3)	130.78(7)	N(5)−Ca(1)−N(7)	111.17(8)
N(2)−Ca(1)−N(3)	134.42(7)	N(4)−Ca(1)−N(6)	168.11(8)
N(4)−Ca(1)−N(5)	99.99(8)	N(1)−Ca(1)−N(6)	90.15(7)
N(1)−Ca(1)−N(5)	128.37(7)	N(2)−Ca(1)−N(6)	86.03(8)
N(2)−Ca(1)−N(5)	95.90(7)	N(3)−Ca(1)−N(6)	137.01(8)
N(3)−Ca(1)−N(5)	88.59(8)	N(5)−Ca(1)−N(6)	70.23(8)
N(4)−Ca(1)−N(7)	110.35(8)	N(6)−Ca(1)−N(7)	68.72(8)
N(1)−Ca(1)−N(7)	104.31(8)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **5**

Ca(1)−N(1)	2.463(2)	Ca(1)−O(1)	2.470(2)
Ca(1)−N(2)	2.374(2)	Ca(1)−O(2)	2.544(2)
Ca(1)−N(3)	3.374(2)	Ca(1)−O(3)	2.528(2)
Ca(1)−N(4)	2.425(2)	Ca(1)−O(4)	2.518(2)
N(1)−Ca(1)−N(3)	173.09(7)	N(1)−Ca(1)−O(2)	82.50(7)
N(2)−Ca(1)−N(4)	107.53(7)	N(3)−Ca(1)−O(1)	84.90(8)
O(1)−Ca(1)−O(4)	166.42(7)	N(3)−Ca(1)−O(4)	85.58(7)
N(1)−Ca(1)−O(1)	96.31(7)	N(3)−Ca(1)−O(3)	91.12(8)
N(1)−Ca(1)−O(4)	92.01(8)		

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **7**

Ca(1)−N(1)	2.378(3)	Ca(1)−N(5)	2.564(3)
Ca(1)−N(2)	2.368(3)	Ca(1)−N(6)	2.613(3)
Ca(1)−N(3)	2.403(3)	Ca(1)−N(7)	2.570(3)
Ca(1)−N(4)	2.389(3)		
N(1)−Ca(1)−N(4)	117.41(10)	N(4)−Ca(1)−N(7)	115.13(10)
N(2)−Ca(1)−N(4)	106.65(9)	N(3)−Ca(1)−N(7)	83.75(9)
N(1)−Ca(1)−N(3)	111.65(10)	N(5)−Ca(1)−N(7)	120.30(13)
N(2)−Ca(1)−N(3)	121.70(10)	N(4)−Ca(1)−N(6)	148.49(10)
N(2)−Ca(1)−N(5)	96.62(11)	N(1)−Ca(1)−N(6)	92.56(10)
N(1)−Ca(1)−N(5)	127.91(11)	N(2)−Ca(1)−N(6)	92.75(10)
N(4)−Ca(1)−N(5)	84.05(10)	N(3)−Ca(1)−N(6)	144.78(8)
N(3)−Ca(1)−N(5)	110.09(10)	N(5)−Ca(1)−N(6)	68.95(10)
N(2)−Ca(1)−N(7)	125.51(10)	N(6)−Ca(1)−N(7)	68.87(10)
N(1)−Ca(1)−N(7)	94.03(10)		

nitrogen bonds of the η^2-pyrazolato ligands are considered to be monodentate donors. Two pyridine molecules are located in the axial positions, whereas the two pyrazolato ligands, one pyridine ligand, and the calcium center define the equatorial plane. The distorted trigonal bipyramidal distortion is characterized by N(5)−Ca−N(6), N(3)−Ca−N(6), N(1)−Ca−N(6), N(1)−Ca−N(7), N(3)−Ca−N(5), N(1)−Ca−N(5), N(2)−Ca−N(4) angles of 174.86(10), 87.53(10), 92.82(10), 88.59(10), 92.29(10), 97.32(10), 113.53(10)°, respectively. These distortions are probably caused by steric interactions between the *tert*-butyl groups of the 3,5-di-*tert*-butylpyrazolato ligands. The calcium−nitrogen bond lengths range between 2.377(3) and 2.414(3) Å for the pyrazolato ligands and between 2.526(3) and 2.564(3) Å for the pyridine donors.

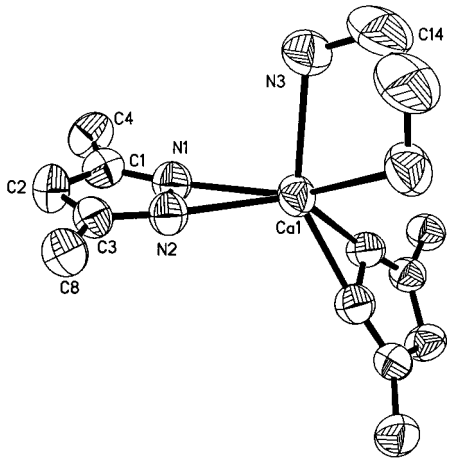


Figure 2. Perspective view of bis(3,5-di-*tert*-butylpyrazolato)(TMEDA)calcium (**3**) with thermal ellipsoids at the 50% probability level. The methyl groups on C(4), C(8), and N(3) have been removed for clarity.

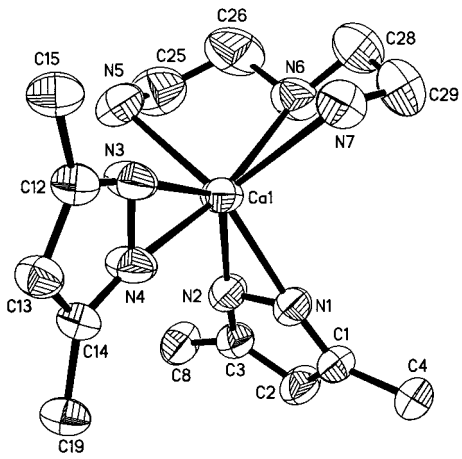


Figure 3. Perspective view of bis(3,5-di-*tert*-butylpyrazolato)(PMDETA)calcium (**4**) with thermal ellipsoids at the 50% probability level. The methyl groups on C(4), C(8), C(15), C(19), N(5), N(6), and N(7) have been removed for clarity.

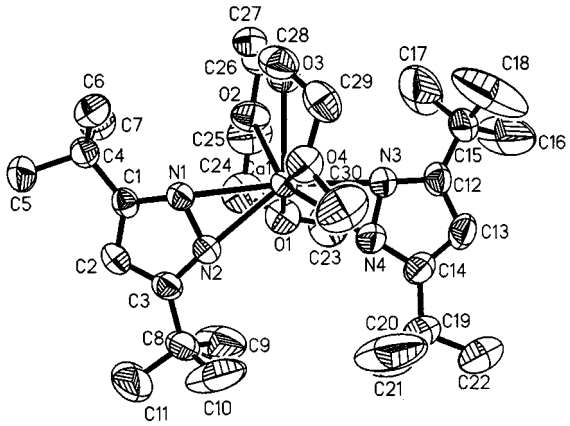


Figure 4. Perspective view of bis(3,5-di-*tert*-butylpyrazolato)(triglyme)calcium (**5**) with thermal ellipsoids at the 50% probability level.

Complex **3** exists as a six-coordinate, monomeric complex with two η^2-pyrazolato ligands and one bidentate TMEDA

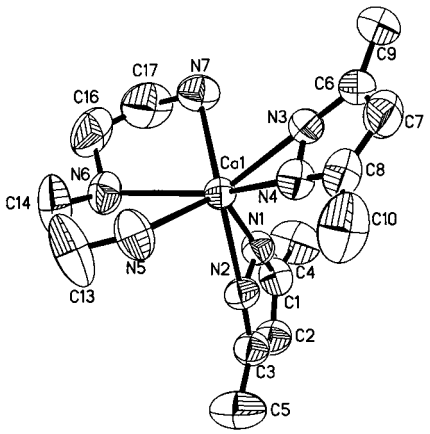


Figure 5. Perspective view of bis(3,5-dimethylpyrazolato)(PMDETA)-calcium (**7**) with thermal ellipsoids at the 50% probability level. The methyl groups on C(4), C(8), C(9), C(10), N(5), N(6), and N(7) have been removed for clarity.

ligand. The molecule in **3** occupies a crystallographic 2-fold axis. There are two independent molecules in the unit cell that are identical within the precision of the experiment. Only data for the molecule containing Ca(1) are discussed herein. The coordination geometry about the calcium center can be described as distorted tetrahedral if the center of the nitrogen−nitrogen bond of each pyrazolato ligand is considered to be a monodentate donor. The distorted tetrahedral geometry is characterized by nitrogen−calcium−nitrogen bond angles that range between 70.3 and 148°. The calcium−nitrogen bond lengths are 2.331-(3) and 2.336(3) Å for the pyrazolato ligands and 2.535(3) Å for the TMEDA ligand. Complex **3** possesses a molecular structure similar to the analogous magnesium complex, which we have recently reported.[22]

Compound **4** crystallizes as a seven-coordinate, monomeric complex with two η^2-pyrazolato ligands and one PMDETA ligand. The calcium−nitrogen bond lengths range from 2.322-(3) to 2.529(3) Å for the pyrazolato ligand and from 2.539(3) to 2.666(3) Å for the PMDETA donor. The nitrogen−calcium−nitrogen bond angles range between 70.23(8) and 168.11(8)°. The asymmetry of the calcium−nitrogen bond lengths associated with the pyrazolato ligand is 0.218 Å. Such large asymmetric bonding of the pyrazolato ligands is probably caused by steric interactions involving the *tert*-butyl groups and the methyl groups of the PMDETA donor. This asymmetry is more pronounced in **4** compared to **3** as a consequence of the increase in coordination number about the calcium ion in **4**.

Compound **5** exists as an eight-coordinate, monomeric complex with one tetradentate triglyme ligand and two pyrazolato ligands bound through their nitrogen atoms in a η^2-fashion. The coordination geometry about the calcium ion can be envisioned as distorted octahedral if the center of the nitrogen−nitrogen bond of each η^2-pyrazolato ligand is treated as a monodentate donor. The two pyrazolato donors are trans to each other within the octahedron, whereas the triglyme ligand coordinates to the calcium center through four approximately coplanar oxygen atoms. The distorted octahedral geometry is characterized by N(1)−Ca(1)−N(3), N(2)−Ca(1)−N(4), O(1)−Ca(1)−O(4), N(1)−Ca(1)−O(1), N(1)−Ca(1)−O(4), N(1)−Ca-(1)−O(2), N(3)−Ca(1)−O(1), N(3)−Ca(1)−O(4), and N(3)−Ca(1)−O(3) angles of 173.09(7), 107.53(7), 166.42(7), 96.31(7), 92.01(8), 82.50(7), 84.90(8), 85.58(7), and 91.12(8)°, respectively. The calcium−nitrogen bond lengths range between 2.374(2) and 2.463(2) Å for the pyrazolato ligands, while the calcium−oxygen bond lengths range between 2.470(3) and 2.544(2) Å for the triglyme donor. The η^2-pyrazolato ligands in **5** are asymmetrically bonded with a difference in calcium−nitrogen bond lengths of 0.089 Å. The asymmetry found in **5** is higher than the related values in **2** and **3** but is significantly less than in **4**. This difference is probably caused by the sterically more congested coordination sphere in **4** relative to those in **2**, **3**, and **5**.

Compound **7** exists in the solid state as a seven-coordinate, monomeric complex with two η^2-pyrazolato ligands and one PMDETA ligand. The calcium−nitrogen bond lengths range between 2.368(3) and 2.403(3) Å for the pyrazolato ligands and between 2.564(3) and 2.613(3) Å for the PMDETA donor. The nitrogen−calcium−nitrogen bond angles range between 68.87-(10) and 148.49(10)°. The asymmetry of the calcium−nitrogen bond lengths associated with the pyrazolato ligand is 0.025 Å. The difference is again probably caused by steric interactions involving the *tert*-butylmethyl groups and the methyl groups of the PMDETA ligand. The asymmetry in **7** is significantly smaller than in **4** because of the sterically less demanding nature of the 3,5-dimethylpyrazolato ligand relative to the 3,5-di-*tert*-butylpyrazolato ligand.

Discussion

A significant feature of complexes **1**−**9** is the η^2-pyrazolato ligand coordination. We recently reported the first example of η^2-pyrazolato ligand coordination among the main group metals in bis(bis(3,5-di-*tert*-butylpyrazolato)magnesium).[22] Given the larger size of the calcium ion, it is perhaps not surprising that the η^2-pyrazolato ligand bonding mode is observed exclusively in **1**−**9**. η^2-Pyrazolato ligands are very common in lanthanide pyrazolato complexes because of the ionic bonding and large sizes of these ions.[32−37] Since the groups 1−3 metal ions exhibit predominant ionic bonding and since the sizes of many of these ions are as large or larger than the lanthanide ions, η^2-pyrazolato ligand coordination should be frequently observed in pyrazolato complexes of the main group metals. We are particularly interested in η^2-pyrazolato ligand coordination, since the steric profile of the η^2-pyrazolato ligand should be similar to that of appropriately substituted 1,3-diketonate ligands. In addition, coordination of both nitrogen atoms of a pyrazolato ligand should minimize undesired side reactions that might be promoted by the presence of an uncoordinated nitrogen atom in an η^1-pyrazolato ligand (e.g., deprotonation, oligomerization). 1,3-Diketonate complexes of the heavier group 2 metals are widely used as source compounds for CVD applications. The results described herein demonstrate that replacement of the 1,3-diketonate ligands by pyrazolato ligands yields similar monomeric complexes. With the appropriate ligands, such pyrazolato complexes can be volatile. Further development may lead to the preparation of volatile group 2 pyrazolato complexes that do not contain metal−oxygen bonds, which would allow the incorporation of the heavier group 2 ions into non-oxide materials.

(32) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M.; Hemling, H.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 874.
(33) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M.; Hemling, H.; Schumann, H. *Aust. J. Chem.* **1994**, *47*, 1223.
(34) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M. *Aust. J. Chem.* **1993**, *46*, 1881.
(35) Cosgriff, J. E.; Deacon, G. B.; Fallon, G. D.; Gatehouse, B. M.; Schumann, H.; Weimann, R. *Chem. Ber.* **1996**, *129*, 953.
(36) Deacon, G. B.; Delbridge, E. E.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **1998**, 543.
(37) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M.; Lee, P. R.; Schumann, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1399.

The crystal structures of **2**−**5** and **7** afford some insight into the structural features that lead to volatility in this general class of complexes. The bulky 3,5-di-*tert*-butylpyrazolato ligand seems to promote volatility, since **5** sublimed partially, while the analogous 3,5-dimethylpyrazolato complex **8** decomposed prior to sublimation. It is likely that the *tert*-butyl groups in **5** help to reduce the lattice energy of the solid by reducing intermolecular interactions. The coordination number of the calcium ion in **5** is 8, which is achieved by coordination to four nitrogen atoms and four oxygen atoms. Previous studies have demonstrated that the coordination spheres of calcium diketonate complexes coordinated to neutral polydentate amines or ethers are saturated with a coordination number of 8.[38,39] Accordingly, the lack of volatility of **2**−**4** could be due to the unsaturated calcium centers in these complexes. While X-ray quality crystals of **6** could not be grown, it is likely that the calcium ion in this complex is also eight-coordinate, with one terminal methoxy group of the tetraglyme moiety not being coordinated by analogy with related 1,3-diketonate complexes of calcium.[38,39]

The fact that **5** is volatile while **6** decomposes prior to sublimation is noteworthy. We suggest that a critical parameter in the thermal stability of **5** and **6** is the steric "fit" of the neutral donor ligand about the metal center. In **5**, the pyrazolato ligands are approximately coplanar with N(1)−Ca(1)−N(3) and N(2)−Ca(1)−N(4) angles of 173.09(7) and 107.53(8)°, respectively. The triglyme ligand coordinates to the calcium center in a plane that approximately bisects the plane of the pyrazolato ligands. This arrangement places the methyl groups of the triglyme ligand as far as possible from the bulky *tert*-butyl groups. However, the bending of the nitrogen−calcium−nitrogen angles to accommodate the triglyme ligand is limited by steric interactions between the *tert*-butyl groups containing quaternary carbons C(8) and C(19). The thermal stability of **5** and related complexes is likely to be related to how easily the neutral donor ligand dissociates from the metal center. Accordingly, we propose that the thermal stability and ability to volatilize of calcium bis(pyrazolato) complexes bearing neutral polydentate ethers or amines will be a critical function of steric interactions between the pyrazolato ligand substituents (e.g., crowding between *tert*-butyl groups containing C(8) and C(19)). Such interactions determine the size of the pocket into which the neutral donor fits. In **5**, it appears that the *tert*-butyl groups exert too large a steric profile and that these steric interactions afford nitrogen−calcium−nitrogen angles that are too large for optimum bonding interactions between calcium and the triglyme ligand. As a result, decomposition of **5** by triglyme ligand loss is competitive with sublimation. Such a proposal may explain the lack of volatility of **6**, since a tetradentate tetraglyme ligand would leave a pendant methoxyethyl substituent in the coordination sphere. Steric interactions between this dangling group and the *tert*-butyl moieties may lead to an enhanced rate of decomposition through tetraglyme loss.

The results of this study suggest that the key to making volatile, thermally stable group 2 bis(pyrazolato) complexes is to optimize the bonding of the neutral donor ligand by minimizing steric interactions within the coordination sphere. It is likely that adjusting the pyrazolato ligand steric profiles in complexes $Ca(R_2pz)_2$(triglyme) will lead to compounds that exhibit enhanced thermal stability compared to **5** and may be suitable for use as source compounds in CVD processes. We are also exploring the synthesis and properties of analogous strontium and barium complexes, as well as complexes containing only nitrogen donor ligands. These results will be published in due course.

Experimental Section

General Considerations. All reactions were performed under an inert atmosphere of argon using either glovebox or Schlenk line techniques. Toluene, tetrahydrofuran, and hexane were distilled from sodium. *N,N,N′N′*-tetramethylethylenediamine, *N,N,N′N′N″*-pentamethyldiethylenetriamine, triglyme, and tetraglyme were purchased from Aldrich Chemical Co. and were dried by distillation from sodium. Pyridine was distilled from calcium hydride. Calcium bromide was purchased from Strem Chemicals, Inc. and was used as received. 3,5-Dimethylpyrazole was obtained from Aldrich Chemical Co. and was used as received. 3,5-Di-*tert*-butylpyrazole was synthesized according to a literature method.[40]

^{1}H and ^{13}C{^{1}H} NMR spectra were obtained at 300 or 75 MHz in benzene-d_6. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of Bis(3,5-di-*tert*-butylpyrazolato)bis(tetrahydrofuran)calcium (1). A 200 mL Schlenk flask was charged with calcium bromide (0.500 g, 2.50 mmol), 3,5-di-*tert*-butylpyrazolatopotassium (1.09 g, 5.00 mmol), and tetrahydrofuran (50 mL). The resultant mixture was stirred at ambient temperature for 18 h during which time a fine white precipitate formed. The volatile components were removed under reduced pressure to afford a white solid. Extraction of this solid with hexane (80 mL) yielded a white suspension, which was filtered through a 2 cm pad of Celite on a coarse glass frit. The resultant clear solution was concentrated under reduced pressure to approximately 30 mL and then cooled at −20 °C to yield **1** as a colorless solid (0.950 g, 69%). ^{1}H NMR (benzene-d_6, 23 °C, δ): 5.84 (s, 2 H, pyrazolato ring C−*H*), 3.45 (m, 4 H, O−C*H*$_2$CH$_2$), 1.38 (s, 32 H, C(C*H*$_3$)$_3$), 1.34 (m, 4H, O−CH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, ppm): 160.33 (s, pyrazolato ring *C*−C(CH$_3$)$_3$), 95.44 (s, pyrazolato ring *C*−H), 67.47 (s, O−*C*H$_2$CH$_2$), 31.93 (s, pyrazolato *C*(CH$_3$)$_3$), 31.65 (s, pyrazolato C(*C*H$_3$)$_3$), 25.41 (s, O−CH$_2$*C*H$_2$). Anal. Calcd for $C_{30}H_{54}CaN_4O_2$: C, 66.38; H, 10.03; N, 10.32. Found: C, 65.86; H, 9.75; N, 11.07.

Preparation of Bis(3,5-di-*tert*-butylpyrazolato)tris(pyridine)calcium (2). A 200 mL Schlenk flask was charged with calcium bromide (0.500 g, 2.50 mmol), 3,5-di-*tert*-butylpyrazolatopotassium (1.09 g, 5.00 mmol), and tetrahydrofuran (50 mL). The resultant mixture was stirred at ambient temperature for 18 h during which time a fine white precipitate formed. The volatile components were removed under reduced pressure to afford a colorless solid. Extraction of this solid with hexane (80 mL) yielded a white suspension, which was filtered through a 2 cm pad of Celite on a coarse glass frit. After the addition of pyridine (0.988 g, 12.5 mmol) in hexane (20 mL), the resultant clear solution was concentrated under reduced pressure to approximately 30 mL and then cooled at −20 °C to yield colorless crystals of **2** (0.810 g, 51%): mp 144−145 °C. IR (Nujol, cm^{-1}): 1593 (s), 1561 (m), 1512 (m), 1485 (vs), 1406 (m), 1358 (s), 1285 (m), 1248 (s), 1216 (m), 1034 (m), 1011 (m), 993 (s), 804 (m), 775 (m), 723 (m), 704 (s). ^{1}H NMR (benzene-d_6, 23 °C, δ): 8.15 (m, 6 H, Py C−*H*), 6.80 (m, 3 H Py C−*H*), 6.50 (m, 6 H, Py C−*H*), 6.40 (s, 2H, pyrazolato ring C−*H*), 1.47 (s, 36 H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, ppm): 159.46 (s, pyrazolato ring *C*−C(CH$_3$)$_3$), 149.93 (s, Py *C*−H), 136.52 (s, Py *C*−H), 123.46 (s, Py *C*−H), 96.89 (s, pyrazolato ring *C*−H), 32.10 (s, pyrazolato *C*(CH$_3$)$_3$), 31.78 (s, pyrazolato C(*C*H$_3$)$_3$). Anal. Calcd for $C_{37}H_{53}CaN_7$: C, 69.88; H, 8.40; N, 15.42. Found: C, 69.66; H, 8.39; N, 15.31.

Preparation of Bis(3,5-di-*tert*-butylpyrazolato)(*N,N,N′,N′*-tetramethylethylenediamine)calcium (3). In a procedure similar to the preparation of **2**, calcium bromide (0.500 g, 2.50 mmol), 3,5-di-*tert*-butylpyrazolatopotassium (1.09 g, 5.00 mmol), and *N,N,N′,N′*-tetramethylethylenediamine (1.16 g, 1.00 mmol) were reacted to yield

(38) Drake, S. R.; Miller, S. A. S.; Williams, D. J. *Inorg. Chem.* **1993**, *32*, 3227.

(39) Hänninen, T.; Mutikainen, I.; Saanila, V.; Ritala, M.; Leskelä, M.; Hanson, J. C. *Chem. Mater.* **1997**, *9*, 1234.

(40) Elguero, J.; Gonzalez, E.; Jacquier, R. *Bull. Soc. Chim. Fr.* **1968**, 707.

colorless crystals of **3** (0.810 g, 74%): dec range 185−195 °C. IR (Nujol, cm^{-1}): 1509 (s), 1494 (vs), 1426 (s), 1400 (m), 1357 (s), 1315 (m), 1294 (s), 1248 (vs), 1220 (s), 1202 (s), 1175 (m), 1154 (s), 1134 (m), 1081 (m), 1038 (s), 1022 (s), 1008 (vs), 997 (s), 940 (s), 770 (s), 725 (s). ^{1}H NMR (benzene-d_6, 23 °C, δ): 6.40 (s, 2H, pyrazolato ring C−*H*), 2.00 (m, 4H, N−C*H*$_2$), 1.90 (s, 12 H, N−C*H*$_3$), 1.40 (s, 36 H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, ppm): 160.24 (s, pyrazolato ring *C*−C(CH$_3$)$_3$), 95.57 (s, pyrazolato ring *C*−H), 57.40 (s, N−*C*H$_2$), 45.34 (s, N−*C*H$_3$), 31.95 (s, pyrazolato *C*(CH$_3$)$_3$), 31.73 (s, pyrazolato C(*C*H$_3$)$_3$). Anal. Calcd for $C_{28}H_{54}CaN_6$: C, 65.32; H, 10.57; N, 16.32. Found: C, 62.71; H, 10.08; N, 16.75.

Preparation of Bis(3,5-di-*tert*-butylpyrazolato)(*N,N,N′,N′N″*-pentamethyldiethylenetriamine)calcium (4). In a procedure similar to the preparation of **2**, calcium bromide (0.500 g, 2.50 mmol), 3,5-di-*tert*-butylpyrazolatopotassium (1.09 g, 5.00 mmol), and *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (0.648 g, 3.75 mmol) were reacted to afford colorless crystals of **4** (0.72 g, 50%): mp 139−141 °C. IR (Nujol, cm^{-1}): 3110 (s), 1510 (vs), 1492 (vs), 1401 (s), 1354 (vs), 1315 (s), 1289 (m), 1246 (vs), 1219 (s), 1204 (vs), 1166 (m), 1101 (m), 1064 (m), 1036 (s), 1015 (vs), 992 (vs), 972 (s), 931 (s), 905 (m), 785 (s), 770 (vs), 722 (s). ^{1}H NMR (benzene-d_6, 23 °C, δ): 6.27 (s, 2H, pyrazolato ring C−*H*), 2.61 (m, 4H, N−C*H*$_2$CH$_2$), 2.30 (m, 4H, N−CH$_2$C*H*$_2$), 2.02 (s, 12 H, N−(C*H*$_3$)$_2$), 1.83 (s, 3 H, N−C*H*$_3$), 1.52 (s, 36 H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, ppm): 158.90 (s, pyrazolato ring *C*−C(CH$_3$)$_3$), 97.74 (s, pyrazolato ring *C*−H), 57.19 (s, N−*C*H$_2$CH$_2$), 55.70 (s, N−CH$_2$*C*H$_2$), 45.81 (s, N−(*C*H$_3$)$_2$), 42.26 (s, N−*C*H$_3$), 32.90 (s, pyrazolato *C*(CH$_3$)$_3$), 32.09 (s, pyrazolato C(*C*H$_3$)$_3$). Anal. Calcd for $C_{31}H_{61}CaN_7$: C, 65.10; H, 10.75; N, 17.14. Found: C, 64.98; H, 10.86; N, 17.06.

Preparation of Bis(3,5-di-*tert*-butylpyrazolato)(triglyme)calcium (5). In a fashion similar to the preparation of **2**, calcium bromide (0.500 g, 2.50 mmol), 3,5-di-*tert*-butylpyrazolatopotassium (1.09 g, 5.00 mmol), and triglyme (0.445 g, 2.50 mmol) were reacted to yield colorless crystals of **5** (1.06 g, 73%): mp 140−141 °C. IR (Nujol, cm^{-1}): 1509 (m), 1491 (s), 1404 (m), 1356 (s), 1318 (m), 1260 (vs), 1221 (m), 1203 (m), 1094 (broad, vs), 1011 (vs), 938 (m), 872 (m), 802 (vs), 723 (m). ^{1}H NMR (benzene-d_6, 23 °C, δ): 6.28 (s, 2 H, pyrazolato ring C−*H*), 3.25 (m, 4 H, C*H*$_2$O−CH$_2$CH$_2$), 2.95 (m, 4 H, CH$_2$−O−C*H*$_2$CH$_2$), 2.84 (m, 4 H, CH$_2$−O−CH$_2$C*H*$_2$), 2.81 (s, 6 H, O−C*H*$_3$), 1.61 (s, 32 H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, ppm): 158.21 (s, pyrazolato ring *C*−C(CH$_3$)$_3$), 96.61 (s, pyrazolato ring *C*−H), 69.74 (s, *C*H$_2$−O−CH$_2$CH$_2$), 68.77 (s, CH$_2$−O-*C*H$_2$CH$_2$), 68.69 (s, CH$_2$−O−CH$_2$*C*H$_2$), 58.88 (s, O−*C*H$_3$), 32.91 (s, pyrazolato *C*(CH$_3$)$_3$), 32.12 (s, pyrazolato C(*C*H$_3$)$_3$). Anal. Calcd for $C_{30}H_{56}CaN_4O_4$: C, 62.46; H, 9.78; N, 9.71. Found: C, 62.05; H, 9.78; N, 9.71.

Preparation of Bis(3,5-di-*tert*-butylpyrazolato)(tetraglyme)calcium (6). In a fashion similar to the preparation of **2**, calcium bromide (0.500 g, 2.50 mmol), 3,5-di-*tert*-butylpyrazolatopotassium (1.09 g, 5.00 mmol), and tetraglyme (0.555 g, 2.50 mmol) were reacted to afford **6** as a colorless, sticky solid (0.89 g, 57%): mp 106−107 °C. IR (Nujol, cm^{-1}): 3100 (m), 1511 (s), 1495 (s), 1407 (m), 1357 (vs), 1322 (m), 1302 (m), 1248 (s), 1223 (m), 1203 (m), 1104 (broad, vs), 1021 (s), 1011 (s), 997 (m), 948 (s), 863 (s), 851 (s), 776 (vs), 728 (s). ^{1}H NMR (benzene-d_6, 23 °C, δ): 6.27 (s, 2 H, pyrazolato ring C−*H*), 3.67 (m, 4 H, CH$_3$−O−CH$_2$C*H*$_2$−O−CH$_2$CH$_2$), 3.35 (m, 4 H, CH$_3$−O−CH$_2$-CH$_2$−O−C*H*$_2$CH$_2$), 3.29 (s, 6 H, O−C*H*$_3$), 3.06 (m, 4 H, CH$_3$−O−CH$_2$CH$_2$−O−CH$_2$C*H*$_2$), 2.95 (m, 4 H, CH$_3$−O−C*H*$_2$CH$_2$O−CH$_2$CH$_2$), 1.59 (s, 32 H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, ppm): 158.27 (s, pyrazolato ring *C*−C(CH$_3$)$_3$), 96.71 (s, pyrazolato ring *C*−H), 71.64 (s, CH$_3$−O-*C*H$_2$CH$_2$−O−CH$_2$CH$_2$), 70.10 (s, CH$_3$−O−CH$_2$*C*H$_2$−O−CH$_2$CH$_2$), 68.92 (s, CH$_3$−O−CH$_2$CH$_2$−O-*C*H$_2$CH$_2$), 68.45 (s, CH$_3$−O−CH$_2$CH$_2$O−CH$_2$*C*H$_2$), 58.37 (s, O−*C*H$_3$), 33.12 (s, pyrazolato *C*(CH$_3$)$_3$), 32.10 (s, pyrazolato C(*C*H$_3$)$_3$). Anal. Calcd for $C_{32}H_{60}CaN_4O_5$: C, 61.90; H, 9.74; N, 9.02. Found: C, 63.11; H, 10.05; N, 9.64.

Preparation of Bis(3,5-dimethylpyrazolato)(*N,N,N′,N′N″*-pentamethyldiethylenetriamine)calcium (7). A 200 mL Schlenk flask was charged with potassium hydride (0.200 g, 5.00 mmol), 3,5-dimethylpyrazole (0.480 g, 5.00 mmol), and tetrahydrofuran (50 mL). After the mixture was stirred for 3 h, the gas evolution ceased and the resultant clear solution was added by a cannula to a 200 mL Schlenk flask that had been charged with calcium bromide (0.500 g, 2.50 mmol). The reaction mixture was stirred at ambient temperature for 18 h during which time a fine white precipitate formed. The volatile components were removed under reduced pressure to afford a colorless, sticky solid. After extraction of the residue with toluene (80 mL), the suspension was filtered through a 2 cm pad of Celite on a coarse glass frit. Addition of *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (0.432 g, 2.50 mmol) in toluene (20 mL) resulted in a clear, colorless solution. This solution was concentrated under reduced pressure to a volume of approximately 30 mL and then cooled at −20 °C to yield colorless crystals of **7** (0.66 g, 65%): mp 188−191 °C. IR (Nujol, cm^{-1}): 1512 (vs), 1415 (vs), 1353 (vs), 1339 (m), 1312 (s), 1289 (s), 1168 (s), 1154 (m), 1105 (vs), 1075 (m), 1064 (m), 1026 (vs), 1007 (vs), 969 (s), 943 (s), 791 (vs), 771(vs), 730 (s). ^{1}H NMR (benzene-d_6, 23 °C, δ): 6.18 (s, 2 H, pyrazolato ring C−*H*), 2.43 (s, 12 H, N−(C*H*$_3$)$_2$), 2.28 (m, 4 H, N−C*H*$_2$-CH$_2$), 2.25 (m, 4 H, N−CH$_2$C*H*$_2$), 2.04 (s, 12 H, CC*H*$_3$), 1.52 (s, 3 H, N−C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, ppm): 144.99 (s, pyrazolato ring *C*−C(CH$_3$)$_3$), 104.58 (s, pyrazolato ring *C*−H), 56.69 (s, N−*C*H$_2$CH$_2$), 55.06 (s, N−CH$_2$*C*H$_2$), 45.37 (s, N−(*C*H$_3$)$_2$), 41.35 (s, N−*C*H$_3$), 13.98 (s, pyrazolato C*C*H$_3$). Anal. Calcd for $C_{19}H_{37}CaN_7$: C, 56.54; H, 9.24; N, 24.29. Found: C, 56.49; H, 8.99; N, 24.19.

Preparation of Bis(3,5-dimethylpyrazolato)(triglyme)calcium (8). In a procedure similar to the preparation of **7**, calcium bromide (0.500 g, 2.50 mmol), 3,5-dimethylpyrazole (0.480 g, 5.00 mmol), potassium hydride (0.201 g, 5.00 mmol), and triglyme (0.446 g, 2.50 mmol) were reacted to yield **8** as a colorless, sticky solid (0.55 g, 54%): mp 87−88 °C. IR (Nujol, cm^{-1}): 1510 (s), 1415 (s), 1357 (s), 1285 (m), 1245 (m), 1199 (m), 1093 (broad, vs), 1024 (s), 947 (s), 871 (m), 846 (m), 769 (m), 747 (s). ^{1}H NMR (benzene-d_6, 23 °C, δ): 6.21 (s, 2 H, pyrazolato ring C−*H*), 3.25 (m, 4 H, C*H*$_2$O−CH$_2$CH$_2$), 3.18 (m, 4 H, CH$_2$−O−C*H*$_2$CH$_2$), 3.02 (m, 4 H, CH$_2$−O−CH$_2$C*H*$_2$), 2.99 (s, 6 H, O−C*H*$_3$), 2.50 (s, 12 H, CC*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, ppm): 146.57 (s, pyrazolato ring *C*−C(CH$_3$)$_3$), 104.63 (s, pyrazolato ring *C*−H), 71.78 (s, *C*H$_2$−O−CH$_2$CH$_2$), 70.64 (s, CH$_2$−O−*C*H$_2$CH$_2$), 70.55 (s, CH$_2$−O−CH$_2$*C*H$_2$), 59.78 (s, O−*C*H$_3$), 14.93 (s, pyrazolato C*C*H$_3$). Anal. Calcd for $C_{18}H_{32}CaN_4O_4$: C, 52.92; H, 7.89; N, 13.71. Found: C, 50.40; H, 7.86; N, 12.06.

Preparation of Bis(3,5-dimethylpyrazolato)(tetraglyme)calcium-(II) (9). In a fashion similar to the preparation of **7**, calcium bromide (0.500 g, 2.50 mmol), 3,5-dimethylpyrazole (0.480 g, 5.00 mmol), potassium hydride (0.201 g, 5.00 mmol), and tetraglyme (0.555 g, 2.50 mmol) were reacted to afford **9** as a colorless solid (0.45 g, 40%): mp 75−79 °C. IR (Nujol, cm^{-1}): 3082 (m), 1506 (s), 1405 (s), 1354 (s), 1343 (m), 1321 (m), 1286 (m), 1245 (m), 1196 (m), 1085 (broad, vs), 1025 (s), 1010 (s), 946 (s), 849 (s), 749 (vs), 728 (s). ^{1}H NMR (benzene-d_6, 23 °C, δ): 5.86 (s, 2 H, pyrazolato ring C−*H*), 3.29 (s, 6 H, O−C*H*$_3$), 3.18 (m, 4 H, CH$_3$−O−C*H*$_2$CH$_2$−O−CH$_2$CH$_2$), 3.01 (m, 12 H, CC*H*$_3$), 2.98 (m, 4 H, CH$_3$−O−CH$_2$CH$_2$−O−CH$_2$C*H*$_2$), 2.21 (m, 4 H, CH$_3$−O−CH$_2$C*H*$_2$−O−CH$_2$CH$_2$), 2.15 (m, 4 H, CH$_3$−O−CH$_2$-CH$_2$O−C*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, ppm): 153.10 (s, pyrazolato ring *C*−CH$_3$), 102.80 (s, pyrazolato ring *C*−H), 71.90 (s, CH$_3$−O−*C*H$_2$CH$_2$−O−CH$_2$CH$_2$), 70.41 (s, CH$_3$−O−CH$_2$*C*H$_2$−O−CH$_2$CH$_2$), 70.28 (s, CH$_3$−O−CH$_2$CH$_2$−O−*C*H$_2$CH$_2$), 69.17 (s, CH$_3$−O−CH$_2$CH$_2$O−CH$_2$*C*H$_2$), 58.47 (s, O−C*H*$_3$), 13.46 (s, pyrazolato C*C*H$_3$). Anal. Calcd for $C_{18}H_{32}CaN_4O_4$: C, 53.07; H, 8.02; N, 12.36. Found: C, 52.70; H, 7.95; N, 12.33.

Crystal Structure Determinations of 2−5 and 7. A colorless elongated octahedron of **2** was mounted in a thin-walled capillary under a nitrogen atmosphere. Crystallographic data were collected at room temperature on a Siemens/Bruker automated P4/CCD diffractometer with monochromated Mo radiation. A quantity of 1470 frames were collected for 10 s and integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with Sheldrick's SADABS program, and the structure was solved and refined using the programs of SHELXS-86 and SHELXL-93. The molecule crystallizes as a molecular complex with no associated solvent or ions. The *tert*-butyl groups and coordinated pyridine ligands exhibited their typical disorder. Partial occupancy isotropic carbon atoms were used to describe

the disorder for atoms labeled C5−C7 and C20−C22. Hydrogen atoms were calculated and assigned to ride on the carbons to which they were bound.

A colorless fragment of a crystal of **3** was mounted in a thin-walled capillary under a nitrogen atmosphere. Crystallographic data were collected at room temperature on a Siemens/Bruker automated P4/CCD diffractometer with monochromated Mo radiation. A quantity of 1470 frames were collected for 10 s and integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with Sheldrick's SADABS program, and the structure was solved and refined using the programs of SHELXS-86 and SHELXL-93. The molecule crystallizes as a molecular complex with no associated solvent or ions. The asymmetric unit contains two independent half-molecules. The *tert*-butyl groups exhibit their typical disorder. Hydrogen atoms were calculated and assigned to ride on the carbons to which they were bound.

A colorless rectangular crystal of **4** was mounted in a thin-walled capillary under a nitrogen atmosphere. Crystallographic data were collected at room temperature on a Siemens/Bruker automated P4/CCD diffractometer with monochromated Mo radiation. A quantity of 1500 frames were collected for 10 s and integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with Sheldrick's SADABS program, and the structure was solved and refined using the programs of SHELXS-86 and SHELXL-93. The molecule crystallizes as a molecular complex with no associated solvent or ions. The *tert*-butyl groups exhibit their typical disorder. Hydrogen atoms were calculated and assigned to ride on the carbons to which they were bound.

A colorless crystalline rod of **5** was mounted in a thin-walled capillary under a nitrogen atmosphere. Crystallographic data were collected at room temperature on a Siemens/Bruker automated P4/CCD diffractometer with monochromated Mo radiation. A quantity of 1470 frames were collected for 10 s and integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with Sheldrick's SADABS program, and the structure was solved and refined using the programs of SHELXS-86 and SHELXL-93. The molecule crystallizes as a molecular complex with no associated solvent or ions. The *tert*-butyl groups exhibit their typical disorder. Hydrogen atoms were calculated and assigned to ride on the carbons to which they were bound.

A colorless rod of **7** was mounted in a thin-walled capillary in a nitrogen atmosphere. Crystallographic data were collected at room temperature on a Siemens/Bruker automated P4/CCD diffractometer with monochromated Mo radiation. A quantity of 1470 frames were collected for 10 s and integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with Sheldrick's SADABS program, and the structure was solved and refined using the programs of SHELXS-86 and SHELXL-93. The molecule crystallizes as a molecular complex with no associated solvent or ions. Hydrogen atoms were calculated and assigned to ride on the carbons to which they were bound.

Acknowledgment. We gratefully acknowledge support from the Army Research Office (Grant DAAG55-98-1-0166).

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2**−**5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991049C