

though diamagnetic due to coupling between paramagnetic ligands and the $S = 3/2$ metal ion, shows only broad resonances for ligand *tert*-butyl groups, and Pd(DBSQ)₂ shows a similar NMR spectrum due to coupling between the paramagnetic ligands through the diamagnetic metal.²³ Further, the symmetrical equivalence of the quinone ligands in the structure of Ru(*t*-Bupy)₂(DBQ)₂ with the spherical shape of the thermal ellipsoids of ligand oxygens is inconsistent with a disordered mixed-charge ligand Ru(III) formulation. Cobalt and iron analogues, M(N-N)(DBSQ)-(DBCat) (M = Co, Fe), have been reported with this charge distribution.^{24,25} The Ru^{IV}(Cat)₂ option is consistent with the magnetic property of the complex and is in accord with the tendency for catecholate ligands to stabilize metals in high oxidation states, but the ligand C-O lengths are 0.02 Å shorter than the catecholate value. We conclude from this that there is no good

localized charge formulation for the complex and that the electronic structure of the complex is best described in terms of a delocalized model similar to the 1,2-dithiolene complexes.²⁶ In other studies structural results usually coupled with spectral and magnetic properties have led to localized charge assignments for quinone and metal. This appears to represent the first situation where charge delocalization has been observed for quinone ligands.

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Supplementary Material Available: Tables containing anisotropic thermal parameters and bond distances and angles for [Ru(bpy)₂(DBSQ)](ClO₄) and Ru(*t*-Bupy)₂(DBQ)₂ (6 pages); tables of structure factors for both compounds (28 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectroscopic and X-ray Structural Characterization and Dynamic Solution Behavior of the Neutral Cobalt(II) Alkoxides

[Co{OC(C₆H₁₁)₃}]₂·CH₃OH·¹/₂C₆H₁₂·THF, [Co(OCPh₃)₂]₂·*n*-C₆H₁₄,
 [Co(OSiPh₃)₂(THF)]₂, and Co(OCPh₃)₂(THF)₂

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Reaction of the metal amide [Co{N(SiMe₃)₂}]₂ with the appropriate alcohol or silanol affords several examples of previously undescribed neutral cobalt alkoxides in moderate yields. These are the complexes [Co{OC(C₆H₁₁)₃}]₂·CH₃OH·¹/₂C₆H₁₂·THF (**1**), [Co(OCPh₃)₂]₂·*n*-C₆H₁₄ (**2**), [Co(OSiPh₃)₂(THF)]₂ (**3**), Co(OCPh₃)₂(THF)₂ (**4**), and Co{OC(4-MeC₆H₄)₃}]₂ (5). Compounds 1-4, which have been structurally characterized, are the first authenticated neutral cobalt(II) alkoxides. The structures of compounds 1 and 2 are dimeric with the cobalts bound to two bridging alkoxides and one terminal alkoxide ligand. Each cobalt has trigonal-planar geometry in addition to a central nonplanar Co₂O₄ core. The Co...Co distances (ca. 2.9 Å) are considerably longer than those found in similar amide complexes. In the binuclear complex 3 and the monomeric 4, cobalt has a severely distorted tetrahedral geometry. Other interesting features include the formation of CH₃OH and C₆H₁₂ in the preparation of 1 and the fluxional behavior of complexes 2, 4, and 5 in solution. A range of physical properties, including ¹H NMR, electronic, and IR spectra are also reported. A variable-temperature ¹H NMR study of 2 or its 4-methyl-substituted analogue [Co{OC(4-MeC₆H₄)₃}]₂ (**6**) (derived from 5) showed that the signals due to the bridging and terminal ligands coalesced upon heating in C₇D₈ solution. Energy barriers of 57-58 kJ mol⁻¹ were estimated on the basis of coalescence temperatures and spectral parameters. Crystallographic data with Mo Kα radiation (λ = 0.71069 Å) at 130 K: **1**, *a* = 13.359 (4) Å, *b* = 14.589 (5) Å, *c* = 23.054 (9) Å, α = 72.73 (3)°, β = 77.14 (3)°, γ = 64.86 (3)°, *Z* = 2, triclinic, space group P $\bar{1}$; **2**, *a* = 11.787 (4) Å, *b* = 13.336 (4) Å, *c* = 20.107 (5) Å, α = 81.50 (2)°, β = 80.07 (3)°, γ = 89.40 (3)°, *Z* = 2, triclinic, space group P1; **3**, *a* = 14.203 (2) Å, *b* = 22.060 (5) Å, *c* = 22.269 (3) Å, β = 92.71 (1)°, *Z* = 4, monoclinic, space group P2₁/*n*; **4**, *a* = 18.994 (9) Å, *b* = 9.600 (9) Å, *c* = 23.421 (11) Å, β = 119.66 (3)°, *Z* = 4, monoclinic, space group C2/*c*. For **1**, *R* = 0.076, for **2**, *R* = 0.072, for **3**, *R* = 0.056, and for **4**, *R* = 0.054.

Introduction

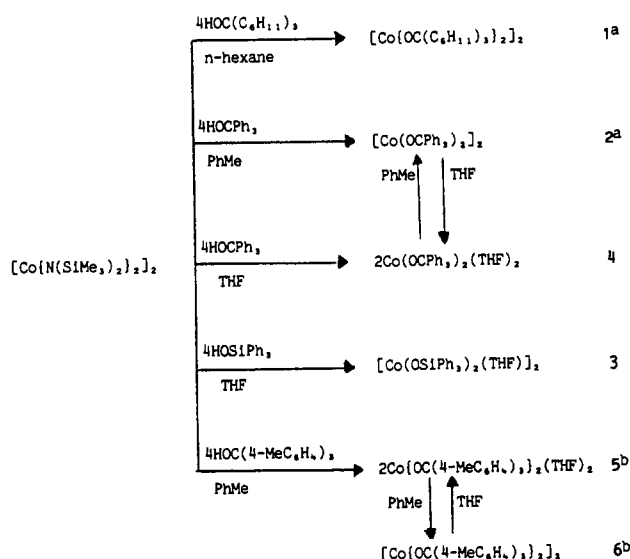
As part of our continuing study of low-coordinate transition-metal complexes, we recently reported the synthesis and structural characterization of the lithium salts of monomeric three-coordinate ionic cobalt(II) alkoxide/amide complexes. These are the species [Co(Cl)(OC-*t*-Bu)₃Li(THF)]₃, [Li(THF)₄][Co{N(SiMe₃)₂}(OC-*t*-Bu)₃]₂, and Li{Co{N(SiMe₃)₂}(OC-*t*-Bu)₃}]₂.¹ These compounds were the first structurally characterized cobalt alkoxides, and they all possess the rare trigonal-planar geometry at the cobalt center.^{1,2} Other features include agostic interactions between ligand CH₃'s and Co or Li, as well as the involvement of Cl⁻ as a bridging ligand between Li⁺ and Co(II).¹ Since the use of lithium alkoxides as ligand-transfer agents invariably gave

products that included either halide or lithium halide as part of the coordination sphere of an ionic complex, we decided to synthesize neutral cobalt alkoxides by the alcoholysis of a cobalt amide. With the very crowded alcohol HOC-*t*-Bu₃, although exchange occurred with [Co{N(SiMe₃)₂}]₂, we have not yet been able to isolate crystals of product suitable for X-ray study. However, with HOC(C₆H₁₁)₃, HOCPh₃, HOC(4-MeC₆H₄)₃, and HOSiPh₃ the products illustrated in Scheme I can be readily isolated and crystallized.

Experimental Section

General Procedures. All reactions were performed by using modified Schlenk techniques under an inert atmosphere of N₂. Solvents were freshly distilled from drying agents and degassed twice before use. Solutions containing the [Co{OC(C₆H₁₁)₃}]₂ complex were the most air-sensitive. The compounds HOC(C₆H₁₁)₃, HOCPh₃, HOC(4-MeC₆H₄)₃, and HOSiPh₃ were purchased from Aldrich or Alfa and used as received; [Co{N(SiMe₃)₂}]₂ was synthesized by a literature procedure.³ Products

- (1) Olmstead, M. M.; Power, P. P.; Sigel, G. *Inorg. Chem.* **1986**, *25*, 1027.
 (2) Bradley, D. C.; Hursthouse, M. B.; Newing, C. W.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 872.

Scheme I. Summary of the Products Arising from the Alcoholysis of $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2]$ 

^a Crystalline species have solvent and other molecules in their lattices. ^b Studied as a solution species only.

1–5 gave satisfactory C and H elemental analyses.

Physical Methods. Electronic spectra were obtained on a Hewlett-Packard 8450A UV/vis spectrometer. Infrared spectra were recorded on an IBM IR/32 spectrometer. ¹H NMR spectra were obtained on a Nicolet 360-MHz FT NMR spectrometer. Isotropic shifts are reported in parts per million (ppm) where $(\Delta H/H_0)_{\text{iso}} = (\Delta H/H_0)_{\text{obsd}} - (\Delta H/H_0)_{\text{dia}}$.

[Co{OC(C₆H₁₁)₃}₂]₂·CH₃OH·¹/₂C₆H₁₂·THF (1). Addition of cold (ca. 0 °C) *n*-hexane (40 mL) to $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (0.68 g, 1.79 mmol) and $\text{HOC}(\text{C}_6\text{H}_{11})_3$ (1.01 g, 3.6 mmol) gave a green solution. After the mixture was stirred overnight at room temperature, a blue-green precipitate was obtained. The solvent was removed under reduced pressure to 25% of the original volume, and THF (30 mL) was added. Gradual heating to 40–50 °C to dissolve the precipitate, followed by slow cooling to –20 °C over 48 h, gave the product 1 as green plates. Filtration gave 0.31 g of 1: 28% yield; mp 210–212 °C; electronic spectrum (nm (ε), in toluene) 648 (248), 582 (101), 424 (164); IR (cm⁻¹) ν(C–O) 1074, 1023 (bridging).

[Co{OCPh₃}₂]₂·*n*-C₆H₁₄ (2). Addition of toluene (100 mL) to $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (1.911 g, 5.02 mmol) and HOCPh_3 (2.61 g, 10.1 mmol) at 0 °C gave an immediate reaction, the mixture initially turning purple and later green. After the mixture was stirred overnight at room temperature, the volume was reduced 50% under reduced pressure and hexane (25 mL) was added. Slow cooling over 20 h to 0 °C gave green crystals suitable for X-ray analysis. Filtration gave 2 (1.25 g): 43% yield; mp 267 °C dec; electronic spectrum (nm (ε)) 670 (174), 616 (151), 420 (69); IR (cm⁻¹) ν(C–O) 1047, 1028, 979 (bridging).

[Co{OSiPh₃}₂(THF)]₂ (3). Addition of THF (50 mL) to $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (1.7 g, 4.5 mmol) and HOSiPh_3 (2.5 g, 9.1 mmol) at 0 °C gave a purple solution that upon overnight stirring yielded a purple precipitate. Solvent was removed under reduced pressure to 50% of the original volume. Toluene (25 mL) was added while the solution was warmed to dissolve the purple material. Slow cooling overnight to –20 °C gave purple crystals suitable for X-ray studies: yield 1.45 g of 3, 47% yield; mp 194 °C dec; electronic spectrum (nm (ε), in toluene) 692 (428), 580 (217), 526 (170); IR (cm⁻¹) ν(C–O) 1109, 1024, 875 (bridging).

Co{OCPh₃}₂(THF)₂ (4). Addition of THF (50 mL) to $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (1.7 g, 4.5 mmol) and HOCPh_3 (2.37 g, 9.1 mmol) at 0 °C gave a green solution that upon overnight stirring yielded a pink precipitate. The volume was reduced by 50% under reduced pressure. Toluene (25 mL) is then added while the solution was warmed to dissolve the pink material. Slow cooling over 20 h to room temperature afforded 4 as red crystals isolated by filtration: yield 1.92 g, 59%; mp 139–141 °C; electronic spectrum in toluene identical with that of 2; IR (cm⁻¹) ν(C–O) 1091, 1057.

Co{OC(4-MeC₆H₄)₃}₂(THF)₂ (5, mp 105 °C). In toluene solution 5 dissociates two molecules of THF to give $[\text{Co}\{\text{OC}(4\text{-MeC}_6\text{H}_4)_3\}_2]$ (6) an analogue of 2. The synthetic procedure for 5 is the same as for 4 with

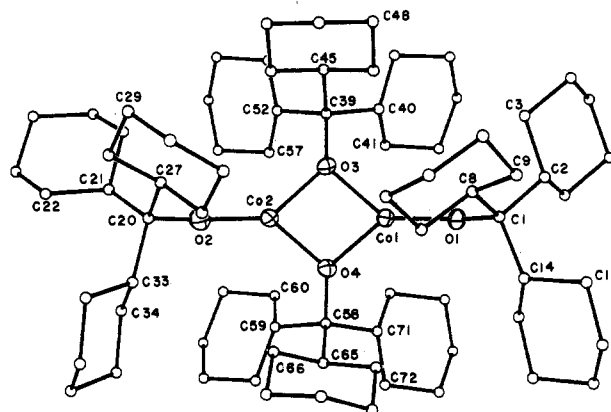


Figure 1. Computer-generated thermal ellipsoid (probability level 50%) plot of 1. Solvent of crystallization molecules and hydrogen atoms are not included.

$\text{HOC}(4\text{-MeC}_6\text{H}_4)$ instead of HOCPh_3 . Electronic spectrum of 6 (nm (ε), in toluene): 656 (163), 612 (160), 458 (112).

X-ray Crystallographic Studies. All X-ray data were collected with a Syntex P2₁ diffractometer equipped with a locally modified Syntex LT-1 device. Crystals of 1–4 were mounted by transferring them from the Schlenk tube under N₂ and immediately covering them with a layer of hydrocarbon oil. A suitable crystal was then selected, attached to a glass fiber with silicon grease, and quickly placed in the low-temperature N₂ stream. Calculations were carried out on a Data General Eclipse computer using the SHELXTL program system. The atom form factors, including anomalous scattering, were from ref 4. The data were corrected for Lorentz, polarization, and absorption effects.⁵

Green plates of $[\text{Co}\{\text{OC}(\text{C}_6\text{H}_{11})_3\}_2]_2 \cdot \text{CH}_3\text{OH} \cdot \frac{1}{2}\text{C}_6\text{H}_{12} \cdot \text{THF}$ (1) were obtained by slow cooling (20 h) of a THF/hexane solution to 0 °C and mounted in the manner described. The structure was solved by the Patterson technique for the triclinic space group *P* $\bar{1}$. Half of a cyclohexane molecule occupies a site near the center of inversion, giving rise to one cyclohexane per unit cell. Also one THF molecule and one CH₃OH molecule were found per asymmetric unit. Since the thermal parameters for all THF atoms were high, no assignment of the oxygen atom was made. All atoms were assigned as carbon. Such a disorder involving carbon and oxygen atoms seems reasonable on the basis that no cation is present to orient the oxygen. In the final cycles of refinement, all cobalt and oxygen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions, and their thermal parameters were given the value 1.2 times the equivalent isotropic thermal parameter of the bonded carbon. Further details of data collection and refinement are in Table I.

X-ray data on $[\text{Co}\{\text{OCPh}_3\}_2]_2 \cdot n\text{-C}_6\text{H}_{14}$ (2) were obtained in a manner identical with that for 1. The structure was solved by the Patterson technique. Half of the *n*-hexane molecule occupies a site near the center of inversion. The final cycles of refinement were carried out in a fashion identical with that for 1. Further details are in Table I.

Purple plates of $[\text{Co}\{\text{OSiPh}_3\}_2(\text{THF})]$ (3) were obtained by slow cooling a concentrated THF/toluene solution to –20 °C. The structure was solved by direct methods. One of the carbons on each of the THF molecules is disordered. Refinement was carried out with variable occupancies. These are labeled C(Na) and their counterpart C(Nb). For C(74a), the occupancy converged at 0.65 (1). For C(76a) the occupancy converged at 0.70 (1). The final refinement procedure was identical with that for 1 and 2 except that silicon atoms were also refined anisotropically.

Red crystals of $\text{Co}\{\text{OCPh}_3\}_2(\text{THF})_2$ (4) were isolated from a cooled THF/toluene solution. The systematic absences were consistent with the space group *C*2/*c* or *Cc*. The structure could be solved and refined to the same *R* value in either space group. *C*2/*c* is preferable because the molecule possesses a crystallographic twofold axis in this space group and because in *Cc* there are some large discrepancies between “equivalent” bonds. In the final cycles of refinement all non-hydrogen atoms were assigned anisotropic thermal parameters and hydrogen atoms were included by using the riding model mentioned previously. Further details are given in Table I. The atomic coordinates and isotropic temperature factors for complexes 1–4 are given in Table II.

(4) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(5) The program XABS was developed by H. Hope and B. Moezzi; it obtains an absorption tensor from $F_o - F_c$ differences.

Table I. Crystal Data and Summary of Data Collection and Refinement^a

	1	2	3	4
formula	C ₈₄ H ₁₅₀ O ₆ Co ₂	C ₇₉ H ₆₇ O ₄ Co ₂	C ₈₀ H ₇₆ O ₆ Si ₄ Co ₂	C ₄₆ H ₄₆ O ₄ Co
fw	1374.2	1198.3	1359.7	721.81
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
conditions	none	none	<i>h</i> 0 <i>l</i> , <i>h</i> + <i>l</i> = 2 <i>n</i> ; 0 <i>k</i> 0, <i>k</i> = 2 <i>n</i>	<i>h</i> <i>k</i> <i>l</i> , <i>h</i> + <i>k</i> = 2 <i>n</i> ; <i>h</i> 0 <i>l</i> , <i>l</i> = 2 <i>n</i>
cryst dimens, mm	0.310 × 0.520 × 0.11	0.325 × 0.350 × 0.70	0.375 × 0.575 × 0.625	0.237 × 0.375 × 0.387
cryst color and habit	dark green plates	green prisms	blue-violet plates	dichroic pink/green plates
temp, K	130	130	130	130
<i>a</i> , Å	13.359 (4)	11.787 (4)	14.203 (2)	18.994 (9)
<i>b</i> , Å	14.589 (5)	13.336 (4)	22.060 (5)	9.600 (8)
<i>c</i> , Å	23.054 (9)	20.107 (5)	22.269 (3)	23.421 (11)
α , deg	72.73 (2)	81.50 (2)		
β , deg	77.14 (3)	80.07 (3)	92.71 (1)	119.66 (3)
γ , deg	64.86 (3)	89.40 (3)		
<i>Z</i>	2	2	4	4
<i>V</i> , Å ³	3860 (2)	3079 (2)	6970 (2)	3711 (4)
<i>d</i> _{calcd} , g/cm ³	1.18	1.29	1.30	1.29
linear abs coeff, cm ⁻¹	5.0	6.2	5.93	5.02
scan speed, deg mm ⁻¹	15	15	30	30
scan width, deg	1.0	1.0	1.0	1.0
max 2 θ , deg	45	50	50	55
ω offset for bkgd, deg	1.0	1.0	1.0	1.0
range of abs factors	1.05–1.29	1.18–1.51	1.20–1.42	1.11–1.26
octants	+ <i>h</i> , ± <i>k</i> , ± <i>l</i>	+ <i>h</i> , ± <i>k</i> , ± <i>l</i>	+ <i>h</i> , + <i>k</i> , ± <i>l</i>	+ <i>h</i> , + <i>k</i> , ± <i>l</i>
no. of variables	399	371	441	231
data/variable	16.0	18.0	16.8	13.1
no. of check reflexns	(3,0,-2), (1,3,6), (2,-1,-3); no decay	(0,2,5), (1,1,2); no decay	(1,2,5), (0,6,4); no decay	(1,1,4), (2,2,4); no decay
<i>R</i> (merge)	0.004	0.005	0.006	0.006
no. of unique data	9979	10833	12273	4163
no. of data used in refinement	6375, <i>I</i> > 3 σ (<i>I</i>)	6680, <i>I</i> > 3 σ (<i>I</i>)	7442, <i>I</i> > 3 σ (<i>I</i>)	3025, <i>I</i> > 2 σ (<i>I</i>)
<i>R</i> (<i>F</i>)	0.076	0.072	0.056	0.054
<i>R</i> _w (<i>F</i>)	0.084	0.077	0.059	0.055
largest Δ / σ	0.019	0.009 for <i>x</i> of C(79)	0.007 for <i>y</i> of C(14)	0.01 for <i>y</i> of C(3)
largest feature in final diff map, e Å ⁻³	1.24, in vicinity of MeOH	1.97 and 1.62, in vicinity of hexane	0.89, in vicinity of disordered THF's	0.62, 1.01 Å from Co

^a All data were taken with Mo K α radiation with $\lambda = 0.71069$ Å by using a ω -scan technique; background offsets were 1° in each case. $R = \sum ||F_o| - |F_c|| / |F_o|$ and $R_w = \sum ||F_o| - |F_c|| w^{1/2} / \sum |F_o w^{1/2}|$ with $[\sigma^2(F_o)]^{-1}$ weighting scheme.

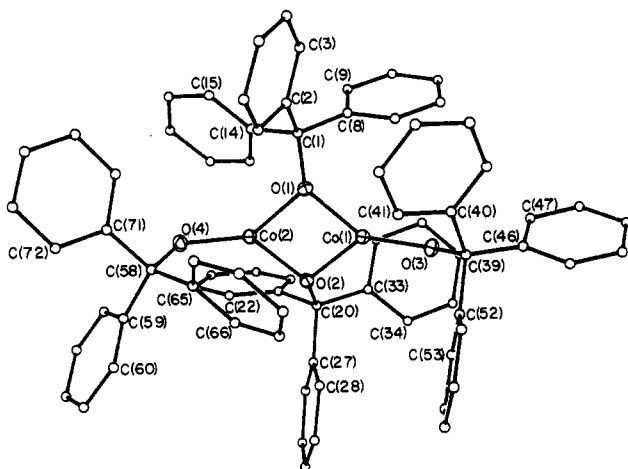


Figure 2. Computer-generated thermal ellipsoid (probability level 35%) plot of 2. The *n*-C₆H₁₄ molecule of crystallization is omitted for clarity.

Results and Discussion

Structures. The title compounds, synthesized by alcoholysis of [Co{N(SiMe₃)₂]₂], are the first structurally characterized neutral cobalt alkoxides.⁶ The structures of complexes 1–4 are illustrated in Figures 1–4. The dimeric structures of 1 and 2

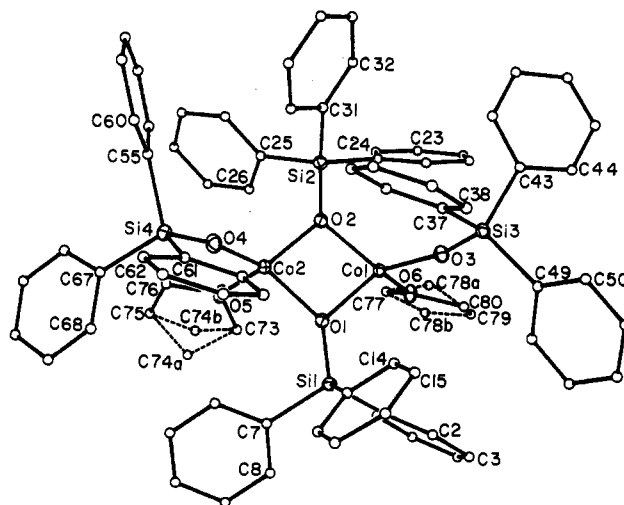


Figure 3. Computer-generated thermal ellipsoid plot (probability level 35%) of 3.

consist of a butterfly Co₂O₄ central core having near-C_{2v} symmetry with each cobalt in the rare trigonal-planar geometry. The low coordination at the metal centers in 1 and 2 is a consequence of the large steric requirements of the -OC(C₆H₁₁)₃ and -OCPh₃ ligands. In 3 each cobalt has a distorted tetrahedral geometry due to the coordination of one THF to each cobalt, giving a central Co₂O₆ core. In contrast to the case for 1 and 2, 4 has a mononuclear pseudotetrahedral cobalt center surrounded by two THF molecules and two OCPH₃ ligands.

Selected bond distances and angles for 1 are given in Table III. The most conspicuous feature of 1 is its dimeric nature. Although

(6) A cobalt(II) *p*-tert-butylcalix[4]arene cluster containing aryl-oxo bonds has been structurally characterized: Olmstead, M. M.; Sigel, G.; Hope, H.; Power, P. P.; Xu, X. *J. Am. Chem. Soc.* **1985**, *107*, 3087. Also a cage cluster with a central Co₄O₄ core has been structurally characterized with the bulky ligand 3,5-di-*tert*-butylcatechol: Olmstead, M. M.; Power, P. P.; Sigel, G., unpublished results.

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{\AA}^2 \times 10^3$) for 1-4

atom	x	y	z	U^a	atom	x	y	z	U^a
Complex 1									
Co(1)	2594 (1)	2092 (1)	2062 (1)	19 (1)*	C(40)	2368 (6)	3124 (5)	3135 (3)	22 (2)
Co(2)	3431 (1)	63 (1)	2887 (1)	23 (1)*	C(41)	1158 (6)	3266 (6)	3176 (4)	28 (2)
O(1)	2475 (4)	3186 (4)	1423 (2)	23 (2)*	C(42)	469 (7)	4335 (6)	2827 (4)	39 (2)
O(2)	4194 (5)	-1219 (4)	3266 (3)	38 (3)*	C(43)	484 (7)	5167 (7)	3093 (4)	40 (2)
O(3)	3242 (4)	1479 (4)	2842 (2)	19 (2)*	C(44)	1663 (7)	5040 (6)	3134 (4)	33 (2)
O(4)	2409 (4)	772 (4)	2262 (2)	20 (2)*	C(45)	2383 (6)	3918 (6)	3455 (3)	28 (2)
O(5)	175 (15)	4129 (13)	5148 (8)	93 (5)	C(46)	4421 (6)	1981 (5)	3256 (3)	19 (2)
C(1)	3053 (6)	3617 (5)	890 (3)	21 (2)	C(47)	4764 (6)	2584 (6)	2643 (3)	25 (2)
C(2)	2727 (6)	4775 (5)	884 (3)	25 (2)	C(48)	5912 (6)	2619 (6)	2614 (4)	30 (2)
C(3)	3186 (6)	4907 (6)	1408 (3)	28 (2)	C(49)	6804 (7)	1547 (6)	2745 (4)	31 (2)
C(4)	2895 (7)	6073 (7)	1376 (4)	44 (2)	C(50)	6477 (6)	918 (6)	3360 (3)	30 (2)
C(5)	1617 (8)	6691 (7)	1411 (4)	46 (2)	C(51)	5331 (6)	900 (5)	3394 (3)	25 (2)
C(6)	1149 (7)	6577 (7)	887 (4)	40 (2)	C(52)	2955 (6)	1316 (5)	3937 (3)	21 (2)
C(7)	1452 (7)	5406 (6)	917 (4)	31 (2)	C(53)	2965 (7)	1665 (6)	4497 (3)	31 (2)
C(8)	4322 (6)	3002 (5)	944 (3)	26 (2)	C(54)	2970 (7)	850 (6)	5085 (4)	36 (2)
C(9)	5116 (7)	3448 (6)	456 (4)	36 (2)	C(55)	1982 (7)	542 (6)	5174 (4)	33 (2)
C(10)	6318 (8)	2882 (7)	643 (4)	46 (2)	C(56)	1912 (7)	222 (6)	4614 (3)	28 (2)
C(11)	6742 (8)	1702 (7)	671 (4)	53 (3)	C(57)	1914 (7)	1067 (6)	4043 (4)	32 (2)
C(12)	5955 (7)	1227 (7)	1126 (4)	43 (2)	C(58)	1694 (6)	429 (5)	2043 (3)	20 (2)
C(13)	4734 (7)	1819 (6)	968 (4)	33 (2)	C(59)	1392 (6)	-362 (5)	2608 (3)	22 (2)
C(14)	2730 (6)	3507 (6)	300 (3)	23 (2)	C(60)	629 (6)	96 (6)	3142 (3)	27 (2)
C(15)	2892 (7)	4278 (6)	-301 (3)	31 (2)	C(61)	636 (7)	-758 (6)	3717 (4)	32 (2)
C(16)	2783 (7)	3963 (6)	-849 (4)	34 (2)	C(62)	211 (7)	-1514 (6)	3606 (4)	34 (2)
C(17)	1659 (7)	3899 (6)	-796 (4)	35 (2)	C(63)	885 (7)	-1937 (6)	3049 (3)	29 (2)
C(18)	1459 (7)	3148 (6)	-195 (4)	37 (2)	C(64)	939 (7)	-1089 (6)	2487 (3)	27 (2)
C(19)	1589 (6)	3471 (6)	353 (4)	30 (2)	C(65)	2410 (6)	-139 (5)	1527 (3)	23 (2)
C(20)	5141 (7)	-2190 (6)	3399 (4)	33 (2)	C(66)	3467 (6)	-1045 (6)	1741 (4)	29 (2)
C(21)	4953 (7)	-2547 (6)	4123 (4)	33 (2)	C(67)	4160 (7)	-1644 (6)	1259 (4)	37 (2)
C(22)	5644 (8)	-3699 (7)	4417 (4)	45 (2)	C(68)	4460 (7)	-913 (7)	680 (4)	43 (2)
C(23)	5250 (8)	-3962 (7)	5110 (4)	45 (2)	C(69)	3410 (7)	-40 (7)	449 (4)	42 (2)
C(24)	5312 (8)	-3231 (7)	5417 (4)	44 (2)	C(70)	2687 (7)	560 (6)	935 (3)	29 (2)
C(25)	4636 (7)	-2111 (6)	5124 (4)	40 (2)	C(71)	715 (6)	1431 (5)	1782 (3)	22 (2)
C(26)	5032 (7)	-1841 (7)	4459 (4)	38 (2)	C(72)	-91 (7)	1255 (6)	1497 (4)	30 (2)
C(27)	6183 (7)	-1904 (7)	3153 (4)	37 (2)	C(73)	-817 (7)	2268 (6)	1111 (4)	40 (2)
C(28)	7287 (7)	-2666 (7)	3397 (4)	40 (2)	C(74)	-1463 (7)	3094 (7)	1490 (4)	40 (2)
C(29)	8176 (8)	-2217 (7)	3169 (4)	47 (2)	C(75)	-688 (7)	3252 (6)	1799 (4)	38 (2)
C(30)	8344 (8)	-1889 (7)	2495 (4)	51 (2)	C(76)	16 (7)	2207 (6)	2192 (4)	35 (2)
C(31)	7271 (8)	-1155 (7)	2237 (5)	53 (3)	C(77)	8540 (11)	2090 (10)	4009 (6)	85 (4)
C(32)	6344 (8)	-1576 (7)	2465 (4)	46 (2)	C(78)	8089 (11)	3808 (10)	4097 (6)	91 (4)
C(33)	5059 (6)	-2938 (6)	3049 (4)	27 (2)	C(79)	7893 (11)	3232 (10)	3695 (6)	91 (4)
C(34)	4045 (6)	-3205 (6)	3313 (4)	30 (2)	C(80)	8849 (14)	3044 (12)	4506 (7)	112 (5)
C(35)	3813 (7)	-3754 (6)	2927 (4)	34 (2)	C(81)	8688 (12)	2164 (11)	4608 (6)	94 (4)
C(36)	4823 (7)	-4725 (6)	2828 (4)	35 (2)	C(82)	739 (14)	-354 (13)	10400 (8)	124 (6)
C(37)	5846 (7)	-4467 (6)	2567 (4)	36 (2)	C(83)	615 (12)	492 (11)	9910 (6)	96 (4)
C(38)	6075 (7)	-3918 (6)	2955 (4)	33 (2)	C(84)	92 (20)	566 (18)	9381 (11)	181 (9)
C(39)	3229 (6)	1978 (5)	3304 (3)	18 (2)	C(85)	961 (18)	4811 (16)	5035 (10)	61 (6)
Complex 2									
Co(1)	841 (1)	3430 (1)	2364 (1)	22 (1)*	C(24)	907 (7)	-800 (6)	1038 (4)	46 (2)
Co(2)	2360 (1)	1697 (1)	2398 (1)	22 (1)*	C(25)	-29 (7)	-217 (6)	990 (4)	42 (2)
O(1)	1422 (3)	2457 (3)	3056 (2)	23 (1)*	C(26)	-1 (6)	817 (5)	1050 (3)	36 (2)
O(2)	1668 (3)	2583 (3)	1711 (2)	23 (1)*	C(27)	1913 (5)	2851 (5)	473 (3)	25 (1)
O(3)	243 (4)	4692 (3)	2278 (2)	26 (1)*	C(28)	2709 (6)	3603 (5)	459 (4)	38 (2)
O(4)	3602 (4)	889 (3)	2418 (2)	28 (1)*	C(29)	3436 (7)	3974 (6)	-162 (4)	53 (2)
C(1)	889 (5)	1919 (4)	3712 (3)	24 (1)	C(30)	3344 (8)	3624 (7)	-743 (4)	57 (2)
C(2)	1540 (5)	2175 (4)	4261 (3)	24 (1)	C(31)	2507 (8)	2915 (7)	-750 (5)	65 (2)
C(3)	986 (6)	2134 (5)	4934 (3)	34 (2)	C(32)	1802 (7)	2513 (6)	-129 (4)	49 (2)
C(4)	1605 (6)	2335 (5)	5431 (4)	42 (2)	C(33)	-29 (5)	2933 (4)	1252 (3)	23 (1)
C(5)	2750 (7)	2572 (6)	5272 (4)	45 (2)	C(34)	-339 (6)	3741 (5)	799 (3)	29 (1)
C(6)	3315 (7)	2598 (6)	4611 (4)	48 (2)	C(35)	-1362 (6)	4243 (5)	952 (3)	35 (2)
C(7)	2715 (6)	2395 (5)	4103 (4)	35 (2)	C(36)	-2110 (6)	3945 (5)	1556 (3)	37 (2)
C(8)	-356 (5)	2263 (4)	3851 (3)	25 (1)	C(37)	-1831 (6)	3136 (5)	2010 (4)	35 (2)
C(9)	-1297 (6)	1598 (5)	3992 (3)	35 (2)	C(38)	-792 (5)	2637 (5)	1858 (3)	28 (1)
C(10)	-2415 (7)	1974 (6)	4105 (4)	42 (2)	C(39)	543 (5)	5665 (4)	2398 (3)	24 (1)
C(11)	-2603 (7)	2999 (5)	4088 (4)	40 (2)	C(40)	959 (5)	5655 (4)	3087 (3)	25 (1)
C(12)	-1669 (6)	3656 (5)	3966 (3)	34 (2)	C(41)	1969 (6)	5039 (5)	3165 (3)	31 (2)
C(13)	-564 (6)	3283 (5)	3852 (3)	31 (2)	C(42)	2347 (6)	4883 (5)	3787 (3)	37 (2)
C(14)	999 (5)	778 (5)	3655 (3)	26 (1)	C(43)	1716 (7)	5240 (5)	4347 (4)	44 (2)
C(15)	1426 (6)	77 (5)	4131 (3)	31 (2)	C(44)	729 (6)	5769 (5)	4279 (4)	40 (2)
C(16)	1575 (6)	-931 (5)	4026 (4)	41 (2)	C(45)	344 (6)	5932 (5)	3653 (3)	29 (1)
C(17)	1309 (6)	-1242 (6)	3444 (4)	42 (2)	C(46)	-536 (5)	6310 (5)	2408 (3)	26 (1)
C(18)	863 (6)	-559 (5)	2971 (4)	40 (2)	C(47)	-1612 (6)	5859 (5)	2541 (3)	36 (2)
C(19)	708 (6)	441 (5)	3078 (3)	31 (2)	C(48)	-2602 (7)	6428 (6)	2614 (4)	45 (2)
C(20)	1131 (5)	2400 (4)	1150 (3)	20 (1)	C(49)	-2537 (7)	7490 (6)	2550 (4)	42 (2)
C(21)	1000 (5)	1260 (5)	1150 (3)	27 (1)	C(50)	-1456 (6)	7950 (5)	2405 (3)	37 (2)
C(22)	1965 (6)	657 (5)	1189 (3)	29 (1)	C(51)	-470 (6)	7361 (5)	2342 (3)	31 (2)
C(23)	1917 (6)	-378 (5)	1138 (3)	38 (2)	C(52)	1511 (6)	6140 (5)	1813 (3)	29 (1)

Table II (Continued)

atom	x	y	z	U^a	atom	x	y	z	U^a
C(53)	1485 (7)	5971 (6)	1154 (4)	43 (2)	C(67)	4427 (6)	4016 (5)	1781 (3)	33 (2)
C(54)	2347 (7)	6374 (6)	623 (4)	57 (2)	C(68)	4788 (6)	4429 (5)	2306 (3)	34 (2)
C(55)	3261 (7)	6933 (6)	741 (4)	50 (2)	C(69)	5212 (6)	3815 (5)	2817 (3)	32 (2)
C(56)	3280 (7)	7115 (5)	1388 (4)	42 (2)	C(70)	5248 (5)	2765 (5)	2815 (3)	28 (1)
C(57)	2409 (6)	6722 (5)	1924 (4)	33 (2)	C(71)	5302 (6)	595 (5)	2915 (3)	31 (2)
C(58)	4786 (5)	1168 (5)	2319 (3)	26 (1)	C(72)	6465 (7)	364 (6)	2851 (4)	48 (2)
C(59)	5394 (6)	825 (5)	1651 (3)	29 (1)	C(73)	6889 (8)	-161 (7)	3431 (4)	64 (2)
C(60)	6323 (6)	1346 (5)	1225 (3)	36 (2)	C(74)	6169 (8)	-406 (7)	4021 (5)	63 (2)
C(61)	6885 (7)	930 (6)	659 (4)	46 (2)	C(75)	5037 (8)	-194 (7)	4098 (5)	65 (2)
C(62)	6530 (7)	18 (6)	521 (4)	53 (2)	C(76)	4597 (7)	306 (6)	3537 (4)	50 (2)
C(63)	5624 (7)	-479 (7)	935 (4)	57 (2)	C(77)	5190 (2)	5166 (10)	4626 (6)	110 (4)
C(64)	5046 (7)	-97 (6)	1498 (4)	42 (2)	C(78)	4607 (13)	5963 (11)	4546 (8)	123 (5)
C(65)	4871 (5)	2326 (5)	2303 (3)	26 (1)	C(79)	4673 (19)	6597 (17)	3800 (11)	201 (8)
C(66)	4475 (5)	2970 (5)	1783 (3)	29 (1)					
Complex 3									
Co(1)	3904 (1)	2817 (1)	7317 (1)	18 (1)*	C(36)	6662 (4)	3427 (3)	8439 (3)	30 (1)
Co(2)	5703 (1)	2211 (1)	7172 (1)	20 (1)*	C(37)	4596 (4)	4641 (2)	7111 (2)	22 (1)
Si(1)	4214 (1)	2391 (1)	5946 (1)	20 (1)*	C(38)	4723 (4)	5198 (3)	6812 (3)	34 (1)
Si(2)	5200 (1)	2559 (1)	8570 (1)	20 (1)*	C(39)	5630 (4)	5412 (3)	6722 (3)	43 (2)
Si(3)	3410 (1)	4325 (1)	7291 (1)	21 (1)*	C(40)	6405 (4)	5087 (3)	6897 (3)	38 (1)
Si(4)	7964 (1)	2599 (1)	6858 (1)	23 (1)*	C(41)	6297 (4)	4536 (3)	7176 (3)	40 (2)
O(1)	4579 (2)	2434 (2)	6650 (2)	22 (1)*	C(42)	5405 (4)	4322 (3)	7286 (3)	34 (1)
O(2)	4977 (2)	2518 (2)	7844 (1)	21 (1)*	C(43)	3112 (3)	4645 (2)	8046 (2)	21 (1)
O(3)	3446 (2)	3605 (2)	7306 (2)	26 (1)*	C(44)	2203 (4)	4826 (2)	8175 (3)	30 (1)
O(4)	6928 (2)	2448 (2)	7059 (2)	30 (1)*	C(45)	1983 (4)	5013 (3)	8750 (3)	34 (1)
O(5)	5774 (2)	1289 (2)	7182 (2)	30 (1)*	C(46)	2665 (4)	5019 (3)	9204 (3)	35 (1)
O(6)	2728 (2)	2347 (1)	7494 (2)	25 (1)*	C(47)	3585 (4)	4841 (3)	9098 (3)	33 (1)
C(1)	2905 (3)	2267 (2)	5902 (2)	21 (1)	C(48)	3799 (4)	4666 (2)	8523 (2)	27 (1)
C(2)	2261 (4)	2674 (2)	5640 (2)	26 (1)	C(49)	2472 (4)	4576 (2)	6719 (2)	22 (1)
C(3)	1296 (4)	2549 (3)	5601 (3)	37 (1)	C(50)	2237 (4)	5185 (3)	6611 (3)	33 (1)
C(4)	970 (4)	2022 (3)	5832 (3)	39 (2)	C(51)	1587 (4)	5352 (3)	6153 (3)	41 (2)
C(5)	1581 (4)	1605 (3)	6101 (3)	35 (1)	C(52)	1142 (5)	4924 (3)	5804 (3)	48 (2)
C(6)	2538 (4)	1729 (2)	6135 (2)	29 (1)	C(53)	1358 (4)	4318 (3)	5894 (3)	47 (2)
C(7)	4765 (4)	1725 (2)	5568 (2)	24 (1)	C(54)	2005 (4)	4148 (3)	6353 (3)	33 (1)
C(8)	4236 (4)	1357 (2)	5176 (2)	30 (1)	C(55)	8708 (4)	2856 (2)	7536 (2)	28 (1)
C(9)	4641 (4)	873 (3)	4878 (3)	37 (1)	C(56)	8614 (4)	2557 (3)	8087 (3)	37 (1)
C(10)	5588 (4)	747 (3)	4981 (3)	36 (1)	C(57)	9138 (5)	2725 (3)	8602 (3)	50 (2)
C(11)	6128 (4)	1112 (3)	5368 (3)	34 (1)	C(58)	9750 (5)	3192 (3)	8581 (3)	52 (2)
C(12)	5728 (4)	1589 (3)	5658 (3)	30 (1)	C(59)	9891 (4)	3498 (3)	8058 (3)	44 (2)
C(13)	4496 (3)	3098 (2)	5525 (2)	22 (1)	C(60)	9354 (4)	3333 (3)	7533 (3)	38 (1)
C(14)	4206 (4)	3663 (2)	5738 (3)	29 (1)	C(61)	7939 (4)	3222 (2)	6278 (2)	25 (1)
C(15)	4323 (4)	4191 (3)	5408 (3)	33 (1)	C(62)	8752 (4)	3410 (3)	5993 (3)	34 (1)
C(16)	4755 (4)	4166 (3)	4866 (3)	36 (1)	C(63)	8704 (4)	3900 (3)	5596 (3)	38 (1)
C(17)	5073 (4)	3612 (3)	4658 (3)	36 (1)	C(64)	7867 (4)	4190 (3)	5460 (3)	41 (2)
C(18)	4940 (4)	3090 (2)	4982 (2)	26 (11)	C(65)	7055 (4)	4005 (3)	5729 (3)	41 (2)
C(19)	4039 (3)	2600 (2)	8941 (2)	22 (1)	C(66)	7097 (4)	3522 (3)	6132 (3)	32 (1)
C(20)	3460 (4)	3097 (2)	8793 (2)	27 (1)	C(67)	8517 (4)	1903 (2)	6527 (2)	24 (1)
C(21)	2581 (4)	3167 (3)	9038 (3)	30 (1)	C(68)	8381 (4)	1778 (3)	5911 (3)	30 (1)
C(22)	2268 (4)	2737 (3)	9430 (3)	35 (1)	C(69)	8687 (4)	1238 (3)	5667 (3)	38 (1)
C(23)	2832 (4)	2241 (3)	9590 (3)	35 (1)	C(70)	9138 (4)	811 (3)	6035 (3)	38 (1)
C(24)	3719 (4)	2181 (3)	9350 (2)	29 (1)	C(71)	9290 (4)	921 (3)	6638 (3)	36 (1)
C(25)	5909 (4)	1883 (2)	8816 (2)	25 (1)	C(72)	8981 (4)	1460 (2)	6881 (3)	31 (1)
C(26)	5573 (4)	1298 (3)	8717 (3)	31 (1)	C(73)	4995 (4)	868 (3)	7052 (3)	37 (1)
C(27)	6097 (4)	787 (3)	8895 (3)	41 (2)	C(74a)	5498 (6)	301 (4)	6809 (6)	38 (3)
C(28)	6995 (4)	859 (3)	9162 (3)	36 (1)	C(74b)	5407 (16)	261 (10)	7181 (15)	47 (9)
C(29)	7353 (4)	1430 (3)	9266 (3)	35 (1)	C(75)	6426 (5)	296 (3)	7164 (3)	56 (2)
C(30)	6812 (4)	1936 (3)	9096 (2)	-27 (1)	C(76)	6666 (4)	968 (3)	7233 (3)	40 (2)
C(31)	5902 (3)	3254 (2)	8777 (2)	21 (1)	C(77)	2686 (4)	1753 (3)	7783 (3)	33 (1)
C(32)	5738 (4)	3595 (3)	9284 (3)	31 (1)	C(78a)	1755 (8)	1775 (5)	8096 (7)	46 (4)
C(33)	6301 (4)	4085 (3)	9453 (3)	40 (2)	C(78b)	1626 (11)	1632 (7)	7789 (10)	20 (6)
C(34)	7041 (4)	4247 (3)	9116 (3)	38 (1)	C(79)	1117 (5)	2158 (3)	7677 (3)	56 (2)
C(35)	7235 (4)	3914 (3)	8608 (3)	34 (1)	C(80)	1791 (4)	2616 (3)	7433 (3)	30 (1)
Complex 4									
Co	5000	4825 (1)	2500	20 (1)*	C(11)	1160 (2)	4058 (3)	333 (2)	30 (1)*
O(1)	3921 (1)	5421 (2)	2101 (1)	22 (1)*	C(12)	1801 (2)	3369 (3)	840 (2)	29 (1)*
O(2)	5161 (1)	3382 (2)	1923 (1)	35 (1)*	C(13)	2536 (2)	4047 (3)	1219 (2)	26 (1)*
C(1)	3463 (2)	6164 (3)	1512 (1)	19 (1)*	C(14)	3286 (2)	7637 (3)	1671 (1)	20 (1)*
C(2)	3929 (2)	6238 (3)	1130 (1)	20 (1)*	C(15)	3165 (2)	7811 (3)	2207 (2)	25 (1)*
C(3)	4675 (2)	6929 (3)	1420 (2)	23 (1)*	C(16)	2946 (2)	9095 (3)	2341 (2)	30 (1)*
C(4)	5139 (2)	6979 (3)	1113 (2)	28 (1)*	C(17)	2838 (2)	10240 (4)	1940 (2)	31 (1)*
C(5)	4863 (2)	6345 (3)	509 (2)	30 (1)*	C(18)	2961 (2)	10079 (3)	1407 (2)	29 (1)*
C(6)	4124 (2)	5663 (3)	214 (2)	30 (1)*	C(19)	3184 (2)	8792 (3)	1275 (2)	24 (1)*
C(7)	3661 (2)	5594 (3)	524 (2)	24 (1)*	C(20)	4627 (2)	2223 (3)	1594 (2)	36 (1)*
C(8)	2637 (2)	5434 (3)	1095 (1)	19 (1)*	C(21)	5164 (2)	1150 (4)	1532 (2)	41 (2)*
C(9)	1983 (2)	6108 (3)	577 (1)	25 (1)*	C(22)	5737 (2)	2046 (4)	1409 (2)	42 (2)*
C(10)	1248 (2)	5437 (3)	199 (2)	27 (1)*	C(23)	5849 (2)	3338 (4)	1814 (2)	35 (2)*

^a Asterisks denote equivalent isotropic U values, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

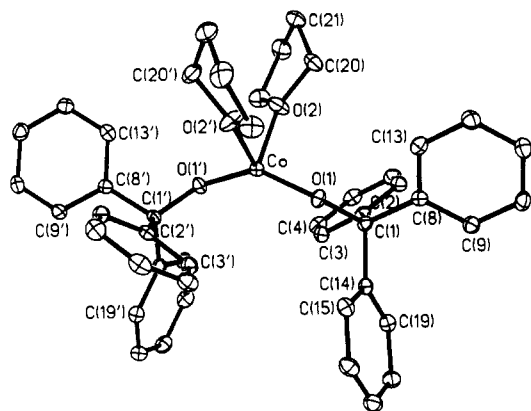


Figure 4. Computer-generated thermal ellipsoid (probability level 35%) plot of **4**.

this type of structure has been reported in the cobalt amides $[\text{Co}(\text{N}(\text{SiMe}_3)_2)_2]_2^7$ and $[\text{Co}(\text{NPh}_2)_2]_2^8$, the only other transition-metal alkoxide similar in structure to **1** is $[\text{Cr}\{\mu\text{-OCH}(t\text{-Bu})_2\}[\text{OC}(t\text{-Bu})_3]_2]_2^9$. Each CoO_3 center is nearly planar with the sum of the angles at cobalt being very close to 360° . The bridging oxygens also have planar coordination. The central Co_2O_4 core has a butterfly shape, being bent along the axis through the bridging oxygen atoms. The dihedral angle between the two CoO_3 planes is 154.5° . The $\text{Co}\cdots\text{Co}$ contact is $2.904(5) \text{ \AA}$, which is much longer than the distances seen in the amides, ca. 2.57 \AA .⁸ The long $\text{Co}\cdots\text{Co}$ distance is contrary to what is expected on the basis of the relative Co-O and Co-N bond lengths. It may be that the planar nature of the bridging oxygens imposes a Co-O-Co angle wider than that required by the bridging amido ligands, which have pseudotetrahedrally disposed orbitals. The smaller angle at the bridging nitrogen then results in a shorter $\text{Co}\cdots\text{Co}$ distance for the amides. Magnetic studies are under way to study this interesting variation in $\text{Co}\cdots\text{Co}$ distances.¹⁰ The wide Co-O-C angles of 145.2 and 158.1° for terminal ligands are common in metal alkoxide complexes.^{1,11} These angles are probably due to $d\text{-}p$ π back-bonding with steric effects also playing a role. The Co-O bond distances for terminal ligands average 1.781 \AA and are as predicted¹ somewhat shorter than Co-O bond distances for terminal ligands in the ionic cobalt complexes $[\text{Li}(\text{THF})_{4.5}][\text{Co}(\text{Cl})(\text{OC}(t\text{-Bu})_2)]_2$ and $[\text{Li}(\text{THF})_{4.5}][\text{Co}(\text{Cl})(\text{OC}(t\text{-Bu})_2)]_2$. As expected, distortions are apparent in the geometry of the central carbon bound to oxygen and the three cyclohexyl groups. The $(\text{C}_6\text{H}_{11})\text{-C-(C}_6\text{H}_{11})$ angles range from 109.4 to 117.0° and $(\text{C}_6\text{H}_{11})\text{-C}$ bond distances from 1.553 to 1.589 \AA . This type of strain from bulky substituents has already been noted in the $\text{OC}(t\text{-Bu})_3$ ligand.¹²

The presence of CH_3OH has not yet been confirmed in the reaction mixture; however, free dicyclohexyl ketone and cyclohexane in solution have been detected by GC/MS. However, a carbon-carbon cleavage of this nature has been observed with the $\text{OC}(t\text{-Bu})_3$ complex $[\text{Cr}\{\mu\text{-OCH}(t\text{-Bu})_2\}[\text{OC}(t\text{-Bu})_3]_2]_2^9$.

The structure of **2** (Figure 2) is in many respects similar to that of **1**, with differences which can be attributed to the slightly larger size of $\text{C}(\text{C}_6\text{H}_{11})_3$ compared to that of CPh_3 . For comparison, selected bond distances and angles are given in Table III. In **2**, each cobalt also has a distorted trigonal-planar geometry. The

Table III. Selected Bond Distances (\AA) and Angles (deg)

Complex 1			
$\text{Co}(1)\cdots\text{Co}(2)$	2.904 (5)	$\text{O}(1)\text{-C}(1)$	1.427 (8)
$\text{Co}(1)\text{-O}(1)$	1.798 (4)	$\text{O}(2)\text{-C}(20)$	1.447 (8)
$\text{Co}(1)\text{-O}(3)$	1.966 (5)	$\text{O}(2)\text{-C}(20)$	1.447 (8)
$\text{Co}(1)\text{-O}(4)$	1.952 (16)	$\text{O}(3)\text{-C}(39)$	1.453 (10)
$\text{Co}(2)\text{-O}(2)$	1.763 (5)	$\text{O}(4)\text{-C}(58)$	1.479 (12)
$\text{Co}(2)\text{-O}(3)$	1.944 (6)	$\text{C}(58)\text{-C}(59)$	1.568 (10)
$\text{Co}(2)\text{-O}(4)$	1.951 (5)	$\text{C}(58)\text{-C}(71)$	1.554 (8)
		$\text{C}(58)\text{-C}(65)$	1.557 (10)
$\text{Co}(1)\text{-O}(3)\text{-Co}(2)$	95.9 (3)	$\text{O}(1)\text{-Co}(1)\text{-O}(4)$	138.4 (3)
$\text{Co}(1)\text{-O}(4)\text{-Co}(2)$	96.1 (3)	$\text{O}(2)\text{-Co}(2)\text{-O}(3)$	139.3 (3)
$\text{O}(3)\text{-Co}(1)\text{-O}(4)$	81.5 (2)	$\text{O}(2)\text{-Co}(2)\text{-O}(4)$	138.5 (3)
$\text{O}(3)\text{-Co}(2)\text{-O}(4)$	82.1 (2)	$\text{Co}(1)\text{-O}(1)\text{-C}(1)$	145.2 (4)
$\text{O}(1)\text{-Co}(1)\text{-O}(3)$	139.1 (3)	$\text{Co}(2)\text{-O}(2)\text{-C}(20)$	158.1 (5)
Complex 2			
$\text{Co}(1)\cdots\text{Co}(2)$	2.910 (2)	$\text{O}(1)\text{-C}(1)$	1.448 (6)
$\text{Co}(1)\text{-O}(1)$	1.964 (4)	$\text{O}(2)\text{-C}(20)$	1.436 (8)
$\text{Co}(1)\text{-O}(2)$	1.982 (4)	$\text{O}(3)\text{-C}(39)$	1.414 (8)
$\text{Co}(1)\text{-O}(3)$	1.814 (4)	$\text{O}(4)\text{-C}(58)$	1.421 (7)
$\text{Co}(2)\text{-O}(1)$	1.968 (4)	$\text{C}(20)\text{-C}(21)$	1.529 (9)
$\text{Co}(2)\text{-O}(2)$	1.963 (4)	$\text{C}(20)\text{-C}(27)$	1.549 (7)
$\text{Co}(2)\text{-O}(4)$	1.811 (4)	$\text{C}(20)\text{-C}(33)$	1.531 (8)
$\text{Co}(1)\text{-O}(1)\text{-Co}(2)$	95.4 (2)	$\text{O}(2)\text{-Co}(1)\text{-O}(3)$	134.1 (2)
$\text{Co}(1)\text{-O}(2)\text{-Co}(2)$	95.0 (2)	$\text{O}(1)\text{-Co}(2)\text{-O}(4)$	134.7 (2)
$\text{O}(1)\text{-Co}(1)\text{-O}(2)$	84.4 (2)	$\text{O}(2)\text{-Co}(2)\text{-O}(4)$	137.5 (2)
$\text{O}(1)\text{-Co}(2)\text{-O}(2)$	84.8 (2)	$\text{Co}(1)\text{-O}(3)\text{-C}(39)$	137.1 (4)
$\text{O}(1)\text{-Co}(1)\text{-O}(3)$	139.1 (1)	$\text{Co}(2)\text{-O}(4)\text{-C}(58)$	129.0 (4)
Complex 3			
$\text{Co}(1)\cdots\text{Co}(2)$	2.916 (2)	$\text{Co}(2)\text{-O}(4)$	1.845 (4)
$\text{Co}(1)\text{-O}(1)$	1.993 (3)	$\text{Co}(2)\text{-O}(5)$	2.036 (3)
$\text{Co}(1)\text{-O}(2)$	1.991 (3)	$\text{Si}(1)\text{-O}(1)$	1.631 (3)
$\text{Co}(1)\text{-O}(3)$	1.858 (3)	$\text{Si}(2)\text{-O}(2)$	1.635 (3)
$\text{Co}(1)\text{-O}(6)$	2.020 (3)	$\text{Si}(3)\text{-O}(3)$	1.589 (4)
$\text{Co}(2)\text{-O}(1)$	1.990 (3)	$\text{Si}(4)\text{-O}(4)$	1.595 (4)
$\text{Co}(2)\text{-O}(2)$	1.977 (3)		
$\text{Co}(1)\text{-O}(1)\text{-Co}(2)$	94.0 (1)	$\text{O}(3)\text{-Co}(1)\text{-O}(6)$	100.9 (1)
$\text{Co}(1)\text{-O}(2)\text{-Co}(2)$	96.5 (1)	$\text{O}(1)\text{-Co}(2)\text{-O}(4)$	125.9 (2)
$\text{O}(1)\text{-Co}(1)\text{-O}(2)$	85.3 (1)	$\text{O}(2)\text{-Co}(2)\text{-O}(4)$	122.3 (2)
$\text{O}(1)\text{-Co}(2)\text{-O}(2)$	85.7 (1)	$\text{O}(1)\text{-Co}(2)\text{-O}(5)$	106.9 (1)
$\text{O}(1)\text{-Co}(1)\text{-O}(3)$	124.6 (1)	$\text{O}(2)\text{-Co}(2)\text{-O}(5)$	111.2 (1)
$\text{O}(2)\text{-Co}(1)\text{-O}(3)$	125.1 (1)	$\text{O}(4)\text{-Co}(2)\text{-O}(5)$	103.7 (2)
$\text{O}(1)\text{-Co}(1)\text{-O}(6)$	111.1 (1)	$\text{Co}(1)\text{-O}(3)\text{-Si}(3)$	161.3 (2)
$\text{O}(2)\text{-Co}(1)\text{-O}(6)$	109.4 (1)	$\text{Co}(2)\text{-O}(4)\text{-Si}(4)$	170.7 (2)
Complex 4			
$\text{Co-O}(1)$	1.872 (2)	$\text{O}(1)\text{-C}(1)$	1.407 (3)
$\text{Co-O}(2)$	2.061 (3)		
$\text{O}(1)\text{-Co-O}(1)'$	144.4 (1)	$\text{O}(1)\text{-Co-O}(2)'$	93.0 (1)
$\text{O}(2)\text{-Co-O}(2)'$	95.5 (2)	$\text{Co-O}(1)\text{-C}(1)$	129.6 (2)
$\text{O}(1)\text{-Co-O}(2)$	111.0 (1)	$\text{Co}(1)\text{-O}(2)\text{-C}(20)$	126.9 (8)

central Co_2O_4 core is only slightly bent with a dihedral angle between CoO_3 planes of 158.9° . This small difference of 4.4° may be a reflection of the less stringent steric requirements of the phenyl rings in the bridging and terminal ligands vs. that of cyclohexyl rings. The Co-O (bridging) and Co-O (terminal) distances average 1.969 and 1.813 \AA and are slightly longer than those in **1**. This might be expected on replacing an alkyl substituent with an aryl ring. The smaller terminal Co-O-CPh_3 angles of 129.0 and 137.1° probably reflect the less demanding steric nature of the phenyl substituent. The $\text{Co}\cdots\text{Co}$ contact in **2** is $2.910(2) \text{ \AA}$, also very close to the value in **1**.

The structure of **3** is illustrated in Figure 3. Important bond lengths and angles are given in Table III. The structure may be regarded as a derivative of **1** or **2** via the coordination of a THF donor to each cobalt resulting in a distorted tetrahedral coordination. Alternatively, the Co_2O_6 core may be viewed as two Co -centered distorted tetrahedra sharing an edge. The THF-Co-OR (terminal) angles average 102.3° , and the core RO-Co-OR (bridging) angles average 85.5° . It is interesting to note that the terminal OSiPh_3 groups have large, almost linear, Co-O-Si angles, 170.7 and 161.3° . This may be in part due to increased

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Table IV. ^1H NMR Isotropic Shifts^a of 2, 3, 4, and 6 at 24 °C in C_6D_6

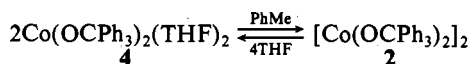
compd	terminal ligand/ppm			bridging ligand/ppm			other features/ppm nonisotropic
	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	
$[\text{Co}(\text{OCPh}_3)_2]_2 \cdot n\text{-C}_6\text{H}_{14}$ (2)	59.2	-23.3	-11.7	-70.1	-46.0	-14.0	1.2, 0.8, 0.4 (C_6H_{14})
$[\text{Co}(\text{OSiPh}_3)_2(\text{THF})_2]$ (3)	19.1	4.2	2.6	-21.8	-4.5	-8.2	4.1, 1.4 ($\text{C}_4\text{H}_8\text{O}$)
$\text{Co}(\text{OCPh}_3)_2(\text{THF})_2$ (4)	57.2	-22.6	-12.5	-71.3	-43.6	-12.5	5.3, 2.1 ($\text{C}_4\text{H}_8\text{O}$)
$[\text{Co}(\text{OC}(4\text{-MeC}_6\text{H}_4)_2)_2]$ (6)	56.4	-22.1	-5.3 ^b	-82.2	-46.3	-11.1 ^b	4.0, 1.6 ($\text{C}_4\text{H}_8\text{O}$)

^aIsotropic shifts reported as $(\Delta H/H_0)_{\text{iso}} = (\Delta H/H_0)_{\text{obsd}} - (\Delta H/H_0)_{\text{dia}}$, where diamagnetic reference shifts were taken as those of the free ligand in CDCl_3 at ambient temperature. ^bShifts refer to the 4-Me group.

crowding at the cobalt center as a result of THF coordination. However, we note that M–O–Si systems frequently have wide angles at oxygen in the terminal Si–O bonds.¹³ Also noteworthy is the fact that both THF's are coordinated in a *cis* fashion across the core. This phenomenon is probably steric in origin since both THF's are coordinated to the most open face of the core. The Co...Co contact in this case is 2.916 (2) Å, very similar to the values seen in 1 and 2.

The treatment of $[\text{Co}[\text{N}(\text{SiMe}_3)_2]_2]$ with HOCPH_3 in the presence of the donor solvent THF gave the monomeric complex $\text{Co}(\text{OCPh}_3)_2(\text{THF})_2$ (4). This THF complexation can be reversed, and 2 may be prepared by dissolving 4 in toluene. The structure of 4 (Figure 4) shows cobalt to have a very distorted tetrahedral geometry. The molecule possesses C_2 symmetry. Selected bond lengths and angles are given in Table III. Each OCPh_3 ligand is oriented about cobalt to minimize steric interactions between substituents. This gives a very large RO–Co–OR angle of 144.4 (1)° and a compressed THF–Co–THF angle of 95.5 (2)°. The Co–OR bond distance of 1.872 (2) Å is slightly longer than in 2 due, presumably, to an increase in the coordination number of cobalt. The Co–THF distance of 2.061 (3) Å is normal.⁵ The general stoichiometry $\text{M}(\text{OR})_2(\text{THF})_2$ has been observed for $\text{M} = \text{Zn}^{14a}$ and has been reported^{14b} for $\text{M} = \text{Cr}, \text{Mn}, \text{R} = 2,6\text{-di-tert-butylphenolate}$.

Spectroscopic Studies. Electronic and IR Spectra. The electronic spectral data for complexes 1–5 is given in the Experimental Section. For compounds 1 and 2 each cobalt is trigonal planar with approximately D_{3h} symmetry. The expected splitting of the ground-state ^4F term involves $^4\text{A}_2', (^4\text{A}_1'', ^4\text{A}_2'')$, $^4\text{E}'$, and $^4\text{E}''$ terms. Three d–d absorptions are seen in the electronic spectrum. If a $^4\text{A}_2'$ ground state is assumed,¹⁵ then the lowest energy transition (648 nm for 1, 670 nm for 2) is probably to the $^4\text{E}'$ state ($^4\text{E}''$ is probably close in energy but is symmetry-forbidden). The bands at 582 nm in 1 and 616 nm in 2 are somewhat less intense and may be due to transitions to the $^4\text{A}_1''$ or $^4\text{A}_2''$ states, which are also probably close in energy.¹⁵ The highest energy transition at ca. 420 nm may be due to excitation to a $^4\text{A}_2'$ state arising from the splitting of the ^4P excited-state free-ion term. The electronic spectrum of 2 is also obtained when 4 is dissolved in toluene, giving a green solution identical in color with that of 2. This indicates the loss of two THF molecules to form the dimer 2 as in the equation



In 3, three transitions are also observed in the electronic spectrum. Each Co is pseudotetrahedrally coordinated by oxygens, and the free-ion ^4F term is split, giving the transitions 694 ($^4\text{A}_2 \rightarrow ^4\text{T}_2$), 576 ($^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{F})$), and 526 nm ($^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{P})$) as tentative assignments for the three absorptions. The ^1H NMR spectra of 4 and 5 show that the two THF molecules are dissociated when dissolved in toluene, and the electronic spectra of the

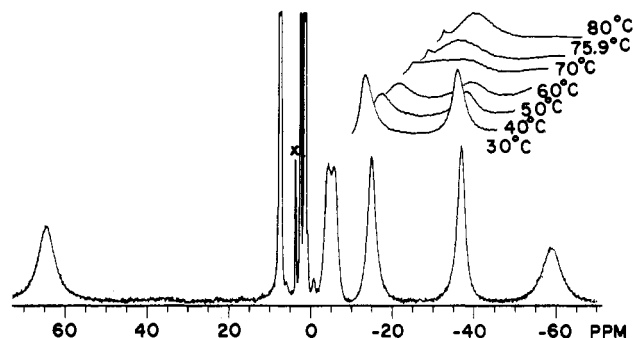


Figure 5. Variable-temperature FT ^1H NMR spectrum of $[\text{Co}(\text{OCPh}_3)_2]_2 \cdot n\text{-C}_6\text{H}_{14}$ (2) in C_7D_8 . Dynamic exchange of bridging and terminal groups is illustrated for meta protons on the phenyl rings.

two compounds are similar to those of 2.

Selected infrared spectral data on complexes 1–4 are given in the Experimental Section. An extensive study on infrared spectra of some metal alkoxides and trialkylsiloxides has been carried out by Bradley et al.¹⁶ Generally $\nu(\text{C–O})$ stretching frequencies in terminal alkoxides are in the range 900–1150 cm^{-1} whereas $\nu(\text{C–O})$ bridging frequencies are somewhat lower than $\nu(\text{C–O})$ terminal frequencies due to the weakening of the C–O bond.¹⁶ For instance, the IR spectrum of 1 shows two broad absorptions at 1074 and 1023 cm^{-1} , which have been assigned to $\nu(\text{C–O})$ terminal and $\nu(\text{C–O})$ bridging stretching frequencies. On the basis of the $\nu(\text{C–O})$ terminal stretching frequencies for the monomer 4, a tentative assignment of bridging $\nu(\text{C–O})$ and terminal $\nu(\text{C–O})$ stretching frequencies has been made for the dimer 2. For complex 3 bands at 1109 and 1024 cm^{-1} correspond to stretching vibrations of terminal Si–O groups, and the band at 875 cm^{-1} corresponds to bridging Si–O groups. Similar assignments have been made on dimeric aluminum trialkylsilanoxides.¹⁷

^1H NMR Spectra. Even though the related paramagnetic transition-metal amides of the bridging type $[\text{M}(\mu\text{-X})\text{X}]_2$ ($\text{X} = \text{amide}$) have been known for a number of years,³ their ^1H NMR spectra have not received much attention. Thus little is known of the dynamic exchange of bridging and terminal groups or the possible dissociation of the complexes into monomeric units. We therefore decided to study the ^1H NMR spectra of 2, 3, and 6 in somewhat greater detail. These spectra provide important information, among which is compound identification and monitoring of product purity. The ^1H NMR spectrum of 2 in C_7D_8 is shown in Figure 5. Table IV gives the isotropic shifts of the peaks in the spectra of 2, 3, 4, and 6.

Because the compounds are paramagnetic, having two apparently weakly coupled¹⁰ d^7 centers, resonances are isotropically shifted. Due to the relatively low symmetry of the metal atom environments both dipolar and contact contributions can be expected. We have made no attempt to calculate the pseudocontact term, which would require the determination of either the single-crystal susceptibility or the g anisotropy. Also due to the lack of comparable data the ratio method cannot be applied with confidence. However, it is apparent from Figure 5 and Table IV

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that the terminal and bridging positions are clearly distinguished for **2**, **3**, and **4**. The para position is clearly identified on the basis of intensity ratio and also through the use of the complex $\text{Co}[\text{OC}(\text{4-MeC}_6\text{H}_2)_3]_2(\text{THF})_2$ (**5**), which dissociated THF in toluene to yield $[\text{Co}[\text{OC}(\text{4-MeC}_6\text{H}_{11})_3]_2]_2$ (**6**). More ambiguous are the assignments of the two most shifted and broadened peaks to the ortho hydrogens, leaving the remaining two peaks to be assigned to the meta hydrogen positions. Similar arguments have been used to assign resonances in phenyl-containing ligands of iron sulfur clusters¹⁸ and porphyrins¹⁹ before unambiguous assignments were made by using substituted phenyls.²⁰ We have assigned the downfield and upfield resonances of **2**, **3**, and **6** to the terminal and bridging groups, respectively. The addition of pyridine-*d*₅ to **5** also lends support to these assignments since only downfield Ph resonances were observed for the complex $\text{Co}[\text{OC}(\text{4-MeC}_6\text{H}_4)_3]_2(\text{py-}d_5)_2$. These assignments are also based on comparisons with terminal and bridging substituents in other transition-metal paramagnetic systems.²¹

Irrespective of the assignments in this work, it is possible to estimate an energy barrier for the dynamic ¹H NMR process seen when solutions of **2** or **6** are heated. No coalescence was observed in the THF-coordinated **3** due to irreversible changes in the

spectrum on heating. Figure 5 shows the changes in the spectrum of **2** when the compound is heated to 80 °C in C₇D₈. Free energies of activation were estimated by using an approximate formula²² based on determinations of coalescence temperature. For **2** the signals for the para hydrogens coalesce at 40 °C, affording a ΔG^\ddagger value of 57.2 kJ mol⁻¹. For the meta hydrogens, which coalesce at 75 °C, a ΔG^\ddagger value of 57.3 kJ mol⁻¹ was calculated; for **6**, very similar values of 58.7 and 56.3 kJ mol⁻¹ were obtained. Evidence for an intramolecular dynamic process comes from experiments similar to those used by Bradley et al. in their study of $[\text{Ta}(\text{OMe})_5]_2$. The addition of free ligand to either **2** or **5** in C₇D₈ solution followed by heating to coalescence showed no evidence of exchange.

Although the above studies do not establish the mechanism for intramolecular exchange, they do show that the complexes are substantially dimeric in solution at room temperature. Further studies on the dynamic ¹H NMR of various dimeric alkoxides and amides are in progress.

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Supplementary Material Available: For the four structure determinations, full tables of bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates and figures illustrating the core atoms of **1** and the ¹H NMR spectra of **2**, **3**, **4**, and **6** in C₆D₆ (26 pages); calculated and observed structure factor tables (139 pages). Ordering information is given on any current masthead page.

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Facile Cleavage of a Phosphido Bridge with H₂. Synthesis, Structures, and Reactivities of the Heterobimetallic Complexes (MeCp)Mn(CO)₂(μ-*t*-Bu₂P)M(COD) (M = Rh, Ir; MeCp = η⁵-C₅H₄Me; COD = 1,5-Cyclooctadiene)

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Reaction of (MeCp)Mn(CO)₂(*t*-Bu₂PLi), generated in situ from (MeCp)Mn(CO)₂(*t*-Bu₂PH) and *n*-BuLi, with [M(COD)Cl]₂ in THF gives the dark red heterobimetallic di-*tert*-butylphosphido bridged complexes (MeCp)Mn(CO)₂(μ-*t*-Bu₂P)M(COD) [MeCp = η⁵-C₅H₄Me; COD = 1,5-cyclooctadiene; M = Rh (**1**) (89%), Ir (**2**) (82%)]. **1** and **2** have been characterized spectroscopically (IR; ¹H, ³¹P NMR) and their structures determined by X-ray crystallography. The complexes are isostructural. The molecular structures consist of a di-*tert*-butyl phosphido (*t*-Bu₂P) unit bridging a Mn-M single bond [**1**, Mn-Rh = 2.708 (2) Å; **2**, Mn-Ir = 2.637 (4) Å]. The COD ligand is bonded to give a roughly planar geometry to Rh (**1**) or Ir (**2**). The geometry at Mn in both complexes is essentially that of a three-legged piano stool (ignoring the metal-metal bond). Neither **1** nor **2** reacts with diazomethane (CH₂N₂) at room temperature in diethyl ether. Both **1** and **2** react with CO (50 psi) and excess PMe₃ although the only isolable compound in both cases is (MeCp)Mn(CO)₂(*t*-Bu₂PH). **1** does not react with H₂ (50 psi), while **2** gives (MeCp)Mn(CO)₂(*t*-Bu₂PH). Crystal data for **1**: C₂₄H₃₇MnO₂PRh, *M*_r 546.38, monoclinic, *P*₂₁/*n* (No. 1014), *a* = 17.740 (4) Å, *b* = 14.808 (3) Å, *c* = 9.051 (1) Å, β = 93.125 (2)°, *V* = 2374.2 (5) Å³, *D*_c = 1.528 g cm⁻³, *Z* = 4, λ(Mo Kα) = 0.71073 Å (graphite monochromator), μ(Mo Kα) = 12.785 cm⁻¹. Methods: MULTAN, difference Fourier, full-matrix least squares. Refinement of 2578 reflections (*I* > 3σ(*I*)) out of 3713 unique observed reflections (3° < 2θ < 48°) gives *R* and *R*_w values of 0.0495 and 0.0581, respectively. Data/parameter ratio = 9.840. Hydrogen atoms were not located. Crystal data for **2**: C₂₄H₃₇IrMnO₂P, *M*_r 635.65, monoclinic, *P*₂₁/*n* (No. 1014), *a* = 17.719 (3) Å, *b* = 14.793 (3) Å, *c* = 9.047 (2) Å, β = 93.113 (2)°, *V* = 2367.9 (5) Å³, *D*_c = 1.775 g cm⁻³, *Z* = 4, λ(Mo Kα) = 0.71073 Å (graphite monochromator), μ(Mo Kα) = 61.892 cm⁻¹. Methods: MULTAN, difference Fourier, full-matrix least squares. Refinement of 2455 reflections (*I* > 3σ(*I*)), out of 2937 unique observed reflections (2° < 2θ < 50°), gives *R* and *R*_w values of 0.0688 and 0.0760, respectively. Data/parameter ratio = 9.742. Hydrogen atoms were not located.

Introduction

As part of a general study of heterobimetallic complexes bearing bulky phosphido (R₂P⁻) ligands, we have recently described a number of mixed-metal complexes of Cr-Rh, Cr-Ni, Cr-Co, and Fe-Ni.^{1,2} The synthesis of these complexes was accomplished

via salt elimination from the reaction of a coordinated lithiated phosphine with a metal-halide moiety (Scheme I). We report here the syntheses, X-ray structures, and preliminary chemical reactivities of two new heterobimetallic complexes; (MeC₅H₄)-Mn(CO)₂(μ-*t*-Bu₂P)M(COD) (M = Rh (**1**), Ir (**2**); COD = 1,5-cyclooctadiene). There are relatively few heterobimetallic

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