Dinuclear Barium Alkoxides and Siloxides Displaying Variable Coordination Numbers and Asymmetric Dispositions of Ligands

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The ammonia-catalyzed reaction of barium granules with Ph_3COH and with $^tBu_3SiOH$ in THF yields $Ba_2(OCPh_3)_4(THF)_3$ and $Ba_2(OSi^tBu_3)_4(THF)$, respectively. These were characterized by elemental analysis, ^1H and ^{13}NMR spectroscopy, and X-ray crystallography as having three bridging and one terminal OR groups. THF ligands occupy terminal sites. Any exchange of terminal and bridging OR ligands is slow on the NMR time scale at 25 °C in aromatic solvents. Crystallographic data: for $Ba_2(OCPh_3)_4(THF)_3\cdot$toluene (at −168 °C), a = 18.242 (5) Å, b = 17.337 (5) Å, c = 26.302 (7) Å, and β = 97.81 (1)° with Z = 4 in space group $P2_1/c$; for $Ba_2(OSi^tBu_3)_4(THF)$ (at −173 °C), a = 19.155 (3) Å, b = 25.489 (4) Å, and c = 13.125 (2) Å with Z = 4 in space group $P2_1nb$.

Introduction

Satisfying the preferred coordination number of a cation as large as Ba^{2+} (ionic radius = 1.35 Å) using monodentate ligands is challenging if polymerization is to be avoided. Thus, $Ba(C_5Me_5)_2$ is monomeric in the vapor phase only.[1,2] Solid $Ba[N(SiMe_3)_2]_2(THF)_2$ is monomeric, but stepwise removal of THF gives dimeric $Ba_2[N(SiMe_3)_2]_4(THF)_n$ where n = 2 and 0.[3] Aryl- and alkoxide ligands yield a variety of further aggregated species including $HBa_5O(OPh)_9(THF)_8$,[4] $H_3Ba_6O(O^tBu)_{11}(OCEt_2CH_2O)(THF)_3$,[4] $H_2Ba_8(O)_2(OPh)_{14}(HMPA)_6$,[5] and $Ba_6O(OC_2H_4OMe)_{10}(HOC_2H_4OMe)_4$.[6] The triphenylsiloxide ligand has been effective in permitting low coordination numbers (5 and 6) and giving monomeric compounds for trivalent yttrium, cerium, and lanthanum. For barium, however, this anion has yielded[7] the aggregate $Ba_3(OSiPh_3)_6(THF)$ with coordination numbers 4 and 5. We have therefore explored the efficacy of the related but larger monoanion Ph_3CO^-, as well as the still larger[8] $Bu^t_3SiO^-$ anion, in the preparation of barium alkoxides of low coordination number. We report here how this approach yields Ba_2^{4+}-containing species with variable coordination number and especially how the Coulomb repulsion of two divalent cations can be overcome by an unusual pattern of alkoxide apportionment.

Experimental Section

All manipulations were carried out under an atmosphere of dry (molecular sieves) argon, with rigorous exclusion of air and moisture. All hydrocarbon and ethereal solvents were dried and distilled from sodium benzophenone ketyl. NMR solvents were dried over 4-Å molecular sieves and stored under argon. Barium metal granules and triphenylcarbinol were purchased from Alfa Chemicals and Aldrich, respectively, and were stored in a drybox under an argon atmosphere; tri-*tert*-butylsilanol was obtained as a gift.[8] Elemental analyses were performed by Oneida Research Services. NMR data were recorded on a Bruker NM-500 NMR spectrometer, using the protio impurities of the deuterated solvents as reference for ^1H and the ^{13}C chemical shifts. Infrared spectra were recorded on a Nicolet 510P FTIR spectrometer, as Nujol mulls between KBr plates.

Table I. Crystallographic Data for $Ba_2(OCPh_3)_4(THF)_3\cdot$toluene$\cdot$THF

chem formula	$C_{88}H_{84}Ba_2O_7\cdot C_6H_5CH_3\cdot C_4H_8O$	space group	$P2_1/c$
		T, °C	−168
a, Å	18.242 (5)	λ, Å	0.710 69
b, Å	17.337 (5)	ρ_{calcd}, g cm^{-3}	1.364
c, Å	26.302 (7)	μ(Mo Kα), cm^{-1}	10.0
β, deg	97.81 (1)	R	0.0486
V, Å^3	8241.08	R_w	0.0480
Z	4		
fw	1692.55		

Synthesis of $Ba_2(\mu_2\text{-}OCPh_3)_3(OCPh_3)(THF)_3\cdot C_7H_8\cdot THF$ (I). Barium metal granules (1.37 g, 10 mmol), Ph_3COH (5.20 g, 20 mmol), and THF (20 mL) were stirred together for 10 min in a Schlenk tube until all the ligand has dissolved. Ammonia gas was bubbled into the reaction mixture for 5 min, during which time a rapid evolution of gas bubbles was observed, indicating that the barium metal was reacting. The solution was then stirred for 5 h, during which time all the metal was consumed to yield a murky brown solution. The solvent and excess ammonia were removed under vacuum to yield a white solid. This was subsequently redissolved in hot toluene (15 mL), and the mixture was filtered to yield a yellow-orange solution. The filtrate was layered with *n*-pentane (16 mL) and left at room temperature (21 °C) for 24 h, during which time a large crop of colorless crystals formed. Yield = 8.36 g (81% based on Ba). Mp: >250° dec. ^1H NMR (500 MHz, 25 °C, toluene-d_8): δ 1.42 (m, THF), 3.46 (m, THF), 6.88 (m, 2 H, Ph), 7.25 (m, 1 H, Ph), 7.46 (m, 2 H, Ph) (*not* altered on cooling to 230 K). ^{13}C NMR (126 MHz, 25 °C, toluene-d_8): δ 25.61 (s, THF), 67.69 (s, THF), 126.14 (s, Ph), 128.25 (s, Ph), 129.15 (s, Ph), 152.98 (s, Ph). Anal. Calcd for $Ba_2O_8C_{99}H_{100}$: C, 70.25; H, 5.96. Found: C, 69.97; H, 5.82.

Crystal Structure Determination of $Ba_2(OCPh_3)_4(THF)_3\cdot C_7H_8\cdot THF$. A crystal of suitable size was cleaved from a large piece of the sample in a nitrogen atmosphere glovebag. The crystal was mounted using silicone grease and was transferred to a goniostat, where it was cooled to −168 °C for characterization and data collection (Table I).[9] A systematic search of a limited hemisphere of reciprocal space revealed intensities with Laue symmetry and systematic absences consistent with space group $P2_1/c$, which was later confirmed by the successful solution of the structure.

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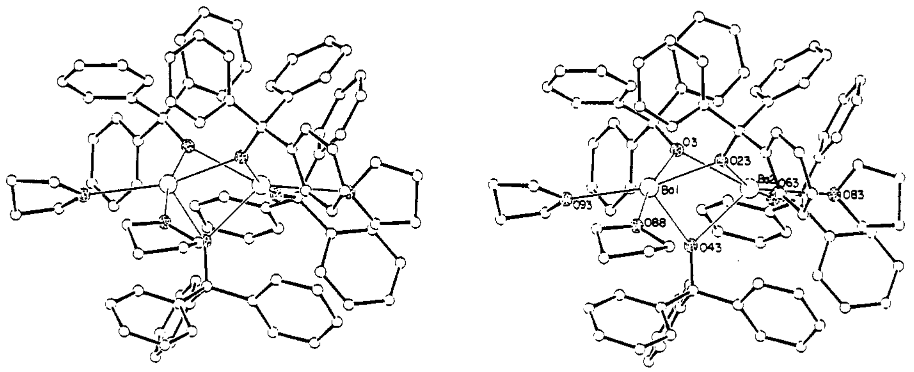

Figure 1. Stereo ORTEP drawing of $Ba_2(OCPh_3)_4(THF)_3$, showing selected atom labeling. Oxygen atoms are stippled.

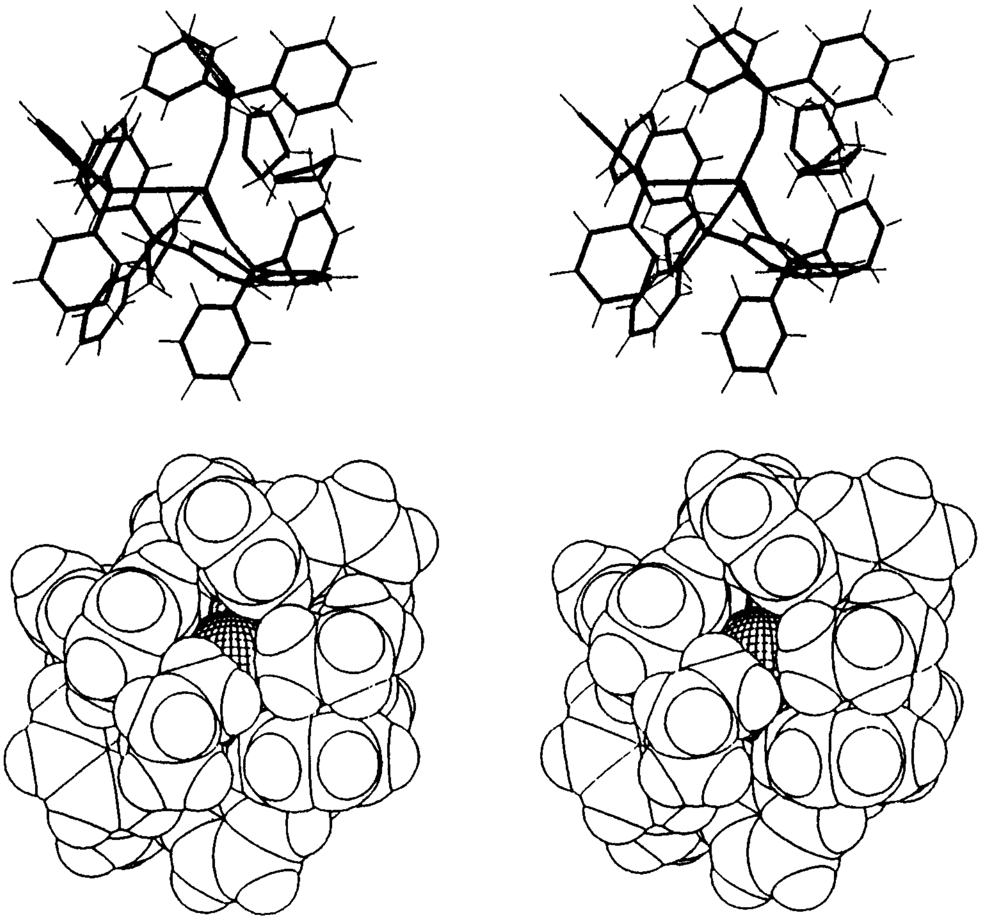

Figure 2. Stereo stick figure and space-filling drawing of $Ba_2(OCPh_3)_4(THF)_3$ viewed down the Ba/Ba direction, showing the blocking of Ba(1) (cross hatched) by two phenyl rings.

Following complete intensity data collection (6° < 2θ < 45°), data processing gave a residual of 0.038 for the averaging of 3169 unique intensities which had been measured more than once. Four standards measured every 400 data showed no significant trends. No correction was made for absorption.

The structure was solved by use of a combination of direct methods (MULTAN78) and Fourier techniques. The barium positions were determined from an initial *E* map, and coordinates of the remaining non-hydrogen atoms were obtained from subsequent iterations of least-squares refinement and difference Fourier calculation. In addition to the molecule of interest, the asymmetric unit contained a molecule of toluene and a molecule of THF, which had been used as solvents during the reaction and subsequent crystallization. Hydrogens were included in calculated positions but were not refined. Hydrogen atom thermal parameters were fixed at 1 Å^2 plus the isotropic thermal parameters. The final difference map was featureless. There were peaks of 0.7–1.5 e/Å^3 in the vicinity of the solvent molecules. All other residual peaks were less than 0.7 e/Å^3. The results of the refinement are shown in Tables II and III and Figures 1 and 2.

Synthesis of $Ba_2(\mu_2\text{-}OSiBu^t_3)_3(OSiBu^t_3)(THF)$ (II). Barium metal granules (0.188 g, 1.37 mmol), Bu^t_3SiOH (0.6 g, 2.76 mmol), and THF (20 mL) were stirred for 3 min in a Schlenk flask until all the ligand had dissolved. Ammonia gas was bubbled into the reaction mixture for 12 min, during which time a slow evolution of gas bubbles was observed, indicating that the barium metal was reacting. The solution was then stirred for 14 h at room temperature, during which time all the metal was consumed to yield a turbid pink solution. The solvent and excess ammonia were removed under vacuum to yield an oily solid. This was redissolved in THF (20 mL), and the solvent again was removed under vacuum to yield a white solid. This was subsequently redissolved in hot toluene (15 mL), and the mixture was filtered to yield a colorless solution. The filtrate was carefully layered with *n*-pentane (15 mL) and left at −20 °C for 2 days, during which time a crop of regularly-shaped crystals formed. Yield = 0.65 g (66% based on Ba). Mp: sublimes at 80 °C (1 Torr). ^{1}H NMR (500 MHz, 25 °C, benzene-d_6): δ 1.12 (s, Bu^t), 1.27 (s, Bu^t) (relative intensity 3:1), 1.57 (s, THF), 3.42 (s, THF). ^{13}C NMR (126 MHz, 25 °C, benzene-d_6): δ 22.74 (s, THF), 29.87 (s, Bu^t), 31.66 (s, Bu^t) (relative intensity 3:1), 67.52 (s, THF). Anal. Calcd for $Ba_2O_5Si_4C_{52}H_{116}$: C, 51.68; H, 9.67. Found: C, 52.58; H, 10.02.

Crystal Structure Determination of $Ba_2(OSi^tBu_3)_4(THF)$. A suitable

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for $Ba_2(OCPh_3)_4(THF)_3$·toluene·THF

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2		10^4x	10^4y	10^4z	$10^{B}{}_{iso}$, Å^2
Ba(1)	2496.5 (2)	2087.8 (2)	1545.7 (1)	17	C(56)	4308 (4)	1649 (4)	1356 (3)	28
Ba(2)	2254.6 (2)	751.5 (2)	2595.6 (2)	17	C(57)	4613 (4)	863 (4)	2394 (3)	25
O(3)	2266 (2)	2249 (2)	2497 (2)	18	C(58)	5348 (4)	833 (5)	2295 (3)	37
C(4)	2201 (3)	2955 (4)	2728 (2)	17	C(59)	5929 (5)	1027 (6)	2667 (3)	44
C(5)	1938 (4)	3563 (4)	2311 (2)	20	C(60)	5786 (4)	1247 (4)	3149 (3)	37
C(6)	1320 (4)	3378 (4)	1953 (3)	23	C(61)	5066 (4)	1239 (4)	3262 (3)	33
C(7)	1085 (4)	3860 (4)	1541 (3)	30	C(62)	4491 (4)	1051 (4)	2885 (3)	23
C(8)	1448 (4)	4549 (4)	1488 (3)	28	O(63)	2766 (2)	572 (3)	3481 (2)	20
C(9)	2050 (4)	4748 (4)	1838 (3)	23	C(64)	2903 (4)	308 (4)	3983 (3)	22
C(10)	2292 (4)	4257 (4)	2244 (2)	20	C(65)	3523 (4)	785 (4)	4294 (3)	22
C(11)	2947 (4)	3218 (4)	3036 (2)	20	C(66)	3654 (4)	1530 (4)	4151 (3)	27
C(12)	3593 (4)	2856 (4)	2958 (3)	22	C(67)	4210 (4)	1972 (4)	4423 (3)	30
C(13)	4278 (4)	3101 (5)	3208 (3)	33	C(68)	4669 (4)	1672 (4)	4840 (3)	28
C(14)	4316 (4)	3713 (4)	3543 (3)	31	C(69)	4541 (4)	922 (4)	4988 (3)	27
C(15)	3670 (5)	4075 (4)	3633 (3)	32	C(70)	3970 (4)	489 (4)	4720 (3)	25
C(16)	2993 (4)	3821 (4)	3385 (3)	25	C(71)	2176 (4)	369 (4)	4227 (3)	20
C(17)	1646 (3)	2899 (4)	3125 (2)	16	C(72)	2135 (4)	626 (4)	4722 (3)	25
C(18)	1070 (4)	3422 (4)	3159 (2)	20	C(73)	1462 (4)	664 (4)	4917 (3)	31
C(19)	613 (4)	3346 (4)	3533 (3)	23	C(74)	818 (4)	436 (4)	4617 (3)	33
C(20)	723 (4)	2760 (4)	3891 (3)	24	C(75)	850 (4)	167 (5)	4130 (3)	33
C(21)	1293 (4)	2235 (4)	3867 (2)	25	C(76)	1518 (4)	136 (4)	3937 (3)	26
C(22)	1743 (4)	2303 (4)	3487 (2)	18	C(77)	3156 (3)	−543 (4)	3983 (3)	18
O(23)	1459 (2)	1134 (2)	1626 (2)	18	C(78)	2896 (4)	−1118 (4)	4287 (3)	35
C(24)	709 (3)	1027 (4)	1456 (2)	17	C(79)	3139 (5)	−1878 (5)	4262 (4)	46
C(25)	273 (4)	954 (4)	1920 (3)	20	C(80)	3642 (4)	−2066 (4)	3945 (3)	37
C(26)	506 (4)	1387 (4)	2360 (2)	19	C(81)	3903 (4)	−1507 (4)	3643 (3)	31
C(27)	141 (4)	1359 (4)	2785 (3)	23	C(82)	3664 (4)	−756 (4)	3666 (3)	24
C(28)	−479 (4)	908 (4)	2782 (3)	30	O(83)	1606 (3)	−713 (3)	2665 (2)	32
C(29)	−729 (4)	486 (4)	2353 (3)	27	C(84)	846 (5)	−919 (5)	2542 (3)	40
C(30)	−359 (4)	504 (4)	1926 (3)	22	C(85)	752 (6)	−1698 (7)	2701 (6)	91
C(31)	586 (3)	296 (4)	1120 (2)	19	C(86)	1525 (6)	−2049 (6)	2762 (5)	64
C(32)	−52 (4)	170 (4)	772 (3)	22	C(87)	1993 (5)	−1378 (5)	2900 (4)	46
C(33)	−146 (4)	−482 (4)	463 (3)	25	O(88)	2538 (3)	1647 (3)	519 (2)	29
C(34)	399 (4)	−1029 (4)	503 (3)	24	C(89)	2423 (4)	869 (4)	318 (3)	32
C(35)	1023 (4)	−929 (4)	845 (3)	27	C(90)	2309 (5)	973 (5)	−262 (3)	37
C(36)	1119 (4)	−279 (4)	1156 (3)	23	C(91)	2776 (5)	1653 (5)	−341 (3)	39
C(37)	409 (4)	1726 (4)	1117 (2)	19	C(92)	2695 (4)	2163 (4)	113 (3)	31
C(38)	−231 (4)	2129 (4)	1184 (3)	26	O(93)	3373 (3)	3364 (3)	1420 (2)	27
C(39)	−478 (4)	2737 (4)	852 (3)	33	C(94)	3197 (4)	3878 (4)	981 (3)	29
C(40)	−87 (4)	2949 (4)	462 (3)	33	C(95)	3628 (4)	4603 (4)	1103 (3)	30
C(41)	551 (4)	2542 (4)	393 (3)	27	C(96)	4309 (4)	4307 (4)	1437 (3)	32
C(42)	783 (4)	1941 (4)	715 (3)	24	C(97)	3995 (4)	3713 (4)	1751 (3)	29
O(43)	3330 (2)	1090 (3)	2049 (2)	23	C(98)	3367 (5)	−4001 (5)	4334 (4)	47
C(44)	3962 (4)	663 (4)	1980 (3)	22	C(99)	3322 (5)	−3932 (5)	4856 (4)	50
C(45)	3776 (4)	−209 (4)	1992 (3)	24	C(100)	2672 (6)	−3821 (6)	5037 (4)	57
C(46)	3093 (4)	−452 (4)	1741 (3)	37	C(101)	2044 (5)	−3776 (6)	4672 (4)	54
C(47)	2883 (5)	−1213 (5)	1743 (4)	50	C(102)	2073 (5)	−3828 (5)	4151 (4)	48
C(48)	3346 (5)	−1762 (5)	1991 (4)	47	C(103)	2738 (5)	−3938 (5)	3980 (4)	43
C(49)	4018 (4)	−1536 (4)	2245 (3)	34	C(104)	2781 (5)	−3961 (6)	3405 (4)	54
C(50)	4233 (4)	−761 (4)	2252 (3)	28	O(105)	2415 (5)	6436 (7)	1205 (4)	117
C(51)	4180 (3)	874 (4)	1446 (3)	23	C(106)	2485 (8)	6484 (14)	685 (4)	156
C(52)	4278 (4)	352 (4)	1060 (3)	27	C(107)	1758 (8)	6493 (10)	426 (5)	96
C(53)	4487 (4)	601 (5)	603 (3)	33	C(108)	1223 (5)	6670 (6)	827 (4)	58
C(54)	4594 (4)	1376 (5)	517 (3)	30	C(109)	1738 (7)	6906 (7)	1254 (5)	68
C(55)	4508 (4)	1900 (4)	894 (3)	28					

[a] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

fragment was cleaved from a larger mass of the extremely air-sensitive crystals in a nitrogen-filled glovebag. The crystal was transferred to the goniostat, where it was cooled to −173 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited orthorhombic symmetry. The systematic extinctions of $hk0$ for $k = 2n + 1$ and of $h0l$ for $h + l = 2n + 1$ identified the possible space groups as *Pmnb* (alternate setting of No. 62) and $P2_1nb$ (alternate setting of No. 33). The structure was solved in the acentric space group $P2_1nb$. Characteristics of the data collection ($6° < 2\theta < 45°$) are shown in Table IV. The crystal chosen for data collection had a small fragment attached, and 50 reflections were rejected due to bad background counts. A plot of the four standard reflections monitored periodically during the data collection showed no systematic trends. No correction for absorption was carried out. The structure was solved with considerable difficulty. Direct methods (SHELXS-86) revealed the two Ba atoms as well as several of the O and Si atoms, i.e., enough to break the false symmetry we encountered in space group *Pmnb* when only the Ba atoms were located. The remaining non-hydrogen atoms were revealed in successive difference Fourier maps. There is evidence of disorder in the molecule. Only the disorder at C(60) was resolved. Only the Ba atoms were refined with anisotropic thermal parameters; all other atoms were refined isotropically. Attempts at refining Si and O atoms with anisotropic thermal parameters resulted in nonpositive definite thermal parameters. An attempt at determining the correct absolute structure for this noncentrosymmetric space group was inconclusive. The final difference map contained numerous peaks of 1 and 2 e/Å^3. The largest peaks were within 1 Å of the Si atoms, indicating some disorder. The unit cell did not appear to contain any voids where solvent of crystallization might be located. The results of the refinement are shown in Tables V and VI and Figure 3.

Results

Syntheses and Spectral Characterization. The rate of the heterogeneous reaction of barium metal with the alcohols in THF was significantly increased by adding a catalytic amount of

Table III. Selected Bond Distances (Å) and Angles (deg) for $Ba_2(OCPh_3)_4(THF)_3$

Ba(1)–O(3)	2.608 (4)	Ba(2)–O(3)	2.609 (4)
Ba(1)–O(23)	2.544 (4)	Ba(2)–O(23)	2.835 (4)
Ba(1)–O(43)	2.551 (5)	Ba(2)–O(43)	2.650 (5)
Ba(1)–O(88)	2.818 (5)	Ba(2)–O(63)	2.409 (4)
Ba(1)–O(93)	2.777 (5)	Ba(2)–O(83)	2.817 (5)
O(3)–Ba(1)–O(23)	76.76 (13)	Ba(1)–O(3)–Ba(2)	89.62 (13)
O(3)–Ba(1)–O(43)	74.73 (14)	Ba(1)–O(3)–C(4)	123.6 (4)
O(3)–Ba(1)–O(88)	167.84 (14)	Ba(2)–O(3)–C(4)	146.8 (4)
O(3)–Ba(1)–O(93)	101.50 (14)	Ba(1)–O(23)–Ba(2)	86.06 (12)
O(23)–Ba(1)–O(43)	85.04 (14)	Ba(1)–O(23)–C(24)	140.3 (4)
O(23)–Ba(1)–O(88)	91.21 (14)	Ba(2)–O(23)–C(24)	128.2 (4)
O(23)–Ba(1)–O(93)	167.23 (14)	Ba(1)–O(43)–Ba(2)	89.96 (14)
O(43)–Ba(1)–O(88)	102.83 (15)	Ba(1)–O(43)–C(44)	137.1 (4)
O(43)–Ba(1)–O(93)	106.86 (14)	Ba(2)–O(43)–C(44)	129.5 (4)
O(88)–Ba(1)–O(93)	90.62 (14)	Ba(2)–O(63)–C(64)	163.5 (4)
O(3)–Ba(2)–O(23)	71.83 (13)	Ba(2)–O(83)–C(84)	128.0 (4)
O(3)–Ba(2)–O(43)	73.07 (13)	Ba(2)–O(83)–C(87)	124.1 (4)
O(3)–Ba(2)–O(63)	102.54 (14)	C(84)–O(83)–C(87)	107.4 (6)
O(3)–Ba(2)–O(83)	155.81 (14)	Ba(1)–O(88)–C(89)	125.3 (4)
O(23)–Ba(2)–O(43)	77.69 (13)	Ba(1)–O(88)–C(92)	124.9 (4)
O(23)–Ba(2)–O(63)	169.49 (13)	C(89)–O(88)–C(92)	109.8 (5)
O(23)–Ba(2)–O(83)	95.78 (13)	Ba(1)–O(93)–C(94)	120.8 (4)
O(43)–Ba(2)–O(63)	109.60 (14)	Ba(1)–O(93)–C(97)	132.1 (4)
O(43)–Ba(2)–O(83)	125.67 (14)	C(94)–O(93)–C(97)	106.8 (5)

Table IV. Crystallographic Data for $Ba_2(OSi^tBu_3)_4(THF)$

chem formula	$C_{52}H_{116}Ba_2O_5Si_4$	space group	$P2_1nb$
a, Å	19.155 (3) Å	T, °C	−173 °C
b, Å	25.489 (4)	λ, Å	0.710 69
c, Å	13.125 (2)	ρ_{calcd}, g cm^{-3}	1.253
V, Å^3	6408.20	μ(Mo Kα), cm^{-1}	13.3
Z	4	R	0.1039
fw	1208.51	R_w	0.1096

ammonia. There was no reaction between barium granules and either Ph_3COH or $^tBu_3SiOH$, at reflux in THF for 3 days, even in the presence of I_2 or $HgCl_2$ catalysts. A high energy stepped ultrasonic probe was also without effect on the Ph_3COH/Ba reactants for 24 h at 25 °C. The ammonia acts to produce H_2 and some barium amide, which then undergoes proton transfer and anion metathesis to give the alkoxide and siloxide compounds. The products are toluene-soluble colorless solids. Addition of pentane to such toluene solutions causes THF solvates to crystallize.

The ^1H NMR spectra of these products establish the presence of THF. Compound I, from triphenylcarbinol, shows proton peaks for only a single type of aryl ring down to 230 K, and the ^{13}C NMR spectrum also shows only one aryl environment. Compound II, from tri-*tert*-butylsilanol, shows two types of siloxide protons (intensity 1:3) and two types of methyl carbons (intensity ~1:3) at 25 °C in toluene-d_8, suggesting possible bridging and terminal structural units.

The identities and structures of I and II were established by X-ray structural studies.

X-ray Diffraction Study of $Ba_2(OCPh_3)_4(THF)_3$. $Ba_2(OCPh_3)_4(THF)_3$ (I) crystallizes with one molecule each of toluene and THF filling holes in the solid lattice. It adopts a structure with three bridging alkoxides (Figure 1). While both metals are five-coordinate, the inequivalence of the terminal ligands gives the two metals distinct environments. Ba(1) has two terminal THF ligands, while Ba(2) has one THF and one terminal Ph_3CO^- ligand, since the fourth THF molecule in the unit cell shows no tendency to interact with barium.

The structure adopted by the M_2X_7 unit resembles that of an M_2X_9 face-shared bioctahedron with two terminal ligands removed. This leaves each metal with a square-pyramidal coordination geometry. The two square pyramids share a triangular face defined by (Figure 1) a basal edge (O(3) and O(23)) and the apex (O(43)). The space below the square base of each pyramid is blocked by two phenyl rings from two different bridging ligands (Figure 2), but there are no contacts from barium to either C or H that qualify as even weak bonds (Ba/C are longer than 3.35 Å and Ba/H longer than 2.94 Å). Distances from Ba to O(THF) span a narrow range (2.77 (5)–2.818 (5) Å, and the THF oxygens are coplanar with their three attached groups (the sum of angles around oxygen is within 0.5° of 360°).

Table V. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $Ba_2(OSi^tBu_3)_4(THF)$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Ba(1)	6420*	2183 (1)	5272 (1)	53
Ba(2)	6435 (3)	805.5 (4)	5069 (1)	29
O(3)	6362 (13)	1504 (6)	3716 (10)	25 (3)
Si(4)	6652 (5)	1501 (3)	2501 (6)	28 (2)
C(5)	5922 (18)	1110 (13)	1902 (24)	35 (6)
C(6)	6020 (21)	929 (15)	726 (30)	56 (9)
C(7)	5257 (23)	1363 (17)	1880 (34)	57 (9)
C(8)	5372 (18)	612 (13)	2410 (25)	37 (6)
C(9)	7592 (25)	1170 (18)	2227 (35)	64 (10)
C(10)	7069 (21)	554 (15)	2558 (28)	47 (8)
C(11)	8161 (31)	1436 (20)	3028 (42)	91 (14)
C(12)	7887 (24)	1263 (17)	1145 (34)	64 (10)
C(13)	6166 (15)	2230 (11)	2022 (21)	29 (6)
C(14)	6193 (18)	2271 (13)	843 (25)	45 (8)
C(15)	5523 (19)	2514 (14)	2382 (27)	46 (8)
C(16)	6708 (20)	2555 (15)	2488 (29)	57 (9)
O(17)	5695 (13)	1454 (9)	5943 (19)	40 (5)
Si(18)	4920 (6)	1467 (4)	6363 (8)	32 (2)
C(19)	4386 (20)	1622 (14)	5219 (27)	47 (7)
C(20)	3677 (22)	1806 (16)	5422 (32)	48 (9)
C(21)	4721 (23)	2024 (16)	4540 (30)	59 (9)
C(22)	4296 (21)	1134 (14)	4498 (28)	51 (8)
C(23)	4371 (18)	687 (12)	6447 (22)	32 (6)
C(24)	3773 (36)	597 (27)	6997 (55)	92 (16)
C(25)	4286 (18)	498 (12)	5306 (23)	36 (6)
C(26)	4922 (21)	274 (14)	6928 (28)	47 (8)
C(27)	5093 (23)	1534 (16)	7854 (31)	59 (9)
C(28)	5372 (37)	2151 (27)	7972 (56)	111 (17)
C(29)	5728 (28)	1164 (21)	8058 (38)	81 (12)
C(30)	4508 (28)	1392 (19)	8719 (37)	78 (12)
O(31)	7426 (12)	1416 (8)	5796 (16)	30 (5)
Si(32)	8101 (6)	1373 (4)	6505 (8)	30 (2)
C(33)	8011 (18)	2039 (13)	7512 (25)	39 (7)
C(34)	7416 (16)	2007 (12)	8087 (22)	22 (5)
C(35)	7990 (17)	2570 (12)	6929 (22)	34 (6)
C(36)	8673 (20)	1947 (14)	8075 (26)	45 (7)
C(37)	8186 (20)	806 (14)	6974 (28)	47 (7)
C(38)	7802 (17)	347 (12)	6320 (24)	33 (6)
C(39)	7790 (21)	726 (14)	8093 (27)	49 (8)
C(40)	9125 (21)	668 (17)	6914 (35)	42 (9)
C(41)	8902 (29)	1884 (20)	6070 (42)	82 (12)
C(42)	9362 (27)	1691 (21)	5230 (38)	67 (12)
C(43)	8426 (23)	2386 (17)	5601 (32)	63 (10)
C(44)	9432 (25)	2066 (18)	7005 (34)	70 (10)
O(45)	6419 (18)	−257 (6)	4685 (12)	38 (3)
C(46)	5840 (33)	−461 (24)	4310 (48)	91 (15)
C(47)	6101 (22)	−1110 (17)	4192 (33)	47 (10)
C(48)	6865 (20)	−1039 (15)	3951 (29)	39 (8)
C(49)	7093 (15)	−576 (11)	4513 (21)	17 (5)
O(50)	6329 (13)	3115 (6)	5570 (12)	33 (4)
Si(51)	6324 (6)	3734 (2)	5690 (5)	22 (1)
C(52)	5620 (29)	3997 (23)	4925 (42)	66 (13)
C(53)	5507 (39)	3733 (30)	4060 (58)	121 (18)
C(54)	5673 (22)	4623 (15)	5001 (31)	47 (8)
C(55)	5086 (32)	3884 (23)	5902 (44)	89 (15)
C(56)	6716 (14)	3894 (11)	7134 (20)	27 (6)
C(57)	6277 (14)	3515 (9)	7788 (17)	21 (5)
C(58)	6525 (19)	4473 (9)	7433 (17)	28 (5)
C(59)	7494 (20)	3773 (15)	7417 (28)	50 (8)
C(60)	7247 (17)	4034 (13)	5136 (24)	23 (6)
C(61)	7515 (18)	4591 (13)	5109 (26)	34 (7)
C(62)	7926 (20)	3687 (14)	4976 (29)	23 (7)
C(63)	7116 (20)	4035 (14)	3718 (26)	17 (7)
C(64)	7796 (41)	3897 (28)	6189 (57)	5 (13)
C(65)	7419 (37)	3694 (26)	4322 (50)	0 (11)

[a] Parameters marked by an asterisk were not varied. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

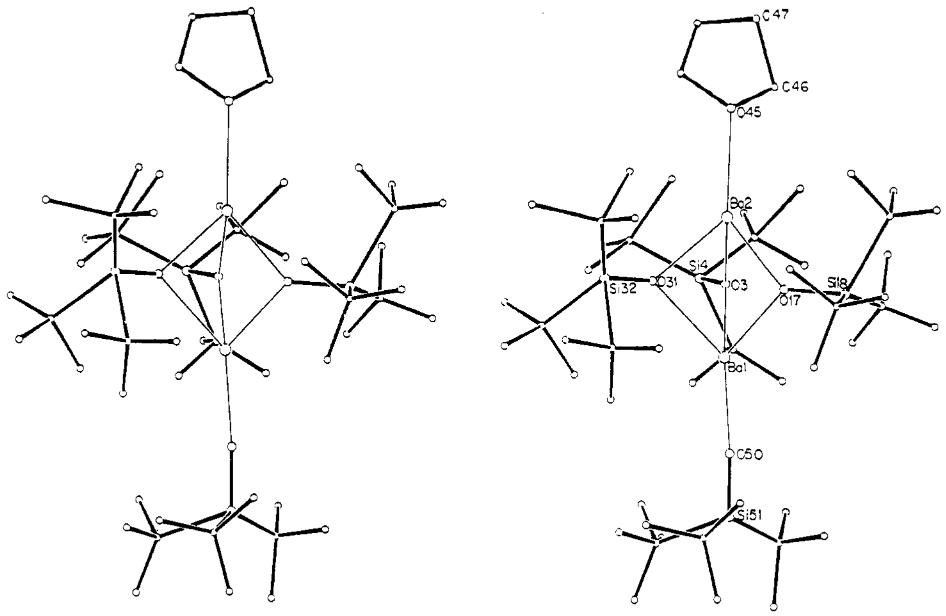

Figure 3. Stereo ORTEP drawing of $\mathrm{Ba_2(OSi^tBu_3)_4(THF)}$, showing selected atom labeling.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $\mathrm{Ba_2(OSi^tBu_3)_4(THF)}$

Ba(1)–O(3)	2.680 (14)	Ba(2)–O(31)	2.633 (21)
Ba(1)–O(17)	2.482 (25)	Ba(2)–O(45)	2.754 (16)
Ba(1)–O(31)	2.832 (21)	Si(4)–O(3)	1.689 (17)
Ba(1)–O(50)	2.413 (16)	Si(18)–O(17)	1.585 (27)
Ba(2)–O(3)	2.518 (14)	Si(32)–O(31)	1.597 (23)
Ba(2)–O(17)	2.461 (24)	Si(51)–O(50)	1.586 (17)
O(3)–Ba(1)–O(17)	76.3 (7)	O(31)–Ba(2)–O(45)	130.9 (8)
O(3)–Ba(1)–O(31)	76.5 (6)	Ba(1)–O(3)–Ba(2)	85.3 (4)
O(3)–Ba(1)–O(50)	139.2 (5)	Ba(1)–O(3)–Si(4)	135.1 (9)
O(17)–Ba(1)–O(31)	77.1 (6)	Ba(2)–O(3)–Si(4)	130.1 (9)
O(17)–Ba(1)–O(50)	129.8 (8)	Ba(1)–O(17)–Ba(2)	90.9 (8)
O(3)–Ba(2)–O(17)	79.8 (7)	Ba(1)–O(17)–Si(18)	129.2 (13)
O(3)–Ba(2)–O(31)	83.0 (7)	Ba(2)–O(17)–Si(18)	135.7 (14)
O(3)–Ba(2)–O(45)	124.4 (5)	Ba(2)–O(31)–Si(32)	139.0 (12)
O(17)–Ba(2)–O(31)	81.3 (7)	C(46)–O(45)–C(49)	116.1 (28)
O(17)–Ba(2)–O(45)	137.7 (9)	Ba(1)–O(50)–Si(51)	174.7 (12)

In contrast, there is pyramidal coordination to two of the bridging alkoxide oxygens (angles at O(23) and O(43) sum to 354.6 and 356.6°, respectively); the third is rigorously planar.

The terminal alkoxide is nearly linear at oxygen (∠Ba–O(63)–C(64) = 163.5 (4)°), and this Ba–O(63) distance is the shortest in the molecule, at 2.409 (4) Å. The Ba–(μ-O) distances fall in the narrow range 2.544 (4)–2.650 (5) Å except for Ba(2)–O(23), the group trans to the terminal alkoxide, which is very long (2.835 (4) Å).

Because the apical and two basal groups in the square pyramids are bridging groups, there are some angular distortions of this polyhedron. Apical-to-basal angles range from 73 to 126° and cis basal-to-basal angles are from 72 to 103°. The open character below the basal plane is clearly indicated by the trans basal-to-basal angles, which range from 156 to 169°.

X-ray Diffraction Study of $\mathrm{Ba_2(OSi^tBu_3)_4(THF)}$. A single-crystal X-ray diffraction study revealed that the molecule has the structure $\mathrm{(^tBu_3SiO)Ba(\mu\text{-}OSi^tBu_3)_3Ba(THF)}$, with each barium four-coordinate. The structure shows some disorder in the *tert*-butyl groups. This particular siloxide has been reported previously to be prone to such disorder.[10] However, the overall molecular structure has been established unambiguously from the X-ray study.

The inner coordination sphere of the molecule has idealized C_{3v} symmetry. All Ba–O(Si) and Ba–O(THF) distances are comparable to those in compound I. The distorted tetrahedral barium centers have compressed angles involving bridging oxygens (76.3 (7)–83.0 (7)°), and expanded angles from bridge to terminal oxygens (124.4 (5)–137.7 (9)°). The terminal siloxide is nearly linear at oxygen (174.7 (12)°).

Discussion

The closest analog of I and II among alkoxides of divalent metals is $\mathrm{Co_2(OCPh_3)_4}$.[11] This adopts the symmetric structure $\mathrm{(Ph_3CO)Co(\mu\text{-}OCPh_3)_2Co(OCPh_3)}$. When THF coordinates to the closely related species $\mathrm{Co_2(\mu\text{-}OSiPh_3)_2(OSiPh_3)_2}$, the structure remains symmetric, $\mathrm{(Ph_3SiO)(THF)Co(\mu\text{-}OSiPh_3)_2Co(THF)(OSiPh_3)}$, with two bridging siloxides. In fact, the many electron diffraction structural studies of MX_2 species throughout the periodic table give no evidence for dimers with an $\mathrm{XM(\mu\text{-}X)_3M}$ structure.[12,13] The question that remains is why, then, the $\mathrm{Ba_2(OR)_4(THF)}_n$ species adopt the asymmetric structure with one terminal and three bridging alkoxides. We suggest that the controlling factor is neither the asymmetry itself nor the retention of (one) terminal alkoxide, but instead the presence of three bridging alkoxides. When two divalent ions are to be held together in a dimetal-containing molecule, the Coulomb repulsion is dramatically larger than when monocations are involved. It is thus effective to shield this repulsion and to develop an attractive force toward the M_2 midpoint, by having three rather than two bridging anions. An alternative explanation, proposed by a reviewer, is that a third bridging alkoxide may efficiently increase the coordination number of barium with minimum intramolecular repulsion. This explains why the $\mathrm{M_2(\mu\text{-}OR)_3}$ structure is adopted for barium (ionic radius 1.35 Å) but not for cobalt (ionic radius 0.745 Å).

Since the siloxide is established to be stereochemically rigid with regard to site exchange of $\mathrm{OSi^tBu_3}$ groups, this means that the double-bridged structure A, an attractive site-exchange intermediate, must lie at least 10–15 kcal/mol above the observed structure.

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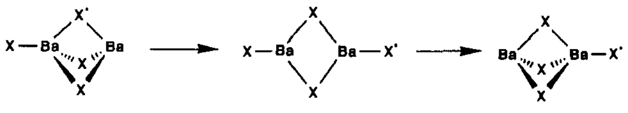
(10) LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6382.

(11) Sigel, G. A.; Bartlett, R. A.; Decker, D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 1773.

(12) Hargittai, M. In *Stereochemical Applications of Gas-Phase Electron Diffraction*; Hargittai, I., Hargittai, M., Eds.; VCH: New York, 1988; Part B, p 383.

(13) A number of compounds have been shown to adopt the $\mathrm{Sn^{II}(\mu\text{-}X)_3M'}$ core structure. This core structure is most appropriate to the general tendency of an $\mathrm{SnX_3^-}$ unit to have a trigonal pyramidal structure with a stereochemically-active lone pair. See: Veith, M.; Rösler, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *21*, 858. Smith, G. D.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1989**, *28*, 618.



A

Finally, it is worth noting that the recently reported[7] structure of Ba$_3$(μ_3-OSiPh$_3$)$_2$(μ-OSiPh$_3$)$_3$(OSiPh$_3$)(THF) may be viewed as the sum of II + Ba(OSiR$_3$)$_2$, wherein two of the μ_2-OSiR$_3$ ligands become μ_3-OSiR$_3$ ligands and the Ba(OSiR$_3$)$_2$ fragments provide two of the three μ-OSiR$_3$ ligands that span the Ba$_3$ triangle.

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Supplementary Material Available: For Ba$_2$(OCPh$_3$)$_4$(THF)$_3$ and Ba$_2$(OSi^{t}Bu$_3$)$_4$(THF), tables of crystallographic details and anisotropic thermal parameters (6 pages); listings of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.