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Bis(*tert*-butylcyclopentadienyl)magnesium, -calcium, -strontium, and -barium Metallocenes

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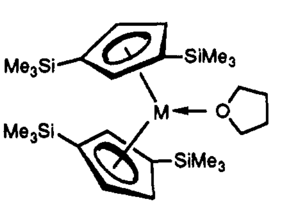
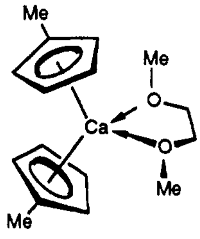
Bis(*tert*-butylcyclopentadienyl)metal derivatives, $M(t\text{-}BuC_5H_4)_2$, M = Mg, Ca, Sr, and Ba, have been prepared by metalation using Mg(*s*-Bu)(*n*-Bu) or metal vapors for the heavier group 2 elements. The Ca, Sr, and Ba compounds are only sparingly soluble in hydrocarbon solvents and have been characterized by using ^{13}C CP/MAS NMR spectroscopy with TOSS pulse sequences. Addition of THF (tetrahydrofuran) to these compounds yields THF adducts that have been isolated as $[M(t\text{-}BuC_5H_4)_2(THF)_2]$ for Ca and Sr. Both have been structurally characterized, along with $[Mg(t\text{-}BuC_5H_4)_2]$. The latter is a regular metallocene: Mg–centroid = 2.00 Å, centroid–Mg–centroid = 180°; crystals are monoclinic, space group $P2_1/n$, a = 6.270 (4) Å, b = 11.213 (3) Å, c = 11.932 (7) Å, β = 96.53°, V = 833.6 Å^3, Z = 2. The THF adducts are isostructural and are monomeric bent metallocenes, with four coordinate metal centers, assuming the cyclopentadienyl ligands to be unidentate: Ca,Sr–centroid = 2.46, 2.61 Å, Ca,Sr–O = 2.40, 2.53 Å, centroid–M–centroid = 133.3, 133.1°, O–M–O = 83.2 (2), 83.1 (2)°; crystals are monoclinic, space group $P2_1/n$, a = 13.527 (4), 13.793 (3) Å, b = 10.057 (4), 10.308 (1) Å, c = 20.254 (7), 20.269 (5) Å, β = 106.24 (1), 107.66 (1)°, V = 2445 (1), 2746 (1) Å^3, Z = 4 (Ca, Sr values, respectively).

Introduction

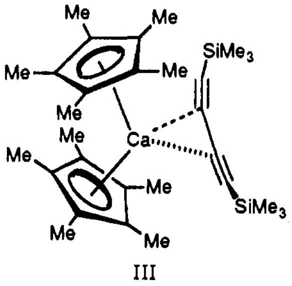
The first structural report of an organometallic compound of the heavier group 2 elements was on bis(cyclopentadienyl)calcium (calcocene) in 1974.[1] Over a decade passed before further structures appeared[2] despite many intervening reports on the synthesis and reactivity of organocalcium, -strontium, and -barium compounds.[3] In the solid state, calcocene is polymeric with the calciums bound to four cyclopentadienyl ligands, in an η^1, η^3, η^5, η^5 fashion;[1] the structures of strontocene, $Sr(C_5H_5)_2$, and barocene, $Ba(C_5H_5)_2$, are thought to be similar.[4] Recent studies demonstrate that simple bent metallocene structures are accessible by incorporating substituents on the cyclopentadienyl ligands[2,5–10] and/or by complexation of the metal centers by Lewis bases such as ethers, as in $[M\{1,3\text{-}(SiMe_3)_2C_5H_3\}_2(THF)]$, **I**, M = Ca, Sr (THF ≡ tetrahydrofuran),[10–12] and $[Ca(C_5H_4Me)_2(DME)]$, **II** (DME ≡ 1,2-dimethoxyethane).[13] In addition, permethylated cyclopentadienyl yields a bent calcocene adduct of a diyne, $[Ca(C_5Me_5)_2\{1,4\text{-}(Me_3Si)_2C_4\}]$, **III**, albeit with the diyne readily displaced by ethers and amines.[14]



I



II



III

The use of bulky pentamethyl- and bis(trimethylsilyl)cyclopentadienyl moieties is well-known to reduce molecular aggregation and often impart higher solubility and volatility of the metallocenes. Barocene, $Ba(C_5H_5)_2$, for example, sublimes at 420–460 °C, "high vacuum",[4] whereas the permethylated barocene, $Ba(C_5Me_5)_2$, sublimes at 130–140 °C, 10^{-3} mmHg.[15] Indeed, greater volatility has led to their use as precursors for organometallic chemical vapor deposition technology.[16] The pentamethylcyclopentadienyl ligand is also featured in the only structural work on a monocyclopentadienyl complex of the heavy

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group 2 elements, viz. $[(\eta\text{-}C_5Me_5)Ca(\mu\text{-}I)(THF)_2]_2$,[17] although a number of complexes of this type have been prepared.[18] A related complex with a group 2 metal bound to a single polyhapto ligand is the calcium carborane, *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$.[19]

Herein we report the metal vapor synthesis of bis(*tert*-butylcyclopentadienyl)metal compounds, $M(t\text{-}BuC_5H_4)_2(THF)_n$, **1a**, M = Ca; **2a**, M = Sr; and **3a**, M = Ba (n = 0) and **1b**, M = Ca; and **2b**, M = Sr (n = 2). This is part of a systematic study of the heavier group 2 elements dealing with varying the degree of steric hindrance of the cyclopentadienyl group; a single *tert*-butyl group will impart less steric hindrance than two isolobal trimethylsilyl groups, which were featured in our earlier study.[11] Thus far, the metal vapor technique has been used to prepare simple metallocenes of calcium and strontium[20] and $M\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2(THF)_n$, M = Ca, Sr, and Ba, n = 0 or 1,[11] and also used to prepare cyclooctatetraene complexes of the same elements, although here the products are derived from metal-to-ligand electron transfer in contrast to C–H bond scission in the reactions of cyclopentadienes. Recently, activated barium powder has been featured in the synthesis of $[Ba(C_5Me_5)_2(THF)_2]$.[21]

We also report the synthesis and structure determination of the unsolvated magnesocene analogue, $[Mg(t\text{-}BuC_5H_4)_2]$, **4**, as a basis for comparison with the more ionic structures for the larger group 2 divalent ions. The parent magnesocene, $[Mg(C_5H_5)_2]$, is monomeric in both the crystalline[22] and gaseous phases[23] as a sandwich species, and while it can reversibly form Lewis base adducts, they cannot be isolated.[24] The highly substituted magnesocene, $[Mg\{\eta\text{-}1,2,4\text{-}(SiMe_3)_3C_5H_2\}_2]$, has a slightly bent sandwich structure in the solid state owing to relief from steric strain.[25] The compound $[Ca\{\mu\text{-}C_5H(i\text{-}Pr)_4\}_2]$ appears to be the only example of a metallocene of the heavier group 2 elements in which the steric hindrance of the ligands is such as to completely block the formation of Lewis base adducts.[10]

Experimental Section

Syntheses were carried out by using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried and then freeze-degassed prior to use. Metals were vaporized from resistively heated tungsten boats attached to water-cooled copper electrodes in a 9-dm^3 vessel. Mg(n-Bu)(s-Bu) was obtained from Alfa Products. All other reagents were obtained from Aldrich. *tert*-Butylcyclopentadiene was prepared according to the published procedure.[26] ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer operating at 250 MHz. The ^{1}H spectra, which were run in deuterated benzene or THF, were referenced to the residual ^{1}H resonances of C_6D_6 (δ 7.15) or d_8-THF (δ 3.58). ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer operating at 62.8 MHz using broad-band proton decoupling. The ^{13}C spectra, which were run in deuterated benzene or THF, were referenced to the ^{13}C resonancnes of C_6D_6 (δ 128.00) or d_8-THF (δ 25.30). ^{13}C CP/MAS NMR spectra were recorded on a Bruker CXP-300 spectrometer operating at 75.4 MHz using broad-band proton decoupling and TOSS pulse sequences to remove spinning side bands; spectra were measured relative to the downfield shift of external adamantane (δ 38.23), and samples were packed in Kel-F inserts, made as described by Merwin et al. for a standard Bruker 7-mm double air bearing probe and a ZrO_2 rotor.[26] ^{25}Mg spectra were recorded on a Bruker CXP-300 spectrometer operating at 116.62 MHz and were run in C_6D_6 and measured relative to external aqueous 0.2 M $MgSO_4$.

Synthesis of $Ca(t\text{-}BuC_5H_4)_2(THF)_n$, n = 0, 1a; n = 2, 1b. Calcium (0.80 g, 20 mmol), *tert*-butylcyclopentadiene (10.0 g, 83 mmol), and hexane (50 cm^3) were cocondensed over ca. 3 h onto the liquid nitrogen cooled walls of the reaction vessel, yielding a black matrix. On warming, a straw-colored slurry devoid of calcium metal particles was obtained. Hexane (100 cm^3) was then added to the reaction vessel. Part of the resulting mixture was siphoned from the vessel as a slurry and dried in vacuo to yield **1a** as a creamy, free flowing, powder (0.90 g, 16%) that can be sublimed (180 °C, 10^{-4} mmHg) as colorless needles of **1a**: mp 301–304 °C; ^{13}C CP/MAS NMR δ 32.0–33.6 (C(Me)$_3$ and Me), 103.7–115.5 (C^2 and C^3), 135.3, 136.5 (C^1). THF was added to the residue in the metal vapor reaction vessel and the mixture siphoned from the vessel. This fraction was dried in vacuo to yield **1b** as a creamy, free flowing, powder (2.04 g, 20%) that can be sublimed (180 °C, 10^{-4} mmHg) as colorless needles of **1a**. Data for **1b**: mp 325–330 °C; ^{1}H NMR (C_6D_6) δ 1.24 (8 H, br m, THF), 1.55 (18 H, s, Me), 3.33 (8 H, br m, THF), 5.88–6.20 (8 H, AA′BB′, H^2 and H^3); ^{13}C{^{1}H} NMR (C_6D_6) δ 25.1 (THF), 32.2 (C(Me)$_3$), 33.0 (Me), 69.0 (THF), 105.9, 106.1 (C^2 and C^3), 135.2 (C^1).

Synthesis of $Sr(t\text{-}BuC_5H_4)_2(THF)_n$, n = 0, 2a; n = 2, 2b. Strontium (2.83 g, 32 mmol), *tert*-butylcyclopentadiene (9.0 g, 74 mmol), and hexane (50 cm^3) were cocondensed over ca. 2 h onto the liquid nitrogen cooled walls of the reaction vessel, yielding a black matrix. On warming to room temperature, a straw-colored slurry devoid of metal particles was obtained. Hexane (100 cm^3) was added to the reaction vessel and part of the resulting mixture siphoned from the vessel as a slurry. This was dried in vacuo to yield **2a** as a creamy free flowing, powder (2.52 g, 24%) that can be sublimed (260 °C, 10^{-4} mmHg) as colorless needles of **2a**: mp 375–380 °C; ^{13}C CP/MAS NMR δ 31.3–33.6 (C(Me)$_3$ and Me), 104.5–114.0 (C^2 and C^3), 134.4, 137.0 (C^1). THF was added to the vessel, and the remaining contents were siphoned from the vessel. This fraction was dried in vacuo to yield **2b** as a creamy, free flowing, powder (5.29 g, 35%) that can also be sublimed (260 °C, 10^{-4} mmHg) as colorless needles of **2a**. Data on **2b**: mp 375–376 °C; ^{1}H NMR (250 MHz, d_8-THF) δ 1.24 (18 H, s, Me), 1.73 (8 H, br m, THF), 3.58 (8 H, br m, THF), 5.53–6.74 (8 H, AA′BB′, H^2 and H^3); ^{13}C{^{1}H} NMR (d_8-THF) δ 26.9 (THF), 32.1 (C(Me)$_3$), 32.1 (Me), 68.2 (THF), 103.7, 106.3 (C^2 and C^3), 135.7 (C^1).

Synthesis of $Ba(t\text{-}BuC_5H_4)_2$, 3a, and a THF Adduct, 3b. Barium (4.28 g, 31 mmol), *tert*-butylcyclopentadiene (7.3 g, 74 mmol), and hexane (50 cm^3) were cocondensed over ca. 2.5 h onto the liquid nitrogen cooled walls of the reaction vessel, yielding a black matrix. On warming to room temperature, a straw-colored slurry devoid of barium metal was obtained. Hexane (100 cm^3) was added to the reaction vessel, and part of the resulting mixture was siphoned from the vessel as a slurry. This was dried in vacuo to yield **3a** as a creamy, free flowing, powder (3.41 g, 29%) that can be sublimed (320 °C, 10^{-4} mmHg) as a glass-like solid. Data for $Ba(t\text{-}BuC_5H_4)_2$, **3**: mp 320 °C (dec); ^{13}C CP/MAS NMR δ 32.3–36.4 (C(Me)$_3$ and Me), 104.9, 109.4 (C^2 and C^3), 135.5 (C^1). THF was added to the vessel, and the remaining contents were siphoned from the vessel. This fraction was dried in vacuo to yield a creamy, free flowing, powder of variable THF content, **3b**, that could be sublimed (320 °C, 10^{-4} mmHg) to give **3a** as a glass-like solid.

Synthesis of $Mg(t\text{-}BuC_5H_4)_2$, 4. Mg(n-Bu)(s-Bu) (11.13 cm^3, 0.7 M, 7.8 mmol) in heptane was added dropwise over 10 min to a stirred solution to *tert*-butylcyclopentadiene (2.0 g, 16.5 mmol)

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Table I. Structural Parameters for $[M(t\text{-}Bu\text{-}C_5H_4)_2(THF)_2]$ (M = Ca (1b), M = Sr (2b))[a]

atoms	1b	2b
M–Centroid(A)	2.462	2.610
M–C(1A	2.797 (6)	2.902 (9)
M–C(2A)	2.790 (6)	2.901 (8)
M–C(3A)	2.716 (6)	2.863 (9)
M–C(4A)	2.665 (6)	2.822 (9)
M–C(5A)	2.706 (6)	2.852 (9)
M–Centroid(B)	2.456	2.599
M–C(1B)	2.803 (6)	2.905 (9)
M–C(2B)	2.793 (7)	2.905 (10)
M–C(3B)	2.700 (7)	2.846 (12)
M–C(4B)	2.653 (6)	2.797 (11)
M–C(5B)	2.709 (6)	2.845 (9)
M–C (av)	2.733	2.864
M–O(1C)	2.405 (4)	2.536 (6)
M–O(1D)	2.398 (4)	2.533 (7)
Centroid(A)–M–Centroid(B)	133.3	133.1
O(1C)–M–O(1D)	83.2 (2)	83.1 (2)
Centroid(A)–M–O(1C)	105.7	105.7
Centroid(A)–M–O(1D)	108.4	108.3
Centroid(B)–M–O(1C)	108.0	107.7
Centroid(B)–M–O(1D)	106.9	107.6

Table II. Structural Parameters for $[Mg(t\text{-}Bu\text{-}C_5H_4)_2]$ (4)[a]

Mg–Centroid	2.00	Mg–C(4)	2.327 (3)
Mg–C(1)	2.354 (3)	Mg–C(5)	2.335 (3)
Mg–C(2)	2.332 (3)	Mg–C (av)	2.336
Mg–C(3)	2.330 (3)		
Centroid–Mg–Centroid	180		

[a] Bond distances are in angstroms and angles in degrees.

Table III. Non-Hydrogen Atom Coordinates for $[Ca(t\text{-}Bu\text{-}C_5H_4)_2(THF)_2]$ (1b)

atom	*x/a*	*y/b*	*z/c*
Ca	0.4839 (1)	0.0313 (1)	0.2345 (1)
Centroid(A)	0.4149 (-)	0.1515 (-)	0.3178 (-)
C(1A)	0.4974 (5)	0.1558 (6)	0.3602 (3)
C(2A)	0.4219 (5)	0.0574 (7)	0.3542 (3)
C(3A)	0.3371 (5)	0.0894 (9)	0.2981 (4)
C(4A)	0.3597 (5)	0.2072 (8)	0.2692 (4)
C(5A)	0.4584 (5)	0.2476 (7)	0.3075 (3)
C(11A)	0.5973 (5)	0.1660 (7)	0.4182 (3)
C(12A)	0.6741 (6)	0.2588 (10)	0.3995 (4)
C(13A)	0.5707 (6)	0.2190 (10)	0.4830 (4)
C(14A)	0.6461 (6)	0.0313 (9)	0.4356 (5)
Centroid(B)	0.6127 (-)	0.0873 (-)	0.1743 (-)
C(1B)	0.5649 (5)	0.1803 (8)	0.1448 (3)
C(2B)	0.5599 (7)	0.0480 (9)	0.1199 (4)
C(3B)	0.6279 (8)	−0.0283 (10)	0.1699 (6)
C(4B)	0.6756 (5)	0.0528 (10)	0.2262 (5)
C(5B)	0.6357 (5)	0.1832 (8)	0.2106 (4)
C(11B)	0.5135 (6)	0.3007 (8)	0.1028 (4)
C(12B)[a]	0.5377 (29)	0.4309 (30)	0.1433 (21)
C(13B)[a]	0.5428 (40)	0.3144 (47)	0.0329 (16)
C(14B)[a]	0.3978 (20)	0.2834 (33)	0.0856 (16)
C(15B)[a]	0.4244 (34)	0.2696 (41)	0.0387 (22)
C(16B)[a]	0.4876 (55)	0.4023 (40)	0.1438 (19)
C(17B)[a]	0.5964 (24)	0.3485 (42)	0.0692 (19)
O(1C)	0.5183 (3)	−0.1908 (4)	0.2790 (2)
C(2C)	0.4483 (6)	−0.2780 (9)	0.3010 (5)
C(3C)	0.5111 (8)	−0.3589 (9)	0.3552 (6)
C(4C)	0.6154 (6)	−0.3603 (9)	0.3460 (5)
C(5C)	0.6146 (5)	−0.2612 (7)	0.2936 (4)
O(1D)	0.3433 (3)	−0.0743 (5)	0.1522 (2)
C(2D)	0.3524 (7)	−0.1956 (10)	0.1160 (5)
C(3D)	0.2578 (9)	−0.2066 (13)	0.0609 (6)
C(4D)	0.1943 (9)	−0.0947 (13)	0.0621 (6)
C(5D)	0.2410 (5)	−0.0251 (9)	0.1252 (4)

[a] Methyl carbons of disordered *tert*-butyl group, C(12B)–C(14B) and C(15B)–C(17B) being the two conformations. Each conformation has a site occupancy of 0.5.

Table IV. Non-Hydrogen Atom Coordinates for $[Sr(t\text{-}Bu\text{-}C_5H_4)_2(THF)_2]$ (2b)

atom	*x/a*	*y/b*	*z/c*
Sr	0.4839 (1)	0.0402 (1)	0.2326 (1)
Centroid(A)	0.4122 (-)	0.1647 (-)	0.3198 (-)
C(1A)	0.4946 (6)	0.1661 (10)	0.3627 (5)
C(2A)	0.4192 (7)	0.0728 (11)	0.3551 (5)
C(3A)	0.3346 (7)	0.1051 (13)	0.2991 (6)
C(4A)	0.3570 (8)	0.2199 (12)	0.2716 (6)
C(5A)	0.4554 (7)	0.2594 (10)	0.3105 (5)
C(11A)	0.5943 (7)	0.1711 (11)	0.4201 (5)
C(12A)	0.6650 (8)	0.2727 (13)	0.4068 (6)
C(13A)	0.5757 (9)	0.2091 (14)	0.4880 (5)
C(14A)	0.6457 (8)	0.0426 (13)	0.4314 (7)
Centroid(B)	0.6223 (-)	0.0956 (-)	0.1740 (-)
C(1B)	0.5736 (8)	0.1845 (13)	0.1426 (6)
C(2B)	0.5711 (10)	0.0543 (16)	0.1191 (7)
C(3B)	0.6400 (14)	−0.0155 (19)	0.1717 (11)
C(4B)	0.6835 (9)	0.0644 (20)	0.2275 (9)
C(5B)	0.6434 (7)	0.1905 (12)	0.2092 (6)
C(11B)	0.5177 (9)	0.2991 (13)	0.0997 (6)
C(12B)[a]	0.4982 (87)	0.3980 (61)	0.1441 (29)
C(13B)[a]	0.5970 (26)	0.3543 (56)	0.0673 (32)
C(14B)[a]	0.4289 (50)	0.2707 (59)	0.0413 (40)
C(15B)[a]	0.5124 (70)	0.2931 (74)	0.0232 (21)
C(16B)[a]	0.4016 (29)	0.2872 (66)	0.0943 (36)
C(17B)[a]	0.5512 (49)	0.4291 (40)	0.1332 (32)
O(1C)	0.5157 (5)	−0.1899 (6)	0.2784 (4)
C(2C)	0.4474 (8)	−0.2693 (13)	0.3038 (8)
C(3C)	0.5072 (11)	−0.3597 (15)	0.3501 (10)
C(4C)	0.6063 (10)	−0.3647 (14)	0.3391 (8)
C(5C)	0.6087 (8)	−0.2617 (11)	0.2913 (7)
O(1C)	0.3362 (5)	−0.0643 (8)	0.1419 (4)
C(2D)	0.3451 (12)	−0.1812 (17)	0.1043 (8)
C(3D)	0.2491 (15)	−0.1969 (21)	0.0515 (10)
C(4D)	0.1830 (13)	−0.0942 (21)	0.0567 (10)
C(5D)	0.2340 (8)	−0.0221 (14)	0.1178 (7)

[a] Methyl carbons of disordered *tert*-butyl group, C(12B)–C(14B) and C(15B)–C(17B) being the two conformations. Each conformation has a site occupancy of 0.5.

Table V. Non-Hydrogen Atom Coordinates for $[Mg(t\text{-}Bu\text{-}C_5H_4)_2]$ (4)

atom	*x/a*	*y/b*	*z/c*
Mg	0.0000 (-)	0.0000 (-)	0.5000 (-)
C(1)	0.1218 (5)	0.0681 (2)	0.3319 (2)
C(2)	0.2629 (6)	0.1110 (3)	0.4236 (3)
C(3)	0.1495 (7)	0.1893 (3)	0.4893 (3)
C(4)	−0.0611 (7)	0.1953 (3)	0.4385 (3)
C(5)	−0.0821 (6)	0.1205 (3)	0.3414 (3)
C(10)	0.1797 (5)	−0.0129 (3)	0.2382 (3)
C(11)	0.3584 (9)	−0.1005 (4)	0.2838 (4)
C(12)	0.2661 (11)	0.0634 (5)	0.1474 (4)
C(13)	−0.0144 (9)	−0.0861 (5)	0.1887 (5)

in hexane (20 cm^3) at 0 °C. The solution was allowed to warm to room temperature and stirred overnight. Volatiles were removed in vacuo to give a pale yellow oil, and the product was sublimed as colorless crystals of **4** at 80 °C (10^{-1} mmHg) (0.88 g, 40%): ^1H NMR (C_6D_6) δ 1.25 (18 H, s, Me), 5.91–5.98 (8 H, AA′BB′, H^2 and H^3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 32.1 ($C(Me)_3$), 32.1 (Me), 103.7, 106.3 (C^2 and C^3), 135.7 (C^1); ^{25}Mg NMR (C_6D_6) δ −88 (br, $\omega_{1/2}$ = 310 Hz, s).

Structure Determinations. Crystals were sealed in capillaries under argon. Suitable crystals of **1b** were grown on storing a saturated THF solution at ca. −30 °C overnight, and for **2b**, crystals were grown by rapid freezing of a saturated THF solution with liquid nitrogen followed by slow thawing to −30 °C. Crystals of **4** were grown by sublimation at 50 °C (10^{-5} mmHg). Unique diffractometer data sets were measured carefully at 296 K to the specified $2\theta_{max}$ limit in conventional ω/θ scan mode by using a Enraf-Nonius CAD4 diffractometer. The structures were solved by the heavy atom method, **1b** and **2b**, or direct methods, **4**, and data for **1b** and **2b** were corrected for absorption (semiempirical ψ scan). Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x,y,z,U_{iso})_H$ were constrained at estimated values for **1b** and **2b** (see below). Conventional residuals on [*F*] at convergence are quoted as *R* and $R'[(\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}]$.

Table VI. Summary of X-ray Diffraction Data for Compounds [M(t-Bu-C_5H_4)$_2$(THF)$_2$] (M = Ca (1b), M = Sr (2b)) and [Mg(t-Bu-C_5H_4)$_2$] (4)

	1b	2b	4
formula	$C_{26}H_{42}O_2Ca$	$C_{26}H_{42}O_2Sr$	$C_{18}H_{26}Mg$
mol wt	426.7	474.2	266.7
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	13.527 (4)	13.793 (3)	6.270 (4)
b, Å	10.057 (4)	10.308 (1)	11.213 (3)
c, Å	20.254 (7)	20.269 (5)	11.932 (7)
β, deg	106.24 (1)	107.66 (1)	96.53 (3)
V, Å^3	2645 (1)	2746 (1)	833.6 (8)
Z	4	4	2
D(calcd), g cm^{-3}	1.07	1.15	1.06
F(000)	936	1008	292
cryst dimens, mm	0.45 × 0.25 × 0.1	0.40 × 0.3 × 0.15	0.35 × 0.3 × 0.3
temp, °C	296	296	296
radiation	Mo Kα (0.71073 Å, graphite monochromator)		
μ, cm^{-1}	2.16	19.31	1.0
$A^*_{\text{min,max}}$	1.00, 1.043	1.00, 1.109	1.0
2θ limit, deg	50	50	50
no. of collected rflns	3918	3744	1786
no. of obsd rflns [$I > 2.5\sigma(I)$]	2432	2326	1102
R	0.061	0.061	0.087
R_w	0.053	0.053	0.097
s	1.56	2.13	1.11

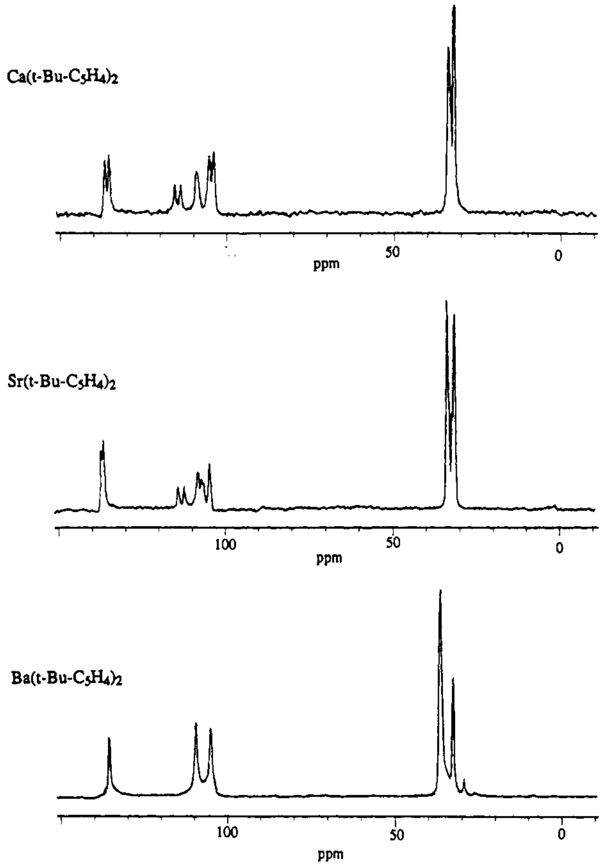

Figure 1. ^{13}C CP/MAS NMR spectra for the complexes, M(t-BuC_5H_4)$_2$, M = Ca, **1a**; M = Sr, **2a**; M = Ba, **3a**.

No extensive, significant extinction effects were found. Neutral-atom complex scattering factors corrected for anomolous dispersion were employed;[28] computation used the SHELXS-86 program system.[29] Crystal data, atom coordinates, and molecular

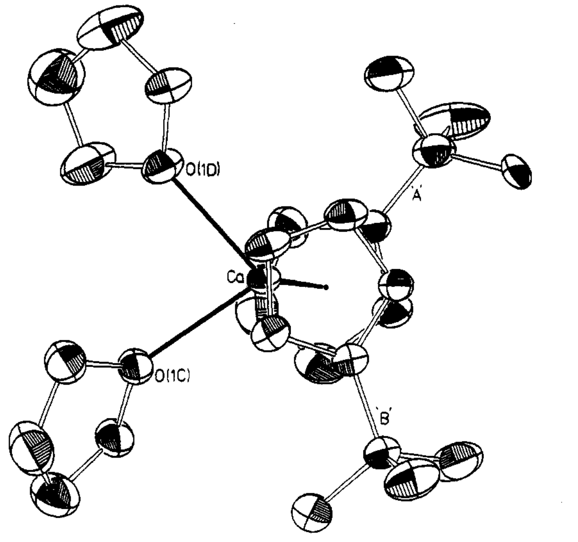

Figure 2. ORTEP drawing of a molecule of [Ca(t-BuC_5H_4)$_2$(THF)$_2$], **1a**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogens are omitted for clarity. Only one of the disordered *tert*-butyl groups of the cyclopentadienyl ring (B) is shown.

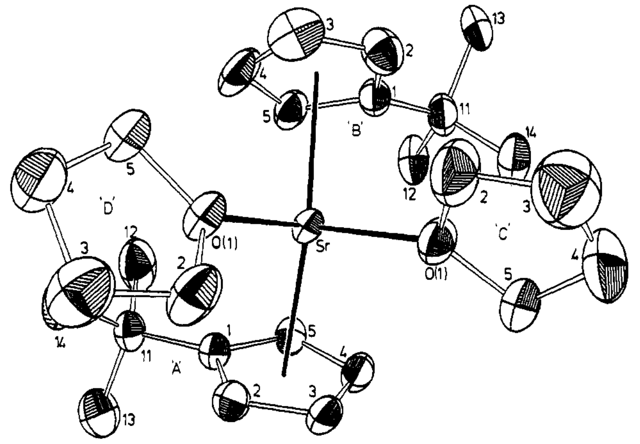

Figure 3. Perspective ORTEP drawing of a molecule of [Sr(t-BuC_5H_4)$_2$(THF)$_2$], **2a**, showing the labeling scheme for crystallographic purposes. Thermal ellipsoids are drawn at the 20% probability level. Hydrogens are omitted for clarity. Only one of the disordered *tert*-butyl groups of the cyclopentadienyl ring (B) is shown.

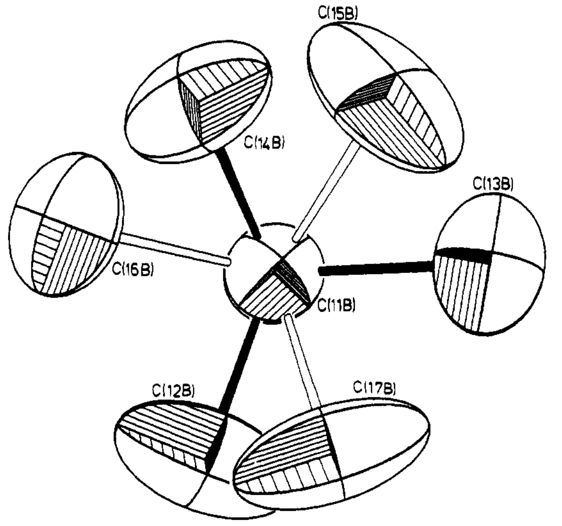

Figure 4. ORTEP drawing of the disorder in the *tert*-butyl group of the cyclopentadienyl ring (B) of [Sr(t-BuC_5H_4)$_2$(THF)$_2$], **2b**. Conformer 1 is shown with solid bonds, while conformer 2 is shown with hollow bonds.

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[28] *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: New York, 1974; Vol. 4.

[29] Sheldrick, G. M. *SHELXS-86, Program for Solution of Crystal Structures*; University of Göttingen: 1986.

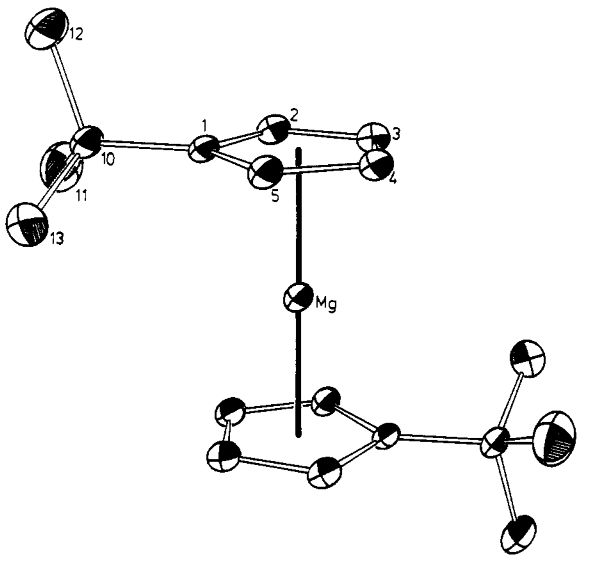
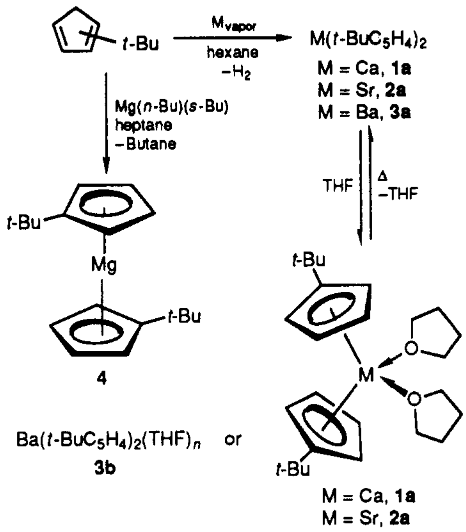


Figure 5. Projection of [Mg(t-BuC$_5$H$_4$)$_2$], **4**, showing the crystallographic labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogens are omitted for clarity.

Scheme I



core geometries are given in Tables I–VI, and molecular projections are in Figures 2–5.

For one of the *tert*-butyl substituents of the cyclopentadienyl rings in each of the structures, **1b** and **2b**, two conformations related by a rotation of 60° along the C1B–C11B vector were clearly visible from Fourier difference maps. These were refined anisotropically with site occupancies fixed at 50%. Average U_{ii}'s for each conformation were approximately equal, Figure 4. No other restrictions were used.

Many hydrogen atom positions were visible from Fourier difference maps in **1b** and **2b**, but all were calculated in idealized, sp^3 or sp^2, positions at a distance of 1.08 Å from the parent carbon atom and were restricted to "ride" along with their parent carbon atoms. No hydrogens were included for the disordered *tert*-butyl substituents. For **4**, H atoms were refined in (x,y,z,U_{iso}).

Discussion

Calcium, Strontium, and Barium Chemistry. Cocondensation of calcium, strontium, or barium vapors with freshly distilled *tert*-butylcyclopentadiene in hexane at −196 °C yielded black matrices that react upon warming to room temperature, affording the corresponding bis(cyclopentadienyl) compounds, M(t-BuC$_5$H$_4$)$_2$, M = Ca, **1a**; Sr, **2a**; Ba, **3a**, Scheme I. They were retrieved from the reaction vessel as straw-colored, pyrophoric, powders. Addition of THF to the initial mixture yields THF adducts that for calcium and strontium have been formulated on the basis of structure determinations (see below) as M(t-BuC$_5$H$_4$)$_2$(THF)$_2$, M = Ca, **1b**, Sr, **2b**. The barium compound failed to give crystals suitable for X-ray work, and microanalyses were unreliable so that the ratio of THF to metallocene entity has not been established.

High-temperature laser spectroscopic studies[30] of the gas-phase reaction of cyclopentadiene with calcium and strontium vapors have detected the cyclopentadienylcalcium and -strontium radicals, M(C$_5$H$_5$)$^\bullet$, M = Ca, Sr. Similar species may be formed as intermediates in the formation of compounds **1–3a** by using metal vapor synthesis.

Compounds **1–3a** have melting points > 300 °C, which is consistent with high ionic character/association, as are the high sublimation temperatures of 180, 260, and 320 °C (10^{-4} mmHg), respectively, and low solubility in hydrocarbon solvents (hexane, benzene, or toluene); the latter precluded recording the solution ^{1}H NMR spectra. Sublimates of **1a** and **2a** are clear, colorless, needle-shaped crystals, up to 2 mm long, unfortunately unsuitable for X-ray structure determinations; compound **3a** sublimes as a liquid, unlike its lighter homologues, and solidifies as a clear, colorless, glass-like solid. Although sublimation presents a viable means of purification of the compounds, they do so with some thermal decomposition, increasing in the order **1a** < **2a** ≪ **3a**. There is then no high yielding method of purification of the Lewis base free metallocenes, **1–3a**.

The THF adducts, **1b** and **2b**, have moderate solubility in THF, ca. 5 g L^{-1}, and can be purified by recrystallization from THF. Compound **1b** has minimal solubility in benzene, unlike the Lewis base free compound, whereas the strontium analogue, **2b**, is insoluble in benzene. The barocene THF adduct, **3b**, is insoluble in both THF and hydrocarbon solvents, which suggests it is oligomeric/ionic in the solid state; compounds **1b** and **2b** are monomeric in the solid state (see below). The THF adducts, **1–3b**, degrade when heated in vacuo at 180, 260, and 320 °C, respectively (10^{-4} mmHg), yielding sublimates of the THF-free compounds **1–3a**. For **2b** and **3b**, complete loss of THF is achieved by a single sublimation, but some of the THF remains with similar treatment of **1b**. The inequality in yield upon sublimation of the THF adducts matches that observed for the unsolvated metallocenes, that is, **1b** > **2b** ≫ **3b**.

Several groups have noted the trend in the ease with which the Lewis bases can be removed from the metallocene adducts of calcium, strontium, and barium, calcium ≪ strontium < barium,[6,9,11] which is also evident in the present study. Indeed, compound **3b** degrades in vacuo at 40 °C to the THF-free compound, cf. with ca. 180 °C for **1b**. The inequality is opposite to that expected if the preferred coordination number of the metal ion was the dominating effect, coordinatively saturated inorganic compounds of barium generally adopting a coordination number of up to 12,[31] considerably more than for calcium and strontium compounds. It appears that the overriding factor is the lower charge density of the larger metal ions results in weaker binding of the Lewis base.[9]

Sublimation temperatures seemingly offer a means of predicting the degree of association in unsolvated metallocenes. Large differences are observed in the sublimation

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(30) O'Brien, L. C.; Bernath, P. F. *J. Am. Chem. Soc.* **1986**, *108*, 5017.

(31) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: New York, 1984; p 574.

temperatures of the more substituted metallocenes relative to the lesser substituted complexes. For example, $Ca(C_5H_5)_2$, $Sr(C_5H_5)_2$, and $Ba(C_5H_5)_2$ sublime at 265, 360–440, and 420–460 °C (high vacuum)[4], respectively, and $Ca(C_5Me_5)_2$, $Sr(C_5Me_5)_2$, and $Ba(C_5Me_5)_2$ sublime at 75, 100–110, and 130–140 °C (10^{-3} mmHg),[4] respectively. The sublimation temperatures observed in this study for the *tert*-butyl-substituted metallocenes of these metals would place the degree of intermolecular association of the unsolvated complexes intermediate between the unsubstituted complexes and the permethylated complexes (which have been shown to exhibit minimal association), and possibly associated to a greater extent than the bis(trimethylsilyl)-substituted complexes, $M\{1,3\text{-}(SiMe_3)_2C_5H_3\}_2$, M = Ca, Sr, Ba, which sublime at ca. 180, 200, and 340 °C, at ca. 10^{-3} mmHg.[11]

Compounds **1**–**3** are all pyrophoric, which together with foregoing solubility problems made spectroscopic characterization difficult. Solution ^1H and ^{13}C NMR data were recorded for compounds **1b** and **2b** only. For the other compounds, ^{13}C CP/MAS NMR spectroscopy with TOSS pulse sequences was used. **3b** was excepted, which readily lost THF during sample preparation at ca. 40 °C in vacuo. Spectra obtained are shown in Figure 1. For **1a** and **2a** there are a number of resonances for each of the "different" carbon positions of the ligand: there are two signals for the C^1 position, and seven signals for the C^2 and C^3 positions resolvable by Gaussian multiplication of the FID's. This shows at least two types of ligands in the crystal lattice, such as found in the solid state of calcocene,[1] and the similarity of the two spectra suggests similar crystal structures for **1a** and **2a**. In contrast, the solid-state ^{13}C NMR spectrum of **3a** consists of single resonances for each of the different carbons of the ligands. This could be either a consequence of the ligand occupying a special position in the crystal lattice and/or more likely due to quadrupolar line broadening by ^{135}Ba and ^{137}Ba nuclei.

Magnesium Chemistry. Compound $[Mg(t\text{-}BuC_5H_4)_2]$, **4**, was prepared using the commercially available $Mg(n\text{-}Bu)(s\text{-}Bu)$, Scheme I, which has previously been used as an entry to both mono- and dicyclopentadienyl complexes of magnesium.[25] Compound **4** was isolated as clear, colorless, crystals in only modest yield owing to the very high solubility of the compound in hydrocarbons. Attempted crystallizations from hexane, benzene, THF, and Et_2O solutions yielded only oils. Solid samples were obtained by sublimation from these oils, which decompose to bright yellow oils on exposure to air. Interestingly, the isolobal compound $[Mg(Me_3SiC_5H_4)_2]$ is a liquid at room temperature.[32]

Compound **4** was characterized by using ^1H and ^{13}C NMR data derived from solution studies and is unexceptional. The ^{25}Mg NMR spectrum consists of a broad singlet at −88 ppm, with $\omega_{1/2}$ = 310 Hz. The resonance lies within the range found previously in a number of magnesocene complexes[24,25] and is well upfield of that of σ-bound dialkylmagnesium complexes.

Structural Studies. In the solid state, compounds **1b** and **2b** are isostructural and isomorphous, being composed of discrete, monomeric, molecules of $[M(t\text{-}BuC_5H_4)_2(THF)_2]$. These can be considered as bent metallocenes with two THF molecules wedged into vacant coordination sites of the metal centers, which are then in distorted, pseudotetrahedral environments, assuming the centroids of each cyclopentadienyl ligand occupy one coordination site, Figures 2 and 3.

Selected geometrical parameters are given in Table I. The Sr–C and Sr–O distances are both ca. 0.13 Å longer than the Ca–C and Ca–O distances, being consistent with the difference in ionic radii of the two metal ions (0.21 Å). The centroid–metal–centroid angles of 133.3 and 133.1°, respectively, compare with those of the solvated complexes, $[M\{1,3\text{-}(SiMe_3)_2C_5H_3\}_2(THF)]$, M = Ca, Sr[11] (135.1°, M = Ca; and 134°, M = Sr), and 134.8° in $[Ca(MeC_5H_4)_2(DME)]$.[13] These "bend" angles are much less than in the monomeric gas-phase structures of $[Ca(C_5Me_5)_2]$ and $[Sr(C_5Me_5)_2]$,[5] being 154 (3) and 149 (3)°, respectively, and the solid-state structure of $Ca(C_5Me_5)_2$, 147.7°, which has minimal intermolecular association.[9] In comparison, the polymeric crystal structure[1] of $Ca(C_5H_5)_2$ has bend angles ranging from 117.5 to 118.9°.

The metal–centroid distances are the largest observed so far for monomeric metallocene complexes of calcium and strontium, being, 2.462, 2.456 and 2.610, 2.599 Å, respectively. For example, the Ca–centroid distances in $[Ca(MeC_5H_4)_2(DME)]$ are marginally less than those in **1b**, 2.399 Å, and also the Ca–centroid and Sr–centroid distances of $[M\{1,3\text{-}(SiMe_3)_2C_5H_3\}_2(THF)]$, M = Ca, Sr, are 2.397 and 2.551 Å, respectively. The average Ca–centroid distance of 2.39 Å in the dimeric complex,[17] $[(C_5Me_5)Ca(\mu\text{-}I)(THF)_2]_2$, compares with these dicyclopentadienyl complexes, whereas the monomeric, unsolvated, gas-phase structures of $[Ca(C_5Me_5)_2]$ and $[Sr(C_5Me_5)_2]$ show considerably shorter metal–centroid distances, 2.312 (6) and 2.469 (6) Å. At the other extreme, the solid-state structure of $Ca(C_5H_5)_2$ has a mean Ca–centroid(η^5) distance of 2.54 Å, this being commensurate with the greater number of ligand contacts in this compound compared to the monomeric species. The two cyclopentadienyl rings in **1b** and **2b** adopt a conformation midway between an eclipsed and a staggered arrangement.

The average Ca–O and Sr–O bond lengths, 2.402 and 2.535 Å, of **1b** and **2b** are longer than the M–O distances in mono(THF) adducts, $[M\{1,3\text{-}(SiMe_3)_2C_5H_3\}_2(THF)]$, M = Ca, Sr, 2.310 (9) and 2.49 (3) Å, also in accordance with the greater solvation of the metal centers in the present structures. The angles subtended at the metal centers by the O atoms, 83.2 (2) and 83.1 (2)°, are larger than the O–Ca–O angle of $[Ca(MeC_5H_4)_2(DME)]$, being, 68.7°, as a consequence of the small bite angle of bidentate DME.

These structures are the first main group structures of the type $(cyclopentadienyl)_2(unidentate)_2metal$, although there is a calocene structure with a bidentate ligand, II,[13] and the structure of **2b** is only the second structure of a organostrontium complex, the other being I.[11] Many of the bis(cyclopentadienyl)lanthanide(II) and cationic-lanthanide(III) compounds exhibit bonding geometries, which correlate with the bent metallocenes of the group 2 metals of nearly the same ionic radii.[9] An example of this is the crystal structure of $Sm(C_5Me_5)_2$, which has an oligomeric bent metallocene structure with close contact between the metal center and a methyl carbon of an adjacent molecule,[33] as in the structure of $Ca(C_5Me_5)_2$.[9] In addition, the metal environment in $[\{CH_2(CH_2C_5H_4)\}_2Yb(THF)_2]$ is remarkably similar to that in **1a**.[34]

The solid-state structure of **4** shows discrete monomeric molecules with crystallographically imposed centrosymmetry. As a consequence, the centroid–Mg–centroid angle is 180°, and the cyclopentadienyl rings are parallel and in a staggered conformation with the *tert*-butyl groups in

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[32] Duff, A. W.; Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G.; Segal, J. A. *J. Organomet. Chem.* **1985**, *293*, 271.

[33] Evans, W. J.; Hughes, L. A.; Hanusa, T. P.; Deodens, R. J. *Organometallics* **1986**, *293*, 271.

[34] Swamy, S. J.; Loebel, J.; Schumann, H. *J. Organomet. Chem.* **1989**, *379*, 51.

trans positions, Figure 5. Such crystallographic conformational constraints are typical of many monosubstituted regular metallocene complexes, as in $[Mn(Me_3SiC_5H_4)_2]$,[35] which is both isostructural and isomorphous with 4.

Important geometrical parameters are given in Table II. The average Mg–C(ring) distance is 2.336 Å, corresponding to a Mg–centroid distance of 2.00 Å, which compares with the Mg–centroid and Mg–C(ring) distances of 2.011 (8), 2.008 (4) and 2.341 (6), 2.339 (4) Å, respectively, observed in the gas-phase structures of $[Mg(C_5Me_5)_2]$[7] and $[Mg(C_5H_5)_2]$,[23] but are significantly longer than the Mg–C(average) bond distances found in the crystal structure of $[Mg(C_5H_5)_2]$,[22] 1.96 and 2.304 Å, respectively. The heavily substituted complex, $[Mg\{\eta^5\text{-}1,2,4\text{-}(SiMe_3)_3C_5H_2\}_2]$,[25] has a longer average Mg–centroid distance of 2.03 Å. This complex also exhibits nonparallel cyclopentadienyl rings and considerable deviations of the trimethylsilyl substituents from the plane of the cyclopentadienyl rings, presumably a consequence of steric interactions between the ligands. The cyclopentadienyl compound, $[Mg\{\eta^5\text{-}1,2,4\text{-}(SiMe_3)_3C_5H_2\}Br(TMEDA)]$,[25] displays yet a larger average Mg–centroid distance of 2.167 Å, as does the analogous unsubstituted complex, $[Mg(\eta^5\text{-}C_5H_5)Br(TMEDA)]$, ca. 2.21 Å (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine).[36]

Acknowledgment. We gratefully acknowledge support of this work by the Australian Research Council.

Supplementary Material Available: Tables SUP1–SUP11, listing thermal parameters, ligand hydrogen parameters, metal core geometries, and ligand non-hydrogen geometries for **1b**, **2b**, and 4 (10 pages); tables of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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(35) Hebendanz, N.; Köhler, F. H.; Müller, G.; Riede, J. *J. Am. Chem. Soc.* **1986**, *108*, 3281.

(36) Johnson, C.; Toney, J.; Stucky, G. D. *J. Organomet. Chem.* **1972**, *40*, C11.

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^{59}Co NMR Study of Cluster Reactions: Solvent and Ligand Effects in Mixed-Metal, Tetrahedral MCo_3 (M = Fe, Ru) Carbonyl Clusters. Crystal Structure of $FeCo_3(\mu_3\text{-}H)(\mu\text{-}CO)_3(CO)_8(PPh_2H)$

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^{59}Co NMR spectroscopy is used to study the site selectivity of reactions between tetrahedral mixed-metal clusters $HMCo_3(CO)_{12}$ (M = Fe (**1a**), M = Ru (**1b**)) and various 2e donor ligands. In the monosubstituted clusters $HMCo_3(CO)_{11}L$ [M = Fe, L = PPh_2H (**2a**), PCy_2H (**4a**), PPh_3 (**5a**), NMe_3 (**6a**), SEt_2 (**7a**); M = Ru, L = PPh_2H (**2b**), PCy_2H (**4b**), PPh_3 (**5b**)] the ligand L is bound to a basal Co atom, generally giving rise to two ^{59}Co NMR resonances in a 2:1 ratio. The variation in chemical shift is examined throughout the series. The reaction of **2a** with a slight excess of Me_3NO in CH_2Cl_2 was monitored by ^{59}Co NMR spectroscopy and gave $HFeCo_3(CO)_{10}(NMe_3)(PPh_2H)$ (**8a**), in which each of the three chemically different Co atoms gives rise to a different resonance. This labile cluster transforms first to **2a** and then to the anion $[FeCo_3(CO)_{11}(PPh_2H)]^-$, owing to decoordination of the amine. Deprotonation of cluster **2a** also occurs in solvents like THF or acetone, which deprotonate the more acidic clusters **1a** or **1b** even more readily. Comparisons are made between disubstituted $FeCo_3$ clusters containing (P, P), (P, N), or (P, S) monodentate donor ligands, which illustrate the sensitivity of ^{59}Co NMR spectroscopy and its diagnostic value for the study of metallosite selectivity in cluster reactions. The structure of **2a** has been determined by X-ray diffraction: space group $P\bar{1}$ with a = 14.615 (5) Å, b = 17.087 (2) Å, c = 11.136 (3) Å, α = 99.20 (1)°, β = 105.94 (2)°, γ = 87.49 (2)°, and Z = 4. The structure was refined to R = 0.029 and R_w = 0.041 on the basis of 5764 reflections having $F_o^2 > 3\sigma(F_o^2)$. There are two independent, almost identical molecules in the asymmetric unit. The cluster has a tetrahedral structure and the phosphine is axially bonded to a basal cobalt atom. The triply bridging hydride ligand was found to be closer to the cobalt atom bearing the PPh_2H ligand.

Introduction

Reactivity studies on mixed-metal cluster compounds require appropriate monitoring and unambiguous identification of the reaction products. This usually involves the use of infrared (particularly for carbonyl clusters) and ^{1}H, ^{13}C, or ^{31}P NMR spectroscopy. Here, we wish to illustrate the potential of ^{59}Co NMR spectroscopy,[1] which has been little used in cluster chemistry.[2]

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(1) (a) Kidd, R. G.; Goodfellow, R. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978. (b) Laszlo, P. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2.

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