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# Metallocalixarenes: Syntheses and X-ray Crystal Structures of Titanium(IV), Iron(III), and Cobalt(II) Complexes of *p-tert*-Butylcalix[4]arene

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**Abstract:** The reactions of the metal amides [Ti(NMe$_2$)$_4$], [Fe{N(SiMe$_3$)$_2$}$_3$], and [(Co{N(SiMe$_3$)$_2$}$_2$)$_2$] with *p-tert*-butylcalix[4]areneH$_4$ (**1**) have resulted in the isolation and structural characterization of the first three $\sigma$-bonded transition-metal derivatives of a calixarene. Complete exchange of the four –OH protons in **1** with [Ti(NMe$_2$)$_4$] gives the complex [{Ti(*p-tert*-butylcalix[4]arene)}$_2$]·6PhMe (**2**) as orange-red crystals. The conformationally mobile cone configuration of **1** acquires rigidity in the titanium complex which exists in a dimeric form with bridging through one of the ligand oxygens resulting in a distorted tetrahedral coordination at titanium. The reactions of **1** with [Fe{N(SiMe$_3$)$_2$}$_3$] or [(Co{N(SiMe$_3$)$_2$}$_2$)$_2$] are more complex and involve –SiMe$_3$ shifts from silylamide groups to a ligand oxygen giving, for iron, an unusual complex of formula [{Fe(NH$_3$)(*p-tert*-butylcalix[4]areneOSiMe$_3$)}$_2$]·3*n*-C$_6$H$_{14}$ (**3**) and the new cluster [Co$_3$(*p-tert*-butylcalix[4]areneOSiMe$_3$)$_2$(THF)]·5PhMe (**4**) for cobalt. The remarkable inclusion of ammonia (which derives from an –N(SiMe$_3$)$_2$ group) in **3** appears to be unprecedented. The cluster **4** also appears to be unique since it is the only structurally characterized cobalt alkoxide. The crystal data at 140 K, Mo K$\alpha$ ($\lambda$ = 0.71069 Å), are as follows: **2**—$a$ = 12.427 (5) Å, $b$ = 13.409 (5) Å, $c$ = 18.754 (13) Å, $\alpha$ = 98.60 (5)°, $\beta$ = 106.26 (4)°, $\gamma$ = 108.33 (3)°, $Z$ = 2, space group $P\bar{1}$, $R$ = 0.067; **3**—$a$ = 12.815 (10) Å, $b$ = 15.061 (13) Å, $c$ = 16.870 (10) Å, $\alpha$ = 111.67 (6)°, $\beta$ = 91.66 (6)°, $\gamma$ = 111.81 (7)°, $Z$ = 2, space group $P\bar{1}$, $R$ = 0.083; **4**—$a$ = 10.152 (10) Å, $b$ = 22.551 (11) Å, $c$ = 27.142 (11) Å, $\beta$ = 105.02 (3)°, $Z$ = 4, space group = $P2_1/n$, $R$ = 0.14.

The calixarenes, illustrated by the example in Figure 1, are formed by condensation of *p-tert*-butylphenol with formaldehyde. They were first prepared by Zinke[1] and co-workers 40 years ago but they have their origins in the work of von Baeyer during the 1870's.[2] An important property of calixarenes is that they possess cavities and form molecular complexes with small molecules.[3] It is this characteristic and their ability to transport metal ions through hydrophobic membranes that has caused the current interest in their physical and chemical properties as models for the in vivo reactions of enzymes. It is also thought that the calixarenes may have similarities to the cyclodextrins which are cyclic oligosaccharides and are known to bind metal salts and organic substrates in their central cavities.[4]

The work of Gutsche and co-workers has allowed the facile synthesis of a variety of calixarenes in good yields,[5] although the development of their syntheses has a long history.[1,2,6] These simple synthetic routes have provided much of the impetus for current investigations. Recent work by Izatt and Christensen has shown that calixarenes are capable of selective ion transport and the formation of neutral complexes with cations through proton loss.[7] Our interest in these compounds stems from work involving transition-metal derivatives of bulky alkoxides such as OC-*t*-Bu$_3$, which display interesting stoichiometries, coordination numbers, and previously unobserved reactions.[8-10] We therefore wished to synthesize transition-metal derivatives of calixarenes to examine any unusual coordination and reactivity which these ligands might induce. For simplicity we have limited our initial work to the synthesis of neutral transition-metal derivatives of *p-tert*-butylcalix[4]areneH$_4$ (**1**), Figure 1. In this paper we describe the synthesis and characterization of the first transition-metal derivatives of *p-tert*-butylcalix[4]areneH$_4$.

## Experimental Section

**General Procedures.** All reactions were performed under N$_2$. Solvents were distilled over Na/K metal and degassed at least twice before use. Anhydrous Ti[N(CH$_3$)$_2$]$_4$ (Alfa) was used as purchased. *p-tert*-Butylcalix[4]areneH$_4$ (**1**),[5] tris{bis(trimethylsilyl)amido}iron(III) (Fe[N(SiMe$_3$)$_2$]$_3$),[11] and bis{bis(trimethylsilyl)amido}cobalt(II) [(Co[N(SiMe$_3$)$_2$]$_2$)$_2$][12] were prepared by literature procedures. $^1$H NMR data were recorded on a Nicolet NT-200 Spectrometer operating at 200 MHz. IR data were recorded on a Perkin-Elmer 180 spectrometer.

**[(Ti{*p-tert*-butylcalix[4]arene})$_2$]·6PhMe (2).** A solution of Ti[N(CH$_3$)$_2$]$_4$ (1.90 mmol, 0.43 g) in toluene (20 mL) was added to a slurry of ligand **1** (1.54 mmol, 1.00 g) in toluene (30 mL). After the solution was stirred for 1 h, **1** dissolved completely, giving a clear orange solution. Slow cooling gave the product as red-orange crystals; 0.69 g, 65%, mp > 360 °C.

**[{Fe(NH$_3$)(*p-tert*-butylcalix[4]areneOSiMe$_3$)}$_2$]·3*n*-C$_6$H$_{14}$ (3).** This synthesis was similar to that described for **2**. A solution of Fe[N(SiMe$_3$)$_2$]$_3$ (0.77 g, 1.43 mmol) in *n*-hexane (20 mL) was added slowly to a slurry of **1** (0.70 g 1.08 mmol) in toluene (30 mL). The ligand dissolved immediately, yielding a brownish-red solution. The reaction was stirred at 60 °C for 1 h and filtered. Reduction of volume and slow cooling afforded the product **3** as red-brown crystals; 0.18 g, 21%, mp > 360 °C.

**[Co$_3$(*p-tert*-butylcalix[4]areneOSiMe$_3$)$_2$THF]·5PhMe (4).** In a similar manner, addition of a solution of Co[N(SiMe$_3$)$_2$]$_2$ (3.1 mmol, 1.16 g) in 50/50 toluene/hexane (40 mL) gave no initial reaction. The mixture was heated to reflux and concentrated to one-half its original volume. Degassed THF (20 mL) was added and the mixture allowed to cool slowly under refrigeration. Brownish-red crystals were obtained in low (ca. 5%) yields.

**X-ray Crystallographic Studies.** All X-ray data were collected with a Syntex P2$_1$ diffractometer equipped with a locally modified Syntex LT-1 low-temperature device. Calculations were carried out on a Data General Eclipse Computer with use of the SHELXTL program system. Structures **2** and **3** were solved by direct methods whereas structure **4** was solved by the Patterson technique. In each case, an absorption correction was applied.[13] Scattering factors and corrections for anom-

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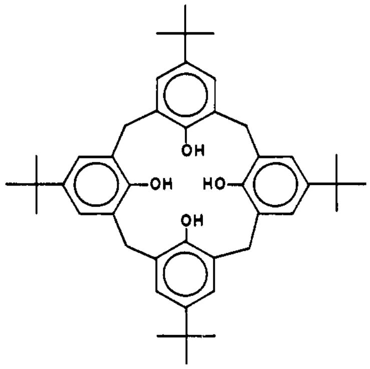


**Figure 1.** Representative drawing of ligand **1**.

**Table I.** Crystallographic Data and Summary of Data Collection and Structure Refinement

| | **2** | **3** | **4** |
|---|---|---|---|
| formula | $C_{130}H_{152}O_8Ti_2$ | $C_{112}H_{170}O_8$-$N_2Si_2Fe_2$ | $C_{133}H_{170}O_9$-$Si_2Co_3$ |
| fw | 1938.47 | 1840.61 | 2145.80 |
| cryst system | triclinic | triclinic | monoclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ |
| $T$, K | 140 | 140 | 140 |
| $a$, Å | 12.427 (5) | 12.815 (10) | 10.152 (10) |
| $b$, Å | 13.409 (5) | 15.061 (13) | 22.551 (11) |
| $c$, Å | 18.754 (13) | 16.870 (10) | 27.142 (11) |
| $\alpha$, deg | 98.60 (5) | 111.67 (6) | |
| $\beta$, deg | 106.26 (4) | 91.66 (6) | 105.02 (3) |
| $\gamma$, deg | 108.33 (3) | 111.81 (7) | |
| $V$, Å$^3$ | 2749 | 2757 | 11914 |
| $Z$ | 1 | 1 | 4 |
| $d_{calcd}$, g cm$^{-3}$ | 1.17 | 1.11 | 1.20 |
| crystal dims, mm | 0.25 × 0.50 × 0.70 | 0.40 × 0.25 × 0.07 | 0.21 × 0.27 × 0.87 |
| radiation | Mo K$\alpha$ $\lambda = 0.71069$ Å | Mo K$\alpha$ $\lambda = 0.71069$ Å | Mo K$\alpha$ $\lambda = 0.71069$ Å |
| $\mu$, cm$^{-1}$ | 2.0 | 3.5 | 4.8 |
| scan type | $\omega$ | $\omega$ | $\omega$ |
| scan range, deg | 1 | 1 | 1 |
| $w$ offset for background, deg | 1 | 1 | 1 |
| scan speed, deg min$^{-1}$ | 60 | 15 | 60 |
| $2\theta$ limits, deg | 50 | 45 | 45 |
| octants | $h \pm k \pm l$ | $h \pm k \pm l$ | $hk \pm l$ |
| no. unique data | 9654 | 7084 | 15596 |
| no. refl used in refinement | 6148 $(I > 3\sigma(I))$ | 2760 $(I > 3\sigma(I))$ | 6837 $(I > 3\sigma(I))$ |
| no. of parameters | 641 | 344 | 515 |
| $R$ | 0.067 | 0.083 | 0.140 |
| $Rw$ | 0.073 | 0.087 | 0.147 |
| GOF | 1.46 | 1.41 | 0.96 |

alous dispersion were from common sources.[14] Hydrogen atoms were included in the refinements with use of a riding model in which idealized positions were recalculated with each least-squares cycle (C–H = 0.96 Å). Atomic coordinates, thermal parameters, hydrogen atom positions, and complete tables of bond distances and angles for all three structures have been deposited as supplementary material. Further details for data collection and refinement are given in Table I.

Orange-red needles of **2** were obtained by slow cooling of the reaction mixture to 5 °C. The crystals were transferred from the Schlenk tube to a hydrocarbon oil under $N_2$. A crystal of suitable dimensions was selected and attached to a glass fiber and immediately placed in the low-temperature nitrogen stream. Solution and refinement of the structure proceeded smoothly. A disordered model for one of the *tert*-butyl groups and one of the toluene molecules was introduced in the refinement.

**Table II.** Selected Internuclear Distances (Å) and Angles (deg) for [{Ti(*p*-*tert*-butylcalix[4]arene)}$_2$]·6PhMe (**2**)

| | |
|---|---|
| Ti–O(1)′ | 1.845 (3)[a] |
| Ti–O(2) | 1.798 (3) |
| Ti–O(3) | 1.813 (3) |
| Ti–O(4) | 1.783 (3) |
| Ti···O(1) | 2.473 (3) |
| Ti···Ti′ | 3.351 (2)[a] |
| O(2)–Ti–O(1)′ | 110.3 (2)[a] |
| O(3)–Ti–O(1)′ | 111.2 (1)[a] |
| O(4)–Ti–O(1)′ | 110.2 (1)[a] |
| O(2)–Ti–O(3) | 98.1 (1) |
| O(2)–Ti–O(4) | 127.0 (1) |
| O(3)–Ti–O(4) | 97.7 (1) |
| Ti′–O(1)′–C(1)′ | 144.9 (3)[a] |
| Ti–O(2)–C(17) | 153.4 (3) |
| Ti–O(3)–C(28) | 118.7 (2) |
| Ti–O(4)–C(39) | 162.9 (3) |

[a] Primed atoms are at symmetry position $-x,-y,1-z$.

**Table III.** Selected Internuclear Distances and Angles (deg) for [{Fe(NH$_3$)(*p*-*t*-butylcalix[4]areneOSiMe$_3$)}$_2$]·3*n*-$C_6H_{14}$ (**3**)

| | |
|---|---|
| Fe–N | 2.10 (1) |
| Fe–O(1) | 1.85 (1) |
| Fe–O(2) | 1.985 (8) |
| Fe–O(3) | 1.82 (1) |
| Fe–O(2)′ | 2.017 (7)[a] |
| Fe···O(4) | 3.79 (1) |
| Fe···Fe′ | 3.258 (2)[a] |
| O(1)–Fe–O(2) | 97.0 (4) |
| O(1)–Fe–O(3) | 120.7 (4) |
| O(2)–Fe–O(3) | 100.2 (4) |
| O(1)–Fe–N | 91.1 (4) |
| O(2)–Fe–N | 154.4 (4) |
| O(3)–Fe–N | 96.3 (5) |
| O(1)–Fe–O(2)′ | 125.8 (4)[a] |
| O(2)–Fe–O(2)′ | 71.4 (3)[a] |
| O(3)–Fe–O(2)′ | 113.5 (4)[a] |
| N–Fe–O(2)′ | 84.2 (4)[a] |
| Fe–O(2)–Fe′ | 108.6 (3)[a] |
| Fe–O(1)–C(1) | 160.1 (6) |
| Fe–O(3)–C(32) | 156.4 (8) |

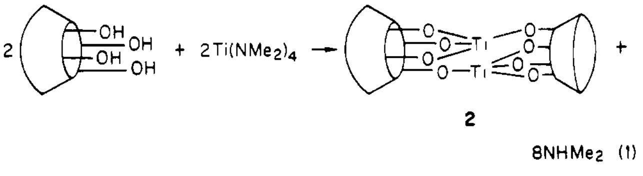
[a] Primed atoms are at symmetry position $1-x$, $1-y$, $-z$.

Red-brown crystals of **3** were obtained by reducing the toluene volume and subsequent slow cooling to −20 °C. Two of the *tert*-butyl groups were disordered in this structure. All three hydrogen atoms of the ammonia molecule appeared in the later difference maps. Their positions were not refined but they were included in the final structure factor calculation at the positions found from the final difference map.

Large red-brown rod-shaped crystals of **4** were obtained by slow evaporation of toluene/hexane and addition of THF followed by cooling to −20 °C. Refinement was carried out with use of isotropic thermal parameters and rigid phenyl groups for the toluenes of crystallization. Carbons of the latter toluenes were assigned a common thermal parameter which was allowed to refine. Not all hydrogens were included due to restrictions of SHELXTL. Important bond distances and angles for **2**, **3**, and **4** are given in Tables II, III, and IV.

## Results and Discussion

**Titanium Complex 2.** The reaction of *p*-*tert*-butylcalix[4]areneH$_4$ with transition-metal amides under mild conditions readily affords the complexes **2**, **3**, and **4**. Complete exchange of all four OH groups in **1** took place when treated with [Ti(NMe$_2$)$_4$] to give the aryloxo complex **2** in good yield, reaction 1. The synthesis



of titanium aryloxides and alkoxides via the reaction of the alcohol with a titanium amide has adequate precedent.[15] These and

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(13) The method obtains an empirical absorption tensor from an expression relating $F_o$ and $F_c$. Hope, H.; Moezzi, B., unpublished results.

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**Table IV.** Selected Internuclear Distances (Å) and Angles (deg) for $[Co_3(p\text{-}t\text{-butylcalix[4]areneOSiMe}_3)_2(THF)]\cdot 5PhMe$ (**4**)

| | |
|---|---|
| Co(1)–Co(2) | 2.760 (4) |
| Co(2)–Co(3) | 2.744 (3) |
| Co(1)···Co(3) | 3.559 (4) |
| (1) Terminal Aryloxy | |
| Co(1)–O(4) | 1.85 (1) |
| Co(3)–O(8) | 1.82 (1) |
| (2) Doubly Bridging Aryloxy | |
| Co(1)–O(2) | 2.02 (1) |
| Co(2)–O(2) | 1.94 (1) |
| Co(2)–O(6) | 1.95 (1) |
| Co(3)–O(6) | 1.93 (1) |
| (3) Triply Bridging Aryloxy | |
| Co(1)···O(3) | 2.43 (1) |
| Co(2)–O(3) | 2.03 (1) |
| Co(3)–O(3) | 2.03 (1) |
| Co(1)–O(7) | 2.03 (1) |
| Co(2)–O(7) | 2.21 (1) |
| Co(3)···O(7) | 2.29 (1) |
| (4) Terminal $OSiMe_3$ | |
| Co(3)–O(5) | 2.17 (1) |
| Co(1)–O(1) | 2.12 (1) |
| (5) Terminal THF | |
| Co(2)–O(9) | 2.11 (1) |
| Co(1)–Co(2)–Co(3) | 80.6 (1) |
| Co(1)–O(4)–C(13) | 133 (1) |
| Co(3)–O(8)–C(57) | 137 (1) |

related complexes have received a considerable amount of attention, particularly in the early literature because of their possible application in coatings and as components in Ziegler–Natta catalysts.[16] More recent attention has focused on the synthesis of coordinatively unsaturated metal alkoxides using large groups such as 2,4,6-tri-*tert*-butylphenol and tri-*tert*-butylcarbinol and also in the use of titanium complexes as asymmetric epoxidation catalysts.[8-10] In spite of this interest a relatively small variety of titanium alkoxide structures have been published. The first such study[17] by Ibers revealed $Ti(OEt)_4$ to have a tetrameric structure wherein each titanium was octahedrally surrounded by ethoxide ligands and the metal centers were linked by doubly or triply bridging –OEt groups. The alkoxides $[\{Ti(OMe)_3(OEt)\}_4]$[18] and $[\{Ti(OMe)_4\}_4]$[19] have similar structures. The structure of $[\{TiCl_2(OPh)_2\}_2]$, on the other hand, is dimeric.[18] Other structural studies on titanium alkoxides have mainly involved mononuclear species of the type $[Ti(\eta^5\text{-}C_5H_5)_2OR(OR')]$ where R or R′ are various aryl groups.[20]

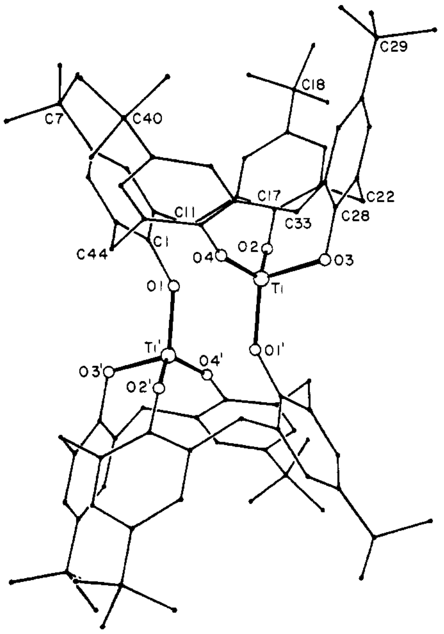

**Figure 2.** Computer-generated drawing of the skeleton of **2** (no hydrogen atoms or toluene molecules are shown).

The complex **2** as shown in Figure 2 may be formally described as a centrosymmetric titanium aryloxide dimer consisting of two Ti(*p*-*tert*-butylcalix[4]arene) units. Earlier work in this laboratory with 16-ane-$N_4$ ligand has also led to a dimeric species with some structural similarities.[21] The Ti–O(2), (3), (4) bond distances (av 1.798 (3) Å) fall within the normal range for titanium–oxygen single bonds; the Ti–O(1)′ distance, 1.845 (3) Å, is somewhat longer.[17-20] The remaining Ti···O(1) contact, 2.473 (3) Å, is about 0.6 Å longer than the other four distances. The disparity in the Ti–O(1) and Ti–O(1)′ distances and the very slight lengthening of the Ti–O(1)′ distance relative to Ti–O(2), Ti–O(3), and Ti–O(4) rules out significant bridging by O(1). As a result, we consider each Ti center to be much closer to four than five coordination with the distortions in the tetrahedral geometry being a consequence of the contraints imposed by the ligand. For example, the wide O(2)–Ti–O(4) angle, 127.0 (1)°, is probably the result of O(2) and O(4) occupying positions across the calixarene ring, and the narrow angles, O(2)–Ti–O(3) and O(3)–Ti–O(4), both ca. 98°, result from these three oxygens occupying adjacent positions in the calixarene. The remaining bond to oxygen involves O(1)′ rather than O(1) primarily because the strain at Ti is thereby much reduced. For example, the O(1)′–Ti–O(2),O(3),O(4) angles are 110.3 (2)°, 111.2 (1)°, and 110.2 (1)°. These are all very close to the tetrahedral value and presumably are relatively strain free. If, on the other hand, Ti were bonded to O(1) instead of O(1)′ two further angles of approximately 98° would result, giving rise to considerably greater strain. This strained bonding scheme would also result in a very unsymmetrical distribution of bonding electrons about Ti, giving rise to a less energetically stable molecule. It may be that during the reaction between $Ti(NMe_2)_4$ and the ligand an intermediate of this type may be produced which then quickly rearranges to the less strained **2**. In addition the rather weak Ti···O(1) interaction is also a result of the calixarene geometry which imposes a close approach, if not bonding, of O(1) to Ti. The Ti···Ti distance is 3.351 (2) Å precluding any significant bonding interaction.

The structural rigidity of **2** compared with **1**[22] was revealed by a variable-temperature $^1H$ NMR study. The $^1H$ NMR spectrum of **2** in chloroform at 25 °C showed two well-resolved sets of doublets at $\delta$ 4.9, 4.67 and $\delta$ 3.66, 3.39 for the bridging methylene groups. These are due to the different environments of the two hydrogen atoms on the methylene group. The different environments are also seen in the free ligand at room temperature or below. At higher temperature rapid interconversion of the cone conformation of **1** causes coalescence. The variable-temperature $^1H$ NMR of **2**, however, showed no coalescence between −30 and +80 °C, indicating a rather more rigid conformation upon complexation to the metal.[22]

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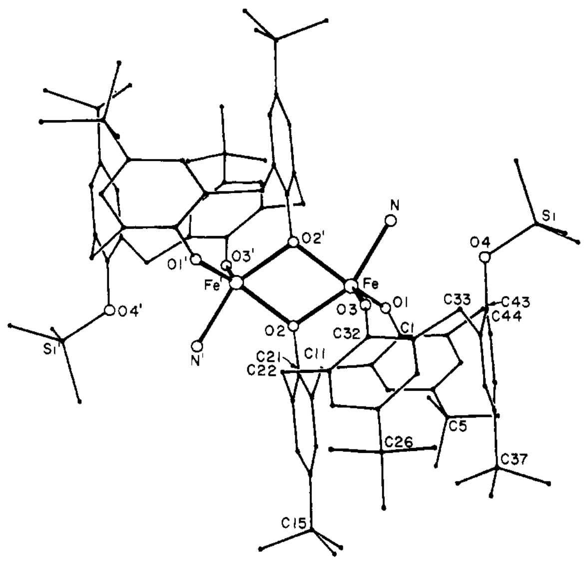


**Figure 3.** Computer-generated drawing of the skeleton of **3** (no hydrogen atoms or hexane molecules are shown).

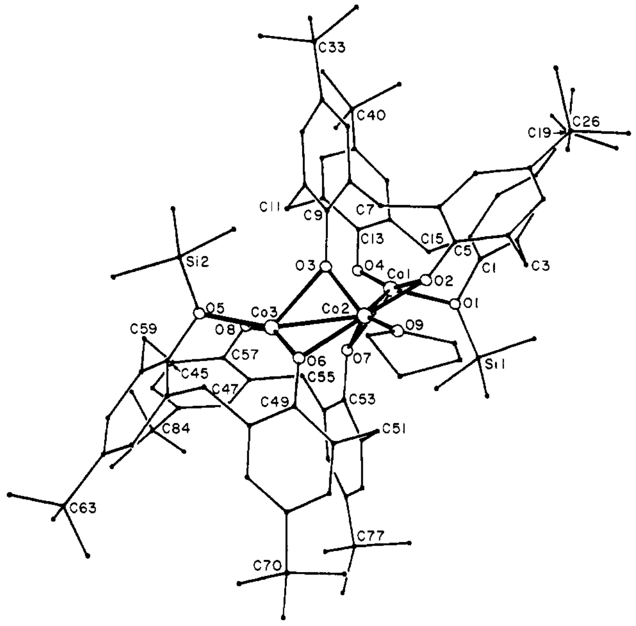


**Figure 4.** Computer-generated drawing of the skeleton of **4** (no hydrogen atoms or toluene molecules have been included).

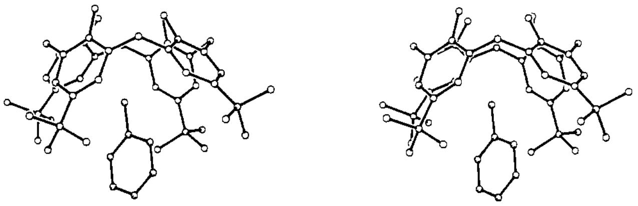
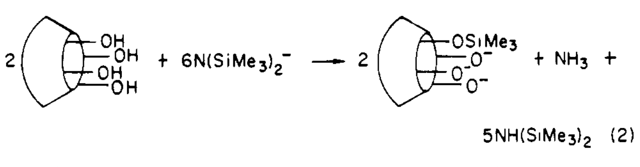


**Figure 5.** Stereoview of one of the ligands in **4** showing the interaction of a toluene with the calixarene.

**Iron and Cobalt Complexes 3 and 4.** We also wished to examine calixarene derivatives of other first-row transition metals. We were particularly interested in the later elements since their alkoxides are among the least well characterized and studied. A problem also arises through the use of metal amide precursors since these complexes are scarce. Until recently only the silyl amides had been well-characterized, although it appears that the diphenyl amide derivatives are also stable.[23] The use of metal silyl amides has a number of other disadvantages: (a) the eliminated amine is not very volatile (cf. $NHMe_2$, bp 7.4 °C), (b) the size of the $-N(SiMe_3)_2$ group may prevent or inhibit reactions through steric hindrance, and (c) the N–Si bond is reactive. Nevertheless, these disadvantages are offset by the ease of preparation of $N(SiMe_3)_2$ derivatives of Mn(II), Fe(III), Co(II), and Cu(I) (the Ni(II) derivative appears to be unstable).[11]

The reactions of $[Fe\{N(SiMe_3)_2\}_3]$ or $[(Co\{N(SiMe_3)_2\}_2)_2]$ with **1** proceed under fairly mild conditions to give **3**, $[\{Fe(NH_3)(p\text{-butylcalix[4]areneOSiMe}_3)\}_2]$, or **4**, $[Co_3(p\text{-}tert\text{-butylcalix[4]areneOSiMe}_3)_2(THF)]$. The yields of these products are not high, but they are reproducible. This may be a consequence of the reactivity of the N–Si bond which, when attacked could lead to a variety of different complexes. The structure of **3** (Figure 3) attests to the lability of the *N*-$SiMe_3$ group. Although the pathway by which **3** formed is not understood it clearly involves an $SiMe_3$ shift from N to O, as outlined in (2). The presence of an ammine ligand on the iron is also noteworthy. A number of N→O $SiMe_3$ shifts are known in the literature,[24] yet we are unaware of any instance of complete $SiMe_3$ stripping of a transition-metal bound $N(SiMe_3)_2$ group, although the reaction between CO and $NaN(SiMe_3)_2$ results in NaCN and $(Me_3Si)_2O$.[25]



(2)

The geometry at iron in **3** (Figure 3) can be described as distorted trigonal pyramidal. The O(1)O(2′)O(3)Fe set forms the equatorial plane with $NH_3$ and O(2) axial (N–Fe–O(2) = 154.4(4)°). The terminal Fe–O distances are normal at ca. 1.84 Å with the bridging Fe–O bonds approximately 2.0 (1) Å. The Fe–N distance is 2.10 Å, close to the values found in other complexes. There is no interaction between the $OSiMe_3$ group and the iron; the Fe–O(4) distance is 3.79 (1) Å. The IR spectrum (Nujol mull) of **3** shows the N–H stretch at 3430 $cm^{-1}$. This is consistent with data on other transition-metal ammine complexes.[26]

The structure of the cobalt complex **4** (Figure 4) is noteworthy in several respects. For example, it is the only reported structure of a cobalt alkoxide or aryloxide.[27] All the ligands on Co(1) or Co(3) are different and the bridging configuration of the $-OSiMe_3$ group is also unique. The coordination about Co(2) is completed by one THF. The Co(1)–Co(2) and Co(2)–Co(3) distances are 2.760 (4) and 2.744 (3) Å. These are close enough to be considered a rather long single bond. The Co(1)–Co(3) distance is quite long at 3.559 (4) Å. The Co–O bond lengths on the ligands surrounding Co(1) offer an interesting illustration of the effects of bond order and length since examples of terminal, doubly bridging, as well as bridging $OSiMe_3$ and terminal THF are included in the coordination sphere. These different types of Co–O bonds are grouped together in Table IV. The expected trends occur: the shortest Co–O bonds, 1.82 (1) and 1.85 (1) Å, are to terminal aryloxy groups, while the longest are to those which are doubly bridging (ca. 2.03 (1) Å). If all these Co–O bonds are counted, Co(1) and Co(3) are six-coordinate and Co(2) is five-coordinate. None of the metals has a coordination geometry that can be described as anything except irregular. There are two long

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interactions of 2.29 (1) Å for Co(3) and O(7) and 2.43 (1) Å for Co(1) and O(3). These are similar to the long interaction seen in the titanium compound. However, in the more complicated cobalt complex it is more difficult to decide whether or not these close contacts represent real bonds or are just a result of geometric constraints imposed by the ligand.

Another feature of interest in these complexes is the possibility of a host–guest interaction, whereby a small molecule fits inside the cone of the calixarene. The crystal structure of the clathrate *p-tert*-butylcalix[4]areneH$_4$·PhMe has already been reported.[28] The cobalt complex **4** crystallizes with five toluene molecules. Two of these are involved in a host–guest interaction. A typical arrangement is shown in Figure 5. The titanium complex **2** crystallizes with three toluenes in the asymmetric unit, and one of these is incorporated into the cone. By contrast, the iron complex **3** has one and one-half molecules of *n*-hexane in the asymmetric unit and neither of these is found within the cone. The reason for this difference in behavior is not immediately obvious, since the cone opening is both flexible and wide. If one takes the distances between opposing carbons bonded to the *tert*-butyl groups as a measure, the openings are 7.49 × 9.18 Å for **2**, 5.44 × 9.60 Å for **3**, and 7.44 × 9.01 and 7.33 × 9.19 Å for **4**.

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**Registry No. 1**, 60705-62-6; **2**, 98719-91-6; **3**, 98705-02-3; **4**, 98719-93-8; Fe(N(SiMe$_3$)$_2$)$_3$, 22999-67-3; Co[N(SiMe$_3$)$_2$]$_2$, 18544-54-2.

**Supplementary Material Available:** Tables of atom coordinates, thermal parameters, complete tables of bond distances and angles, hydrogen coordinates and structure factors (24 pages). Ordering information is given on any current masthead page.

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# Highly Reactive Organolanthanides. Systematic Routes to and Olefin Chemistry of Early and Late Bis(pentamethylcyclopentadienyl) 4f Hydrocarbyl and Hydride Complexes

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**Abstract:** The reaction of the organolanthanide complexes $Cp'_2MCl_2^-Li(ether)_2^+$, $Cp' = \eta^5\text{-}(CH_3)_5C_5$, M = La, Nd, Sm, and Lu, with $LiCH[Si(CH_3)_3]_2$ provides a straightforward route to the broad class of ether- and halide-free bis(pentamethylcyclopentadienyl) lanthanide alkyls, $Cp'_2MCH[Si(CH_3)_3]_2$. These complexes were characterized by standard analytical methodology. The M = Nd complex crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a cell of dimensions (−100 °C) $a$ = 11.045 (9) Å, $b$ = 23.554 (7) Å, $c$ = 11.648 (9) Å, and $\beta$ = 103.10 (6)°. Least-squares refinement led to a value for the conventional $R$ index (on $F$) of 0.078 for 4287 independent, absorption-corrected reflections having $I > 3\sigma(I)$. The molecular structure consists of monomeric $Cp'_2NdCH[Si(CH_3)_3]_2$ units with a "bent-sandwich" $Cp'_2Nd$ configuration: (ring centroid)–Nd–(ring centroid) = 134.4°. The $CH[Si(CH_3)_3]_2$ fragment is coordinated to the $Cp'_2Nd$ group in a highly unsymmetrical fashion with a Nd–C $\sigma$-bond distance of 2.517 (7) Å and a rather short secondary contact to a single methyl carbon atom of 2.895 (7) Å. Spectroscopic data suggest that this interaction is higly metal-to-carbon in character. The $Cp'_2NdCH[Si(CH_3)_3]_2$ complexes react with $H_2$ under mild conditions to yield the corresponding hydrides $(Cp'_2MH)_2$. These complexes are extremely active homogeneous ethylene polymerization catalysts with turnover frequencies exceeding 1800 s$^{-1}$ (25 °C, 1 atm of ethylene pressure) for M = La. Activities are in the order La ≥ Nd ≫ Lu. The kinetics of this process and the molecular weight characteristics of the resulting polymer are severely limited by mass transport effects; evidence is presented that these are "living" polymers and that chain transfer by $\beta$-hydride elimination is not important. For La and Nd, propylene and 1-hexene react rapidly at −10 °C to yield equal quantities of the disproportionation products alkane + metal $\eta^3$-alkenyl. Butadiene undergoes reaction with these hydrides to yield $\eta^3$-crotyl complexes, and significant polymerization does not occur. For 1-hexene under low $H_2$ (or $D_2$) pressure at room temperature, some formation of 2-methylundecane is also observed. The analogous reaction of cyclohexene with these hydrides is sluggish and appears to produce an $\eta^1$-cyclohexenyl complex. There is no evidence for cyclohexene oligomers. Although unreactive toward olefins, $Cp'_2NdCH[Si(CH_3)_3]_2$ reacts with CO to yield a dimeric dionediolate.

Much of the recent development of early transition- and f-element hydrocarbyl and hydride chemistry can be attributed to the beneficial characteristics of bis(pentamethylcyclopentadienyl) ($Cp'_2$) supporting ligation.[2-4] However, in contemplating comparative studies of isoelectronic, isoleptic 4f/5f systems,[5,6] it was evident to us that routes to lanthanide $Cp'_2MR$ and $(Cp'_2MH)_2$

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[1] (1) (a) Technische Universität Berlin. Work performed while a visiting scholar at Northwestern University. (b) Northwestern University. (c) Staff crystallographer, Northwestern University. (d) Technische Universität Berlin.

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