= 965 Hz), 41.8 (m), 20.1 (dm, J_{PF} = 881 Hz) ppm; ^{19}F NMR 50.2 (dm, J_{PF} = 878 Hz, 1 F), 38.7 (t, J_{FH} = 8 Hz, 3 F), 38.5 (t, J_{FH} = 8 Hz, 3 F), 36.0 (dm, J_{PF} = 947 Hz, 1 F) ppm. MS Calcd for $C_{14}H_{12}F_8FeN_3O_2P_3$: 555. Found: 555. Anal. Calcd: C, 30.30; H, 2.18; N, 7.57. Found: C, 30.36; H, 2.24; N, 7.68.

For **20**: IR 3080, 3060, 2940 (w, CH), 1180 (vs, PN) cm^{-1}; ^{1}H NMR δ 4.92 (m, 2 H), 4.89 (m, 2 H), 4.65 (m, 2 H), 4.46 (dq, J_{HCOP} = 10 Hz, J_{HCCF} = 8 Hz, 2 H), 4.34 (m, 4 H), 4.32 (m, 2 H); ^{31}P NMR 39.2 (m), 16.7 (dm, J_{PF} = 877 Hz) ppm; ^{19}F NMR 56.1 (dm, J_{PF} = 879 Hz, 1 F), 38.4 (t, J_{FH} = 8 Hz, 6 F), 38.1 (t, J_{FH} = 8 Hz, 3 F) ppm. MS Calcd for $C_{16}H_{14}F_{10}FeN_3O_3P_3$: 635. Found: 635. Anal. Calcd: C, 30.26; H, 2.22; N, 6.61. Found: C, 30.22; H, 2.07; N, 6.69.

For **21**: IR 3080, 2940 (w, CH), 1170 (vs, PN) cm^{-1}; ^{1}H NMR δ 4.95 (m, 1 H), 4.91 (m, 2 H), 4.88 (m, 1 H), 4.67 (m, 1 H), 4.64 (m, 1 H), 4.52 (dq, J_{HCOP} = 10 Hz, J_{HCCF} = 8 Hz, 2 H), 4.51 (dq, J_{HCOP} = 10 Hz, J_{HCCF} = 8 Hz, 2 H), 4.35 (m, 2 H), 4.33 (m, 2 H); ^{31}P NMR 46.9 (dm, J_{PF} = 942 Hz), 41.1 (m), 21.7 (m) ppm; ^{19}F NMR 39.6 (dm, J_{PF} = 942 Hz, 1 F), 37.9 (t, J_{FH} = 8 Hz, 3 F), 37.8 (t, J_{FH} = 8 Hz, 6 F) ppm. MS Calcd for $C_{16}H_{14}F_{10}FeN_3O_3P_3$: 635. Found: 635. Anal. Calcd: C, 30.26; H, 2.22; N, 6.61. Found: C, 30.36; H, 2.31; N, 6.55.

Attempted Reaction of Sodium Trifluoroethoxide (10 Equiv) with 10. A sample of $N_4P_4F_4(\eta\text{-}C_5H_4)_4Ru_2$ (**10**) (100 mg, 0.19 mmol) was dissolved in THF–benzene-d_6 (4:1, 2 mL) in a 10-mm NMR tube. Sodium trifluoroethoxide (1.9 mmol) in THF (2 mL) was added. The tube was degassed, sealed under vacuum, and heated to 75 °C for 14 days. No reaction was observed by both ^{31}P and ^{19}F NMR spectroscopy. In addition, no precipitate of NaF, an insoluble byproduct of the substitution reaction, was observed in the tube.

X-ray Structure Determination for 1a, 3a, 7, and 10. Our general X-ray structure technique has been described in earlier papers[2], and only the details related to the present work will be given here.

Crystals of **1a**, **3a**, and **7** were obtained from dichloromethane–hexane solutions and were mounted along the longest axis. Crystals of **10** were grown from toluene. The structures of **1a**, **3a**, and **7** were solved by direct methods, and that of **10** was resolved by Patterson and Fourier techniques. In the final cycles of full-matrix least-squares refinement, all non-hydrogen atom positional parameters and anisotropic thermal parameters were refined. The positional parameters for the hydrogen atoms of **1a**, given fixed, arbitrary thermal parameters (B = 5.0 Å^2), were located from a difference Fourier electron density map and were refined. The positional parameters and thermal parameters for the hydrogen atoms of **3a**, **7**, and **10** (B = 5.0 Å^2) were fixed in calculated positions (C–H = 0.97 Å) during the later cycles of refinement.

Acknowledgment. We thank the U.S. Army Research Office for the support of this work and for the X-ray diffractometer provided through a DOD equipment grant. We also thank J. L. Desorcie for obtaining some of the high-field ^{31}P and ^{1}H NMR spectra.

Registry No. **1a**, 89179-03-3; **1b**, 89179-04-4; **2a**, 84462-63-5; **3a**, 89179-06-6; **3b**, 89179-07-7; **4a**, 102735-99-9; **4b**, 102736-11-8; **5a**, 102736-00-5; **5b**, 102736-12-9; **6**, 102849-13-8; **7**, 102736-01-6; **8a**, 102736-02-7; **9b**, 102736-03-8; **10**, 103002-51-3; **12**, 2713-48-6; *cis*-**13**, 102849-14-9; *trans*-**13**, 102736-04-9; **14**, 102736-05-0; **15**, 102736-06-1; **16**, 102745-11-9; **17**, 102736-07-2; **19**, 102736-08-3; **20**, 102736-09-4; **21**, 102736-10-7; **22**, 95784-56-8; lithioferrocene, 1271-15-4; 1,1′-dilithioferrocene, 33272-09-2; dilithioruthenocene, 60898-13-7; lithioruthenocene, 89179-17-9; chloromercuriferrocene, 1273-75-2; ruthenocene, 1287-13-4.

Supplementary Material Available: Appendix A, analysis of NMR spectra, and tables of interatomic distances and bond angles (Tables X, XIV, XVII, and XXI), least-squares planes (Tables XII and XIX), anisotropic thermal parameters (Tables XI, XV, XVIII, and XXII), and calculated structure factors (Tables XIII, XVI, XX, and XXIII) (126 pages). Ordering information is given on any current masthead page.

Formation and Molecular Structures of η^5-Pentabenzylcyclopentadienyl and η^5-Pentaphenylcyclopentadienyl Dicarbonyl Derivatives of Cobalt and Rhodium

John W. Chambers,[1a] Andrew J. Baskar,[1b,c] Simon G. Bott,[1b] Jerry L. Atwood,*[1b] and Marvin D. Rausch*[1a]

Departments of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, and University of Alabama, University, Alabama 35486

Received September 10, 1985

Improved synthetic routes to pentabenzylcyclopentadiene (1) and pentaphenylcyclopentadiene (2) have been developed. Reactions of 1 and 2 with $Co_2(CO)_8$ in refluxing toluene have afforded (η^5-C_5Bz_5)Co(CO)$_2$ (3) and (η^5-C_5Ph_5)Co(CO)$_2$ (5) in yields of 67% and 9%, respectively. Reaction of 1 with n-butyllithium in THF at 0 °C has produced C_5Bz_5Li (7), whereas reaction of 2 with sodium amide in refluxing toluene has afforded C_5Ph_5Na (8) in 84% yield. Both 7 and 8 react with $[Rh(CO)_2Cl]_2$ in THF to produce (η^5-C_5Bz_5)Rh(CO)$_2$ (4) and (η^5-C_5Ph_5)Rh(CO)$_2$ (6), respectively. Single-crystal X-ray diffraction studies on 3 and 5 have been undertaken. Compound 3 crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions a = 12.753 (7) Å, b = 14.877 (8) Å, c = 18.28 (1) Å, β = 108.58 (5)°, and Z = 4 for d_{calcd} = 1.28 g cm^{-3}. Compound 5 crystallizes in the orthorhombic space group $Pbca$ with unit cell dimensions a = 13.66 (1) Å, b = 20.44 (4) Å, c = 20.600 (5) Å, and Z = 8 for d_{calcd} = 1.30 g cm^{-3}. Full-matrix least-squares refinement led for 3 to a final R value of 0.042 for 2398 observed reflections and for 5 to a final R value of 0.054 for 1779 observed reflections. Compound 3 exhibits a nonsymmetric placement of the benzyl substituents, while the phenyl substituents of 5 are symmetrically placed and canted an average of 55.8° with respect to the cyclopentadienyl ring.

Since the first definitive study on η^5-pentamethylcyclopentadienyl derivatives of the metals in 1967,[2] the η^5-C_5Me_5 ligand has played an important role in the development of organometallic chemistry. Replacement of

0276-7333/86/2305-1635$01.50/0

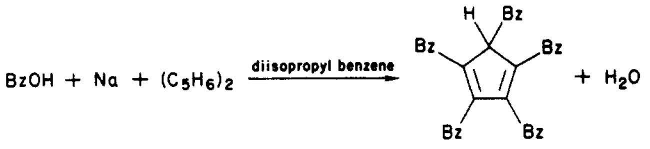
all hydrogen atoms by methyl substituents alters both the steric and electronic influence of the η^5-cyclopentadienyl ring, resulting in differing reactivities, stabilities, solubilities, and spectral properties of (η^5-pentamethylcyclopentadienyl)metal complexes relative to their well-known (η^5-cyclopentadienyl)metal counterparts.[3]

More recently, studies concerning η^5-pentaphenylcyclopentadienyl derivatives of the metals have been undertaken, based in part on the availability of alkali-metal salts of pentaphenylcyclopentadiene.[4,5] Compared to η^5-Cp and η^5-C_5Me_5, the η^5-C_5Ph_5 ligand appears to be an electron-withdrawing substituent[6] and imparts enhanced kinetic stability to metal derivatives, presumably due to its large volume.[7] In contrast, no reports have yet appeared in the literature concerning (η^5-pentabenzylcyclopentadienyl)metal compounds, although such systems might also be anticipated to exhibit chemical and physical properties different from their η^5-Cp analogues.

In this paper, we describe the formation and properties of the first η^5-pentabenzylcyclopentadienyl derivatives of the transition metals,[8] (η^5-C_5Bz_5)$Co(CO)_2$ (3) and (η^5-C_5Bz_5)$Rh(CO)_2$ (4), as well as an improved procedure for the synthesis of the parent organic compound pentabenzylcyclopentadiene (1). For comparative purposes, the η^5-pentaphenylcyclopentadienyl analogues (η^5-C_5Ph_5)$Co(CO)_2$ (5) and (η^5-C_5Ph_5)$Rh(CO)_2$ (6) derived from pentaphenylcyclopentadiene (2) have also been prepared. In order to investigate steric effects in these very bulky organometallic compounds, single-crystal X-ray diffraction studies on 3 and 5 have been undertaken.

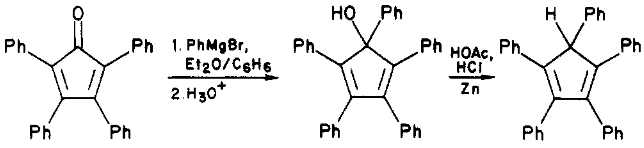
Results and Discussion

Synthetic and Spectral Studies. The synthesis of pentabenzylcyclopentadiene developed during this study is a modification of the original preparation reported by Hirsch and Bailey.[9] After our first few attempts at this synthesis failed, we found it was crucial to predry the benzyl alcohol and the diisopropylbenzene. After the reaction was completed and the solvent removed by distillation, the original preparation called for vacuum distillation of the product at ca. 250–275 °C (0.8 mmHg) from a Claisen flask.[9] We found that this step was very tedious and unnecessary and that trituration of the reaction residue with methanol would dissolve enough of the impurities to allow the product to solidify. The crude product could then be further purified by recrystallization from methanol to give 1 in 28% yield.



1

We have synthesized pentaphenylcyclopentadiene by a modification of the earlier methods of Ziegler and Schnell[10] and Slocum and co-workers.[5] The preparation involves a two-step procedure starting with tetraphenylcyclopentadienone. The first step proceeded in a straightforward manner and produced pentaphenylcyclopentadien-1-ol in 62% yield after recrystallization. Attempts to improve the yield of this step by utilizing phenyllithium were not successful, and the desired product was not obtained.



2

Subsequent reduction of the carbinol with hydroiodic and hypophosphoric acids in glacial acetic acid solution[5] was unsuccessful in our hands, since the color and melting point of the reduction product were inconsistent with those reported for 2. An alternative approach using zinc dust in glacial acetic acid and concentrated hydrochloric acid at reflux was successful, and 2 could be obtained in 66% yield after recrystallization from xylene. While the melting point of 2 obtained in this manner (242–248 °C) was virtually identical with the original melting point reported by Ziegler and Schnell (244–248 °C),[10] we subsequently noted that use of 2 at this level of purity resulted in lower yields of organometallic derivatives and increased purification problems. However, we found that further purification of the product by Soxhlet extraction with hexane followed by recrystallization from 1:1 heptane/toluene gave 2 as light yellow crystals, mp 251–252 °C, and this material was used in subsequent experiments.

Both 1 and 2 were readily converted to their lithium and sodium salts, respectively. The most successful synthesis of (pentabenzylcyclopentadienyl)lithium (7) involved a reaction between 1 and *n*-butyllithium in THF solution at 0 °C.[11] Under these conditions, the metalation reaction

$$1 + n\text{-BuLi} \xrightarrow{\text{THF, 0 °C}} \underset{7}{C_5Bz_5Li} + n\text{-BuH}$$

took place relatively rapidly, and THF solutions of 1 became deep red almost immediately upon addition of the *n*-butyllithium.

Tsutsui and co-workers reported the formation of (pentaphenylcyclopentadienyl)sodium (8) from a reaction of 2 and sodium metal in refluxing toluene.[4] We have found that both sodium hydride and sodium amide in refluxing toluene are more convenient and satisfactory for the generation of 8. A reaction between 2 and sodium amide, for example, produced 8 in 84% yield. The air-sensitive product was isolated and purified by filtration on a frit under nitrogen, followed by washing with dry hexane and drying in vacuo.

$$2 + NaNH_2 \xrightarrow[\Delta]{\text{toluene}} \underset{8}{C_5Ph_5Na} + NH_3$$

The synthesis of the cobalt complexes 3 and 5 were modeled after the procedure developed by Rausch and

---

[1] (a) University of Massachusetts. (b) University of Alabama. (c) Present address: Lehigh University, Bethlehem, PA.

[2] King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.

[3] (a) Miller, E. J.; Landon, S. J.; Brill, T. B. *Organometallics* **1985**, *4*, 533. (b) Calabro, D. C.; Hubbard, J. L.; Blevins, C. H., II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6389. Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. King, R. B. *Coord. Chem. Rev.* **1976**, *20*, 155. See also references cited therein.

[4] Zhang, R.; Tsutsui, M.; Bergbreiter, D. E. *J. Organomet. Chem.* **1982**, *229*, 109.

[5] Slocum, D. W.; Duraj, S.; Matusz, M.; Cmarik, J. L.; Simpson, K. M.; Owen, D. A. *Abstr. Pap.—Am. Chem. Soc.* **1983**, *186th*, PMSE 75; *Metal-Containing Polymeric Systems*; Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Jr., Eds.; Plenum: New York, 1985; p 59.

[6] Broadley, K.; Lane, G. A.; Connelly, N. G.; Geiger, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 2486.

[7] Heeg, M. J.; Janiak, C.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4259.

[8] Decabenzylgermanocene, -stannocene, and -plumbocene have also been synthesized and their structures established by X-ray methods: Chambers, J. W.; Heeg, M. J.; Janiak, C.; Rausch, M. D.; Schumann, H.; Zuckerman, J. J. *Abstr. Pap.—Am. Chem. Soc.* **1985**, *189th*, INOR 24.

[9] Hirsch, S. S.; Bailey, W. J. *J. Org. Chem.* **1978**, *43*, 4090.

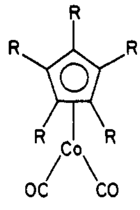
[10] Zieger, K.; Schnell, B. *Justus Liebigs Ann. Chem.* **1925**, *445*, 266.

[11] This method was originally developed by C. Janick and J. J. Zuckerman (personal communication, 1984).

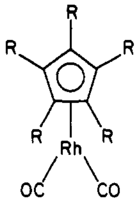
Table I. Crystal Data for $[(C_5Bz_5)Co(CO)_2]$ (3) and $[(C_5Ph_5)Co(CO)_2]$ (5)

	3	5
compd	$CoO_2C_{42}H_{35}$	$CoO_2C_{37}H_{25}$
mol wt	630.7	560.55
space group	$P2_1/n$	*Pbca*
cell constants		
a, Å	12.753 (7)	13.66 (1)
b, Å	14.877 (8)	20.44 (4)
c, Å	18.28 (1)	20.600 (5)
β, deg	108.58 (5)	...
cell vol, $Å^3$	3287 (1)	5752 (1)
molecules/unit cell (*Z*)	4	8
ρ(calcd), g cm^{-3}	1.28	1.30
μ(calcd), cm^{-1}	5.55	6.26
radiation	Mo Kα	Mo Kα
max cryst dimens, mm	0.5 × 0.5 × 0.5	1.0 × 1.0 × 1.0
scan width, deg	$0.8 + 0.2 \tan \theta$	$0.8 + 0.2 \tan \theta$
std reflctns	600, 060, $00\overline{10}$	800, 080, $00\overline{10}$
decay of stds.	<1%	<2%
reflctns measd	3714	3198
hkl range	0–12, 0–14, −17–17	0–13, 0–19, 0–19
2θ range, deg	2–40	2–40
obsd reflctns ($I > 2\sigma(I)$)	2398	1779
no. of parameters varied	406	211
GOF	1.36	2.9
R	0.042	0.054
R_w	0.041	0.056

Genetti for the synthesis of $(\eta^5\text{-}C_5H_4R)Co(CO)_2$ (R = H, $SiMe_3$, Ph).[12] Initial attempts to form 3 via the conventional method of stirring the reactants 1 and $Co_2(CO)_8$ in methylene chloride at reflux gave 3 in only very low yield (2%). Use of refluxing toluene as the solvent did afford 3 in 65% yield, however. A similar reaction between 2 and $Co_2(CO)_8$ in refluxing toluene likewise produced 5. The yield of 5 following purification by column chromatography and crystallization was very low (9%), although no attempt was made to optimize the conditions. Both 3 and 5 were characterized by elemental analyses as well as by their ^1H NMR, IR, and mass spectra.



3, R = Bz
5, R = Ph



4, R = Bz
6, R = Ph

A second product (air-sensitive, dark green) was obtained in low yield from the reaction between 1 and $Co_2(CO)_8$. Preliminary characterization of the freshly chromatographed solution by IR spectroscopy indicated that the compound possessed both terminal and bridging carbonyl groups (ν_{CO} = 1955 and 1815 cm^{-1}). These carbonyl stretching frequencies are very similar to those found in the corresponding cyclopentadienylcobalt dimer complex $[(\eta^5\text{-}C_5H_5)Co(CO)]_2(\mu\text{-}CO)$ (ν_{CO} = 1965, 1814 cm^{-1})[13] and suggest that our product has a similar structure. Further characterization studies are currently in progress.

$(\eta^5$-Pentaphenylcyclopentadienyl)dicarbonylrhodium (6) has been produced by the reaction of 8 and $[Rh(CO)_2Cl]_2$ in refluxing THF solution. The low yield (13%) of 6 obtained in this reaction may be due to the use of a basic solvent such as THF.[5] The corresponding pentabenzyl analogue 4 was formed from a reaction between 7 and $[Rh(CO)_2Cl]_2$ in THF solution at 0 °C. Both 4 and 6 were characterized by elemental analysis as well as by their ^1H NMR, IR, and mass spectra.

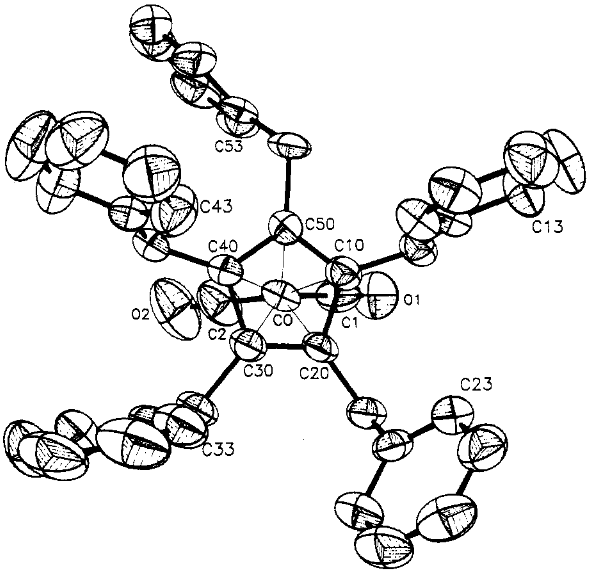


Figure 1. Labeling of atoms in $(\eta^5\text{-}C_5Bz_5)Co(CO)_2$. Benzyl atoms are numbered sequentially after the cyclopentadienyl carbon to which they are bonded. The ORTEP diagram shows 50% probability thermal vibrational ellipsoids.

A second product (air-sensitive, dark blue) was also obtained from the reaction between 7 and $[Rh(CO)_2Cl]_2$. IR spectral analysis of the freshly chromatographed product indicated both terminal and bridging carbonyl groups at 1960 and 1815 cm^{-1}, respectively. When attempts were made to purify the compound via crystallization, the resulting deep blue solid exhibited an IR spectrum that possessed only a single weak carbonyl stretch at 1735 cm^{-1}. The initially formed product appears to be similar to the pentamethylcyclopentadienyl analogue $[(\eta^5\text{-}C_5Me_5)Rh(CO)]_2(\mu\text{-}CO)$,[14] whereas the product after attempted crystallization is reminiscent of the novel dinuclear complex $[(\eta^5\text{-}C_5Me_5)Rh(CO)]_2$.[14-16] Further

---

[12] Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *38*, 3888.

[13] Vollhardt, K. P. C.; Bercaw, J. E.; Bergman, R. G. *J. Organomet. Chem.* **1975**, *97*, 283.

[14] Herrmann, W. A.; Plank, J.; Bauer, C.; Ziegler, M. L.; Guggolz, E.; Alt, R. *Z. Anorg. Allg. Chem.* **1982**, *487*, 85.

[15] Nutton, A.; Maitlis, P. M. *J. Organomet. Chem.* **1979**, *166*, C21.

Table II. Final Atomic Coordinates for 3

atom	*x/a*	*y/b*	*z/c*
Co	0.79476 (6)	0.33262 (5)	0.65751 (4)
C(1)	0.8196 (5)	0.4379 (5)	0.6960 (4)
O(1)	0.8376 (4)	0.5098 (3)	0.7209 (3)
C(2)	0.6822 (6)	0.3130 (5)	0.6804 (4)
O(2)	0.5994 (5)	0.2954 (4)	0.6936 (3)
C(10)	0.9369 (4)	0.3185 (4)	0.6302 (3)
C(20)	0.8439 (4)	0.3272 (4)	0.5587 (3)
C(30)	0.7735 (4)	0.2559 (4)	0.5577 (3)
C(40)	0.8202 (4)	0.2020 (4)	0.6273 (3)
C(50)	0.9222 (4)	0.2406 (4)	0.6694 (3)
C(11)	1.0389 (4)	0.3777 (4)	0.6546 (3)
C(12)	1.1368 (4)	0.3384 (4)	0.6374 (3)
C(13)	1.2356 (6)	0.3849 (4)	0.6608 (4)
C(14)	1.3265 (6)	0.3513 (6)	0.6456 (5)
C(15)	1.3223 (6)	0.2724 (6)	0.6059 (4)
C(16)	1.2252 (6)	0.2256 (4)	0.5825 (3)
C(17)	1.1343 (5)	0.2586 (4)	0.5987 (3)
C(21)	0.8282 (4)	0.4014 (4)	0.4998 (3)
C(22)	0.8725 (5)	0.3801 (4)	0.4348 (3)
C(23)	0.9828 (5)	0.3864 (4)	0.4428 (3)
C(24)	1.0227 (5)	0.3669 (4)	0.3830 (4)
C(25)	0.9506 (7)	0.3387 (5)	0.3116 (4)
C(26)	0.8418 (7)	0.3329 (5)	0.3035 (3)
C(27)	0.8014 (5)	0.3529 (5)	0.3623 (4)
C(31)	0.6603 (4)	0.2373 (4)	0.4980 (3)
C(32)	0.6553 (5)	0.1540 (4)	0.4519 (3)
C(33)	0.7309 (6)	0.1355 (5)	0.4159 (4)
C(34)	0.7229 (8)	0.0598 (7)	0.3700 (4)
C(25)	0.636 (1)	0.0017 (7)	0.3611 (5)
C(36)	0.5618 (9)	0.0190 (7)	0.3978 (6)
C(37)	0.5696 (6)	0.0939 (5)	0.4421 (3)
C(41)	0.7732 (4)	0.1151 (4)	0.6441 (3)
C(42)	0.8312 (5)	0.0336 (4)	0.6261 (3)
C(43)	0.9153 (6)	0.0380 (4)	0.5957 (4)
C(44)	0.9699 (6)	−0.0380 (6)	0.5832 (4)
C(45)	0.9392 (8)	−2.1198 (6)	0.6000 (5)
C(46)	0.8567 (9)	−0.1262 (5)	0.6296 (5)
C(47)	0.8002 (7)	−0.0505 (6)	0.6418 (4)
C(51)	1.0079 (4)	0.2026 (4)	0.7426 (3)
C(52)	0.9663 (4)	0.1667 (5)	0.8036 (3)
C(53)	0.9121 (5)	0.2194 (5)	0.8412 (4)
C(54)	0.8776 (6)	0.1842 (7)	0.9011 (4)
C(55)	0.8991 (7)	0.0962 (8)	0.9231 (4)
C(56)	0.9537 (7)	0.0443 (5)	0.8859 (5)
C(57)	0.9865 (6)	0.0788 (5)	0.8260 (4)

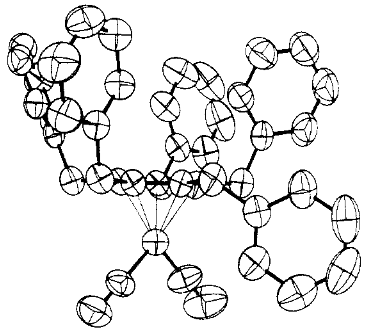


Figure 2. An alternative view of **3**, showing the orientation of the series 50 benzyl group.

Table III. Final Atomic Coordinates for 5

atom	*x/a*	*y/b*	*z/c*
Co	0.24131 (8)	0.14183 (5)	0.19154 (5)
C(1)	0.1890 (8)	0.0930 (6)	0.1309 (6)
O(1)	0.1548 (6)	0.0692 (5)	0.0883 (5)
C(2)	0.1289 (8)	0.1713 (6)	0.2117 (5)
O(2)	0.0545 (6)	0.1936 (5)	0.2235 (5)
C(10)	0.3562 (5)	0.2097 (4)	0.1944 (4)
C(11)	0.3574 (6)	0.2742 (4)	0.1634 (4)
C(12)	0.3125 (6)	0.2842 (4)	0.1028 (4)
C(13)	0.3215 (7)	0.3437 (4)	0.0720 (5)
C(14)	0.3718 (7)	0.3937 (5)	0.0990 (5)
C(15)	0.4152 (7)	0.3861 (5)	0.1598 (4)
C(16)	0.4076 (6)	0.3253 (4)	0.1908 (5)
C(20)	0.3895 (6)	0.1508 (4)	0.1638 (4)
C(21)	0.4398 (5)	0.1466 (4)	0.1003 (4)
C(22)	0.4194 (6)	0.0987 (4)	0.0553 (4)
C(23)	0.4724 (7)	0.0951 (5)	−0.0011 (5)
C(24)	0.5449 (7)	0.1389 (5)	−0.0132 (5)
C(25)	0.5656 (7)	0.1868 (5)	0.0296 (5)
C(26)	0.5158 (6)	0.1904 (4)	0.0877 (4)
C(30)	0.3770 (5)	0.0980 (4)	0.2098 (3)
C(31)	0.4082 (6)	0.0289 (4)	0.1982 (4)
C(32)	0.3420 (7)	−0.0220 (4)	0.1982 (4)
C(33)	0.3761 (8)	−0.0870 (5)	0.1871 (5)
C(34)	0.4688 (8)	−0.0967 (6)	0.1780 (5)
C(35)	0.5355 (8)	−0.0497 (5)	0.1775 (5)
C(36)	0.5056 (7)	0.0160 (5)	0.1880 (5)
C(40)	0.3399 (5)	0.1235 (4)	0.2683 (4)
C(41)	0.3256 (6)	0.0867 (4)	0.3297 (4)
C(42)	0.3995 (7)	0.0481 (4)	0.3541 (4)
C(43)	0.3878 (8)	0.0117 (5)	0.4118 (5)
C(44)	0.2991 (7)	0.0142 (5)	0.4423 (5)
C(45)	0.2260 (7)	0.0518 (4)	0.4200 (4)
C(46)	0.2384 (7)	0.0880 (4)	0.3636 (4)
C(50)	0.3245 (6)	0.1927 (3)	0.2589 (4)
C(51)	0.2969 (5)	0.2398 (4)	0.3109 (4)
C(52)	0.3440 (6)	0.2375 (4)	0.3700 (4)
C(53)	0.3231 (7)	0.2826 (4)	0.4181 (5)
C(54)	0.2524 (8)	0.3294 (5)	0.4073 (5)
C(55)	0.2048 (7)	0.3327 (5)	0.3499 (5)
C(56)	0.2276 (6)	0.2879 (4)	0.3012 (4)

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

Bond Distances			
Co–C(1)	1.705 (7)	Co–C(2)	1.644 (7)
Co–C(10)	2.038 (5)	Co–C(20)	2.093 (5)
Co–C(30)	2.095 (5)	Co–C(40)	2.074 (5)
Co–C(50)	2.083 (5)	C(1)–O(1)	1.156 (7)
C(2)–O(2)	1.185 (7)	Co–Cent	1.686 (6)
Bond Angles			
C(1)–Co–C(2)	96.0 (3)	Co–C(1)–O(1)	178.5 (6)
Co–C(2)–O(2)	176.2 (7)	Cent–Co–C(1)	132.6 (3)
Cent–Co–C(2)	130.4 (3)	C(10)–C(11)–C(12)	114.0 (4)
C(20)–C(21)–C(22)	114.3 (4)	C(30)–C(31)–C(32)	114.5 (5)
C(40)–C(41)–C(42)	113.1 (5)	C(50)–C(51)–C(52)	117.5 (4)

structural studies on these new dinuclear complexes are currently in progress.

X-ray Crystallographic Studies. The X-ray structural study demonstrates that crystals of **3** consist of discrete molecules of (η^5-C_5Bz_5)Co(CO)$_2$, separated by normal van der Waals distances. Selected interatomic distances and angles are presented in Table IV. Figure 1 shows the scheme used in labeling the atoms, while Figure 2 shows an alternative view of the molecule. The cobalt–cyclopentadienyl centroid distance is 1.69 Å, and the Co(CO)$_2$ moiety is seen to be situated such that its projection intersects the bonds between cyclopentadienyl carbons C(10)–C(20) and C(30)–C(40). The same orientation of the Co(CO)$_2$ fragment relative to the cyclopentadienyl ligand was found by Dahl[21] for (η^5-C_5Me_5)-Co(CO)$_2$, where the distance Co–centroid = 1.703 Å. In the latter compound, the noncylindrical field produced by the planar Co(CO)$_2$ moiety was found to differentiate the

---

(16) Bailey, W. I.; Collins, D. M.; Cotton, F. A. *J. Organomet. Chem.* **1979**, *165*, 373.

(17) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

(18) SHELX, a system of computer programs for X-ray structural studies by G. M. Sheldrick, University of Cambridge, Cambridge, England, 1976.

(19) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(20) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(21) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277.

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

Bond Distances			
Co–C(1)	1.71 (1)	Co–C(2)	1.70 (1)
Co–C(10)	2.096 (7)	Co–C(20)	2.112 (7)
Co–C(30)	2.093 (7)	Co–C(40)	2.112 (7)
Co–C(50)	2.073 (8)	C(1)–O(1)	1.15 (1)
C(2)–O(2)	1.14 (1)	Co–Cent	1.70 (1)
Bond Angles			
C(1)–Co–C(2)	89.5 (5)	Co–C(1)–O(1)	177 (1)
Co–C(2)–O(2)	177 (1)	Cent–Co–C(1)	135.1 (6)
Cent–Co–C(2)	134.3 (6)		

cyclopentadienyl bonds by length: the bonds intersected by a carbonyl projection are relatively longer and those not intersected are shorter. The same situation is encountered in 3, where C(10)–C(20) = 1.463 (6) Å and C(30)–C(40) = 1.460 (7) Å (longer, intersected bonds) and C(20)–C(30) = 1.386 (7) Å, C(40)–C(50) = 1.407 (7) Å, and C(10)–C(50) = 1.407 (7) Å (shorter, nonintersected bonds). The cyclopentadienyl fragment is planar to within 0.02 Å, and the methylene carbons of the benzyl groups are not coplanar: C(21) and C(31) are below the plane (0.01 and 0.07 Å, respectively) and toward the cobalt atom, and C(11), C(41), and C(51) are above the plane (0.07, 0.09, and 0.15 Å, respectively). The large deviation from planarity by C(51) is caused by the unique orientation of this benzyl substituent. From Figure 2 it is seen that four of the phenyls of the benzyl groups are situated above the cyclopentadienyl ring and away from the Co(CO)$_2$ moiety, while one phenyl ring, belonging to the series 50 benzyl, is in an orientation below the cyclopentadienyl plane and approaching the cobalt dicarbonyl. Steric rather than electronic[22] effects are thought to cause this effect, since the nonbonding contact between C(12) and C(42) is 0.41 Å shorter than the closest nonbonding approach of similar, nonadjacent phenyl carbons: i.e., the "gap" between C(12) and C(32) is 6.59 Å and accommodates the series 20 phenyl ring; the "gap" between C(22) and C(42) is 6.35 Å and accommodates the series 30 phenyl; the "gap" between C(12) and C(42) is 5.94 Å and precludes placement of the series 50 phenyl between series 10 phenyl and series 40 phenyl. A stereoscopic packing diagram for 3 is included in the supplementary material.

Solution of the X-ray structural data for 5 demonstrates that discrete molecules of (η^5-C$_5$Ph$_5$)Co(CO)$_2$ exist in the crystal separated by normal van der Waals distances. Selected interatomic distances and angles are presented in Table V. Figure 3 shows the scheme used in labeling the atoms and illustrates the difference in placement of the cyclopentadienyl ligand relative to the Co(CO)$_2$ moiety in 3 and 5. The Co–centroid distance is 1.70 Å and is comparable to the Co–centroid distances in the pentabenzyl compound (1.69 Å) and the pentamethyl compound (1.703 Å). A nonequivalence of cyclopentadienyl bonds is apparent, however, when a comparison is made of cyclopentadienyl bonds intersected and not intersected by the Co(CO)$_2$ projection. The intersected bond, C(20)–C(30) = 1.45 (1) Å, is again relatively longer than the four nonintersected bonds, C(10)–C(20) = 1.43 (1) Å, C(30)–C(40) = 1.41 (1) Å, C(10)–C(50) = 1.44 (1) Å, and C(40)–C(50) = 1.44 (1) Å, although the accuracy of the structural determination precludes mathematical significance. The cyclopentadienyl ring is planar to within 0.02 Å, and the phenyl ipso carbons are above this plane and away from the cobalt atom an average of 0.11 Å, ranging from 0.02 to 0.19 Å. The phenyl substituents are arranged in a paddlewheel orientation and canted relative to the cyclopentadienyl frame an average of 55.8°, ranging from 50.4° to 68.2°. In contrast, the twist angles in (η^3-C$_3$Ph$_3$)Co(CO)$_3$ range from 2.9° to 23.5° and those[24] of (η^4-C$_4$Ph$_4$)Co(η^5-C$_5$H$_5$) range from 31.6° to 41.7°. The steric crowding caused by five phenyl substituents increases the twist angle of 5 relative to the triphenyl and tetraphenyl complexes. A stereoscopic packing diagram for 5 is included in the supplementary material.

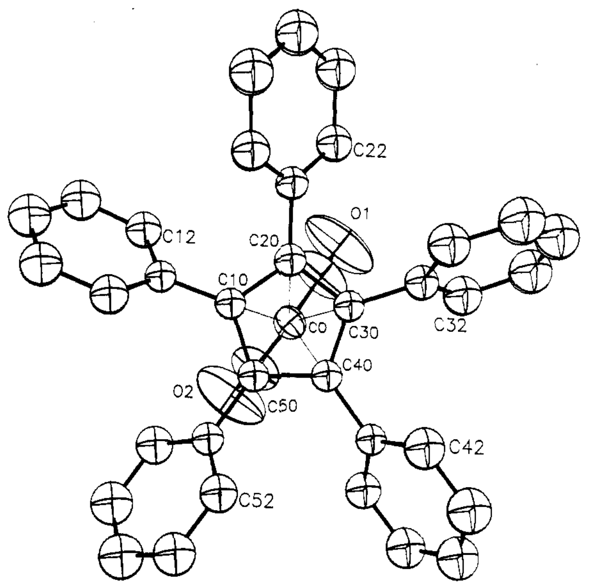


Figure 3. Labeling of atoms in (η^5-C$_5$Ph$_5$)Co(CO)$_2$. The numbering scheme is similar to that in Figure 1.

The precision of the data collection does not allow an absolute assignment of the relative electron-withdrawing properties of the pentabenzyl- and pentaphenylcyclopentadienyl ligands (compared to pentamethylcyclopentadienyl) as evidenced by the carbonyl carbon to oxygen bond distances. Relevant bond distances are as follows: C(1)–O(1) = 1.156 (7) Å and C(1)–O(2) = 1.185 (7) Å for 3, C(1)–O(1) = 1.14 (1) Å and C(2)–O(2) = 1.15 (1) Å for 5, and C(1)–O(1) = 1.137 (6) Å and C(2)–O(2) = 1.134 (6) Å for related distances in the pentamethylcyclopentadienyl complex.

Experimental Section

All operations were carried out under a nitrogen atmosphere by using Schlenk tube techniques except where specified. The nitrogen was deoxygenated with BTS catalyst and dried with sulfuric acid and molecular sieves (4 A). IR spectra were recorded on a Perkin-Elmer Model 1310 infrared spectrophotometer. ^{1}H NMR spectra were recorded on Varian A-60 or XL-300 spectrometers. Mass spectra were recorded on a Perkin-Elmer Hitachi RMU 6L spectrometer. Melting points were obtained in sealed capillaries under nitrogen and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA 01003. Chromatography columns were packed dry under nitrogen by using 5% deactivated and deoxygenated neutral grade alumina. Benzene, pentane, hexane, toluene, and methylene chloride were dried over calcium hydride and then distilled under argon. Ethyl ether and tetrahydrofuran (THF) were predried over sodium and distilled under argon from sodium–benzophenone. Dicyclopentadiene (95%) and tetraphenylcyclopentadienone were ob-

---

[22] The closest approach of the series 50 benzyl to the cobalt atom is 3.627 (6) Å. See: Bleeke, J. R.; Burch, R. R.; Coulman, C. L.; Schardt *Inorg. Chem.* **1981**, *20*, 1316 for an example of "allylic-like" bonding of a benzyl ligand.

[23] Chiang, T.; Kerber, R. C.; Kimball, S. D.; Halpern, J.; Riley, D. P.; Chan, A. S. *Inorg. Chem.* **1979**, *18*, 1687.

[24] Rausch, M. D.; Westover, G. F.; Mintz, E.; Reisner, G. M.; Bernal, I.; Clearfield, A.; Troup, J. M. *Inorg. Chem.* **1979**, *18*, 2605.

tained from Aldrich Chemical Co., whereas sodium amide (97%) was obtained from Morton Thiokol, Inc., Alfa Products. Diisopropylbenzene (Pfaltz and Brauer, mixture of isomers) and bromobenzene (Aldrich) were stirred overnight with calcium hydride and filtered before use. Benzyl alcohol (Aldrich) was refluxed over calcium oxide for 2 h and then distilled. $Co_2(CO)_8$ was obtained from Strem Chemicals, Inc., while $[Rh(CO)_2Cl]_2$ was prepared by a literature method.

Pentabenzylcyclopentadiene (1). A 1000-mL three-necked flask (with a fourth opening to accommodate a ground glass thermometer) was equipped with an overhead paddle stirrer, ground glass thermometer, gas inlet valve (with a 24/40 standard taper opening stoppered with a glass stopper), and a Dean-Stark trap attached to a reflux condenser. The latter was connected to a mercury overpressure valve. After the system was evacuated and back-flushed with nitrogen three times, it was charged with 313.9 g (2.90 mol) of dried benzyl alcohol. Stirring was initiated, and 23.0 g (1.00 mmol) of sodium metal, cut into small pieces, was carefully added. Upon addition, the mixture became cloudy with warming. Stirring was continued for 1.5 h with heating if necessary to maintain a temperature of ca. 80 °C until all the sodium was consumed. Then 250 mL of dry diisopropylbenzene was added, followed by a solution of 6.9 g (0.05 mol) of 95% dicyclopentadiene in 50 mL of diisopropylbenzene. The mixture was heated at reflux so as to maintain a temperature of ca. 200 °C. After 30 h of refluxing at this temperature, the mixture consisted of a thick viscous white solution, and ca. 8 mL of water had collected in the Dean–Stark trap. After being cooled the reaction mixture was extracted from the flask with ca. 500 mL of benzene, and the extracts were washed twice with 250-mL portions of water and dried over anhydrous magnesium sulfate. The benzene was removed by atmospheric distillation, leaving ca. 250 mL of an orange oil. The latter was subsequently vacuum distilled at ca. 80 °C (0.5 torr), leaving ca. 90 mL of a viscous orange residue. To the residue was added 80 mL of methanol, and the mixture was stirred via an overhead paddle stirrer for 3 h. During this period, the crude product began to coagulate as an off-white solid. The methanol was decanted, and the crude product was triturated with heating in 250 mL of fresh methanol. After being cooled, the product was recrystallized from additional fresh methanol. White crystals formed which were collected by suction filtration and dried overnight under high vacuum, affording 14.3 g (28%) of product, mp 68–70 °C (lit.[9] 69.2–75.7 °C).

Pentaphenylcyclopentadien-1-ol. A 500-mL, three-necked flask was equipped with a gas inlet valve, a pressure-equalizing addition funnel, a magnetic stirring bar, and a reflux condenser which was connected to a mercury overpressure valve. After the system was evacuated and back-flushed with nitrogen three times, it was charged with 10.0 g (0.026 mol) of tetraphenylcyclopentadienone followed by 150 mL of dry benzene. A solution of phenylmagnesium bromide, prepared from 1.2 g (0.05 mol) of magnesium and 8.16 g (0.052 mol) of dry bromobenzene in ca. 50 mL of dry ethyl ether, was transferred via a cannula to the addition funnel and added dropwise with stirring. When ca. two-thirds of the reagent had been added, the deep violet color of solution faded into orange-yellow. After the addition was complete, the reaction mixture was allowed to stir for 2 h, followed by the dropwise addition of 100 mL of 1 M sulfuric acid. The mixture was transferred to a 1000-mL separatory funnel, and the aqueous layer was drawn off and discarded. The organic layer was washed twice with 100-mL portions of water and subsequently dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by rotary evaporation at water aspirator pressure, leaving a yellow residue. Rotary evaporation was continued for 1 h under high vacuum to remove unreacted bromobenzene. The residue was dissolved in 500 mL of 1:1 heptane/*n*-propanol solution with mild heating. Upon cooling, the resulting crystals which had formed were collected by suction filtration, washed with additional cold 1:1 heptane/*n*-propanol solution, and air-dried, affording 7.44 g (62%) of product as fine yellow crystals, mp 176–178 °C (lit.[10] mp 175–176 °C).

Pentaphenylcyclopentadiene (2). A 500-mL, three-necked flask was equipped with an overhead paddle stirrer and reflux condenser. Pentaphenylcyclopentadien-1-ol (10.0 g, 0.0216 mol) was placed in the flask and suspended in 200 mL of glacial acetic acid. The mixture was heated to reflux with stirring. Once the starting material had dissolved, a pressure-equalizing addition funnel was attached to the third neck of the flask. Concentrated hydrochloric acid (10 mL) was carefully added dropwise over a 30-min period, causing the solution to become orange with vigorous refluxing. The mixture was allowed to reflux an additional 1.5 h, followed by the addition of 5.64 g (0.0864 mol) of zinc dust, which resulted in a yellow reaction mixture and gas evolution. After an additional 2-h reflux period, the mixture was allowed to cool and the solvent removed by rotary evaporation over a steam bath. The resulting residue was dissolved in 500 mL of hot xylene and filtered hot. The filtrate was allowed to cool to room temperature and crystals began forming within 1 h. The product was collected by suction filtration and dried in a vacuum drying oven, affording 6.43 g (66%) of product as fine pale yellow crystals, mp 242–248 °C (lit.[10] mp 244–246 °C). Pentaphenylcyclopentadiene can be further purified by Soxhlet extraction with hexane for 48 h, followed by recrystallization of the resulting precipitated solid from 1:1 heptane/toluene, mp 251–252 °C.

(η^5-Pentabenzylcyclopentadienyl)dicarbonylcobalt (3). A 500-mL, three-necked flask was equipped with a magnetic stirring bar, gas inlet value, and a reflux condenser connected to a mercury overpressure valve. After the system was evacuated and back-flushed with nitrogen three times, 6.92 g (0.0134 mol) of pentabenzylcyclopentadiene and 150 mL of dry toluene were added. Dicobalt octacarbonyl (2.24 g, 0.0065 mol) was subsequently added under nitrogen. Upon addition, the mixture became dark red, and was heated with stirring at gentle reflux for 12 h, during which time it became olive green. Refluxing was continued for an additional 12 h, after which time the reaction mixture was cooled to room temperature and transferred to a Schlenk tube, and the solvent was removed by high vacuum. The residue was adsorbed onto ca. 10 g of 5% deactivated alumina and placed on a 1.5 × 30 cm column packed dry with 5% deactivated alumina under nitrogen. Elution with dry hexane removed a light yellow band which contained a small amount of unreacted pentabenzylcyclopentadiene. Continued elution with 4:1 pentane/benzene removed an orange band which upon cooling to −20 °C for 48 h produced orange-red needles. The mother liquor was decanted, concentrated, and recooled to −20 °C to yield additional crops of crystals, affording altogether 5.47 g (67%) of product, mp 131–133 °C. The crystals when dried under high vacuum appeared to be air-stable for several weeks, although slow decomposition was noted after this period: ^1H NMR ($CDCl_3$) δ 3.54 (10 H, s, CH_2), 6.9–7.2 (25 H, m, C_6H_5); IR (pentane) ν_{CO} 2020, 1960 cm^{-1}; MS, *m/e* 630 (M^+). Anal. Calcd for $C_{42}H_{35}CoO_2$: C, 79.99; H, 5.59. Found: C, 80.02; H, 5.64.

Further elution of the column with 2:1 ethyl ether/benzene developed a deep green band. After elution, this fraction was also cooled at −20 °C for several days to afford ca. 250 mg of a deep green, air-sensitive solid: IR (C_6H_6) ν_{CO} 1955, 1815 cm^{-1}.

(η^5-Pentaphenylcyclopentadienyl)dicarbonylcobalt (5). Using the same reaction apparatus as described above, the system was charged with 3.5 g (7.8 mmol) of pentaphenylcyclopentadiene, 250 mL of dry toluene, and 1.3 g (3.8 mmol) of dicobalt octacarbonyl. After 24 h at reflux, the solvent was removed and the residue was adsorbed onto ca. 3 g of deactivated alumina and was chromatographed on a 2.5 × 50 cm alumina column. Elution with 1:1 pentane/benzene produced a red band which was collected, and the solvent removed. The residue was redissolved in a minimum amount of dry methylene chloride and ca. 25 mL of dry hexane was carefully layered above it. After the mixture was left standing at room temperature for 48 h, small purple crystals formed at the interface, resulting in 0.40 g (9%) of product: mp 189–196 °C dec; ^1H NMR ($CDCl_3$) δ 7.2 (m, Ph); IR (KBr) 2000, 1945 cm^{-1} (m, ν_{CO}); MS, *m/e* 560 (M^+). Anal. Calcd for $C_{37}H_{25}CoO_2$: C, 79.28; H, 4.49. Found: C, 79.14; H, 4.34.

(η^5-Pentabenzylcyclopentadienyl)dicarbonylrhodium (4). A 500-mL, three-necked flask was equipped with a gas inlet valve, a magnetic stirring bar, and a reflux condenser connected to a mercury overpressure valve. The flask was flushed several times with nitrogen followed by the addition of 1.50 g (2.90 mmol) of pentabenzylcyclopentadiene and 75 mL of dry THF. The solution was cooled to ca. 0 °C with stirring, and 2.0 mL of 1.5 M *n*-butyllithium in hexane (3.0 mmol) was added via a syringe. The reaction mixture turned dark red upon addition and was allowed to stir for an additional 30 min at 0 °C. $[Rh(CO)_2Cl]_2$ (0.57 g, 1.46 mmol) was then added under nitrogen. Upon addition, the solution became blue-green. The reaction mixture was stirred for 24 h, during which time it was allowed to warm to room temperature. After removal of the solvent, the residue was adsorbed onto ca. 2 g of 5% deactivated alumina and chromatographed as described above. Elution with ca. 250 mL of dry hexane removed unreacted starting material, while elution with 3:1 dry pentane/toluene developed an orange band. The latter was concentrated to approximately one-half volume and cooled at −20 °C for 3 days to produce 465 mg (24%) of 4 as bright orange crystals: mp 88–90 °C; ^{1}H NMR ($CDCl_3$) δ 3.67 (10 H, s, CH_2), 6.9–7.2 (25 H, m, C_6H_5); IR (pentane) ν_{CO} 2030, 1970 cm^{-1}; MS, *m/e* 674 (M^+). Anal. Calcd for $C_{42}H_{35}O_2Rh$: C, 74.77; H, 5.23. Found: C, 74.88; H, 5.02.

Further elution of the column with 3:1 dry toluene/ether developed a blue band which was collected. The solution was concentrated to ca. one-fourth volume and cooled at −20 °C for 5 days, producing 50 mg of deep blue crystals: mp 214–216 °C; ^{1}H NMR ($CDCl_3$) δ 3.51 (10 H, s, CH_2), 6.86 (10 H, q, Ar), 7.06 (15 H, t, Ar); IR (pentane) ν_{CO} 1960, 1815 cm^{-1}; MS, *m/e* 1292 ($(M - CO)^+$). Anal. Calcd for $C_{83}H_{70}O_3Rh_2$: C, 75.44; H, 5.34. Found: C, 74.89; H, 5.55.

(Pentaphenylcyclopentadienyl)sodium (8). A 500-mL, three-necked flask equipped as above was purged with dry nitrogen. Pentaphenylcyclopentadiene (1.30 g, 2.91 mmol), sodium amide (0.11 g, 2.82 mmol), and 100 mL of dry toluene were added, and the mixture was heated to gentle reflux with stirring. The mixture gradually became red, and evolution of ammonia was observed. After 24 h, the mixture was allowed to cool to room temperature, and a white precipitate formed. The solid was collected on a frit under nitrogen, was washed with dry pentane until the washings were clear, and was dried under high vacuum to afford 1.11 g (84%) of 8 as a fine white, air-sensitive powder.

(η^5-Pentaphenylcyclopentadienyl)dicarbonylrhodium (6). A reaction apparatus analogous to that described above was purged with dry nitrogen, followed by the addition of 0.96 g (2.1 mmol) of (pentaphenylcyclopentadienyl)sodium, 0.40 g (1.03 mmol) of $[Rh(CO)_2Cl]_2$, and 150 mL of dry THF. Upon heating to reflux, the reaction mixture became dark brown. After 24 h, the mixture was allowed to cool to room temperature, the solvent was removed in vacuo, and the residue was adsorbed onto ca. 2 g of deactivated alumina. The resulting solid was chromatographed on a 1.5 × 30 cm alumina column. Elution with hexane brought down a yellow band. Continued elution with pentane/benzene developed an orange band which was collected, concentrated, and cooled to −20 °C. Two crops of orange crystals amounting to 160 mg (13%) were obtained: mp 190–192 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.06 (m, C_6H_5); IR (KBr) ν_{CO} 2040, 1975 cm^{-1}; MS, *m/e* 604 (M^+). Anal. Calcd for $C_{37}H_{25}O_2Rh$: C, 73.52; H, 4.17. Found: C, 73.74; H, 4.38.

Further elution with 3:1 pentane/benzene developed a deep blue band. This product proved to be highly air-sensitive and was not further characterized.

Collection of X-ray Diffraction Data and Solution of Structure for $[(C_6H_5CH_2)_5C_5Co(CO)_2]$ (3). Single crystals of the air-sensitive compound were crystallized from 4:1 pentane/benzene and sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 24 accurately centered reflections are given in Table I.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the $\theta/2\theta$ scan technique as previously described.[17] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects.

Calculations were carried out with the SHELX system of computer programs.[18] Neutral atom scattering factors were taken from Cromer and Waber[19] for Co. Scattering factors stored within the SHELX program were used for other atoms. The scattering for Co was corrected for the real and imaginary effects of anomalous dispersion by using the compilations of Cromer and Liberman.[20] The position of the cobalt atom was located from a Patterson map, and subsequent difference Fourier maps revealed the remaining non-hydrogen atoms. Full-matrix least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.11$. Further refinement with anisotropic thermal parameters led to $R = 0.064$, and a difference Fourier map was used to locate the hydrogen atoms. Inclusion of these with fixed isotropic thermal parameters led to a final $R = 0.042$, and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2} = 0.041$. The final values of the positional parameters are given in Table II.

Collection of X-ray Diffraction Data and Solution of Structure for $[(C_6H_5)_5C_5Co(CO)_2]$ (5). Data collection and initial structure refinement proceed as for 3. Data collection parameters are given in Table I. Due to a paucity of data, only the $C_5Co(CO)_2$ moiety was refined anisotropically, and refinement converged at $R = 0.054$ and $R_w = 0.056$. The final values of the positional parameters are given in Table III.

Acknowledgment. We gratefully acknowledge research support from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank Larry Kool for assistance in obtaining some of the mass spectra and Johnson-Matthey, Inc., for a loan of rhodium trichloride.

Registry No. 1, 67209-29-4; 2, 2519-10-0; 3, 102539-04-8; 4, 102539-05-9; 5, 90502-88-8; 6, 102539-06-0; 8, 82207-56-5; $Co_2(CO)_8$, 10210-68-1; $[Rh(CO)_2Cl]_2$, 14523-22-9; BzOH, 100-51-6; $(C_5H_6)_2$, 77-73-6; PhBr, 108-86-1; pentaphenylcyclopentadien-1-ol, 2137-74-8; tetraphenylcyclopentadienone, 479-33-4.

Supplementary Material Available: Tables showing positional parameters, anisotropic thermal parameters, observed and calculated structure factor amplitudes, best planes data, complete bond lengths and angles, and packing diagrams (39 pages). Ordering information is given on any current masthead page.