Organometallics 1986, 5, 1405–1411

Synthesis, Molecular Structure, and Molybdenum Complexes of 1,1′-Bis(diphenylphosphino)cobaltocene

Daniel L. DuBois,* Charles W. Eigenbrot, Jr., Alex Miedaner, and James C. Smart

Solar Energy Research Institute, 1617 Cole Boulevard, Golden, Colorado 80401

R. Curtis Haltiwanger

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Received October 17, 1985

The synthesis of 1,1′-bis(diphenylphosphino)cobaltocene (1), $(C_5H_4PPh_2)_2Co$, from $TlC_5H_4PPh_2$ and $CoCl_2$ is described. The ligand 1 coordinates to one $Mo(CO)_4$ fragment as a chelating bidentate ligand to form $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ (2) and to two $Mo(CO)_5$ fragments as a bridging bidentate ligand to form $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$ (3). Molecular structure determinations have been carried out on compounds 1 and 3. Compound 1 crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a = 8.5966$ (16) Å, $b = 18.765$ (4) Å, $c = 8.8137$ (15) Å, $\beta = 99.702$ (14)°, $Z = 2$, and $\rho = 1.32$ g cm^{-3}. The structure was solved from 1735 observed reflections ($F > 6\sigma(F)$) and refined to final residuals of $R = 0.033$ and $R_w = 0.041$. Compound 3 crystallizes in the monoclinic space group $C2/c$ with $a = 16.651$ (5) Å, $b = 12.669$ (6) Å, $c = 26.322$ (9) Å, $\beta = 99.42$ (2)°, $Z = 4$, and $\rho = 1.47$ g cm^{-3}. The structure was solved from 1474 reflections ($F > 6\sigma(F)$) and refined to final residuals of $R = 0.048$ and $R_w = 0.060$. The puckering of the substituted cyclopentadienyl ring of 1 is interpreted with the aid of molecular orbital calculations. Cyclic voltammetry of 1 and $Fe(C_5H_4PPh_2)_2$ (4) and their complexes indicate that substitution of the cyclopentadienyl ring and coordination of 1 and 4 to molybdenum carbonyl fragments affects both the redox potential and electrochemical reversibility of electron-transfer processes occurring at cobalt and iron.

Introduction

The use of 1-(diphenylphosphino)cyclopentadienide as a bridging ligand for the synthesis of homo- and heterobimetallic complexes has been demonstrated by a number of research groups.[1-11] Part of the impetus for these studies is the hope that such heterobimetallic complexes might exhibit unusual catalytic activity by virtue of their ability to activate substrate molecules at two different metal sites. A second area in which heterobimetallic complexes derived from $C_5H_4PR_2$ ligands may be of interest is redox catalysis. In particular, the relatively high electron-transfer rates of metallocenes[12] make their incorporation into redox catalysts attractive. This incorporation could be affected by using substituted metallocenes as ligands. Such ligands may enhance the electron-transfer properties of the catalysts as well as act as electron-storage devices. What effects substitution of the cyclopentadienyl ligands may have on the structural and electrochemical properties of the parent metallocene is not clear, however. We have attempted to answer some of these questions here.

In this paper we report the reaction of $Tl(C_5H_4PPh_2)$ with $CoCl_2$ to form $Co(C_5H_4PPh_2)_2$, the oxidation of $Co(C_5H_4PPh_2)_2$ to the known $[Co(C_5H_4PPh_2)_2]PF_6$ salt in high yield, and reactions of $Co(C_5H_4PPh_2)_2$ with $Mo(CO)_4$(norbornadiene) and excess $Mo(CO)_6$ to form $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ and $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$, respectively. The $Co(C_5H_4PPh_2)_2$ ligand and one of its complexes, $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$, have been characterized by molecular structure determinations. In addition, $Co(C_5H_4PPh_2)_2$ and its molybdenum complexes have been characterized by magnetic susceptibility, infrared spectroscopy, and cyclic voltammetry. Extended Hückel calculations have been carried out on $Co(C_5H_4PH_2)_2$, in an effort to gain further insight into the origin of the puckering of the cyclopentadienyl rings, which is observed in the structure of 1.

Experimental Section

Tetrahydrofuran (THF), toluene, diethyl ether, and dimethoxyethane (DME) were purified by distillation from sodium benzophenone ketyl and purged with N_2. Except where mentioned, all reagents and products were handled with the exclusion of air by standard Schlenk techniques. $ClPPh_2$ (Aldrich) was distilled and purged with N_2 prior to use. Infrared spectra were obtained on a Perkin-Elmer 599B spectrophotomer. A Varian E109 spectrometer was used for obtaining EPR spectra. A JEOL FX90Q FT NMR spectrometer equipped with a tunable, variable-temperature probe was used to collect ^{13}C, ^{1}H, and ^{31}P NMR spectra. Me_4Si was used as an internal reference for ^{1}H and ^{13}C spectra. A capillary filled with phosphoric acid was used as an external reference for ^{31}P spectra, all of which were proton decoupled. Electrochemical measurements were carried out with a Princeton Applied Research Model 173 potentiostat equipped with a Model 179 digital coulometer and a Model 175 universal programmer. A Houston Instruments Model 2000 X-Y recorder was used for plotting cyclic voltammograms. A silver wire dipped in HCl and dried was used as a pseudoreference electrode, and ferrocene was used as an internal standard. A carbon disk electrode (IBM) was used as the working electrode, and a platinum wire was used as the counter electrode. Magnetic susceptibility measurements were performed at three different fields on a

---

(1) Rudie, A.; Lichtenberg, D. W.; Katcher, M. L.; Davison, A. *Inorg. Chem.* **1978**, *17*, 2859.

(2) LeBlanc, J. C.; Moise, C.; Maisonnat, A.; Poilblanc, R.; Charrier, C.; Mathey, F. *J. Organomet. Chem.* **1982**, *231*, C43.

(3) Schore, N. E.; Benner, L. S.; Labelle, B. E. *Inorg. Chem.* **1982**, *20*, 3200.

(4) Casey, C. P.; Nief, F. *Organometallics* **1985**, *4*, 1218. Casey, C. P.; Bullock, R. M.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1591.

(5) Cullen, W. R.; Kim, T.-J.; Einstein, F. W. B.; Jones, T. *Organometallics* **1983**, *2*, 714. Cullen, W. R.; Kim, T.-J.; Einstein, F. W. B.; Jones, T. *Organometallics* **1985**, *4*, 346.

(6) Butler, I.; Cullen, W. R.; Kim, T.-J.; Rettig, S. J.; Trotter, J. *Organometallics* **1985**, *4*, 972.

(7) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

(8) Rausch, M. D.; Edwards, B. H.; Rogers, R. P.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 3882.

(9) For a review of substituted cobaltocenes, see: Sheats, J. E. *J. Organomet. Chem. Rev.* **1979**, *7*, 461.

(10) Mathey, F.; Lampin, J.-P. *Tetrahedron* **1975**, *31*, 2685.

(11) Schore, N. E.; Sundar, S. *J. Organomet. Chem.* **1980**, *184*, C44.

(12) Sharp, M.; Petersson, M.; Edström, K. *J. Electroanal. Chem.* **1980**, *109*, 271. Yang, E. S.; Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1975**, *79*, 1049. Geiger, W. E., Jr.; Smith, D. E. *J. Electroanal. Chem.* **1974**, *50*, 31. Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1.

0276-7333/86/2305-1405$01.50/0

Faraday balance.[13,14] Elemental analyses were performed by Spang Microanalytical Laboratories.

$TlC_5H_4PPh_2$.[15] To 2.5 g (14 mmol) of $NaC_5H_5{\cdot}DME$[16] in a 500-mL side-arm round-bottomed flask was added 250 mL of dry, oxygen-free diethyl ether. To the stirred white suspension was added via syringe 2.6 mL (14 mmol) of $ClPPh_2$. The mixture was stirred for 2 h at room temperature. The white solid was removed by filtration and washed with two 25-mL portions of diethyl ether to yield a clear, colorless filtrate. The laboratory lights were dimmed, and TlOEt (1.0 mL, 3.5 g, 14 mmol) was added via syringe to the filtrate held at −78 °C. The cold bath was removed and aluminum foil wrapped around the flask. After 2 h at room temperature, the resulting off-white solid was isolated by filtration (cannula) washed with Et_2O (50 mL), and dried under vacuum. The solid was Soxhlet extracted into 125 mL of THF under N_2 for 1 day, to yield an insoluble gray material and a cloudy solution. The solution was filtered hot. Cooling the solution to room temperature resulted in the formation of pale yellow crystals. Further cooling to −25 °C overnight, followed by filtration yielded 4.44 g of crystalline $TlC_5H_4PPh_2$ (70% based on $NaC_5H_5{\cdot}DME$). Anal. Calcd for $C_{17}H_{14}PTl$: Tl, 45.05; P, 6.83; C, 45.01; H, 3.11. Found: Tl, 44.89; P, 6.83; C, 44.93; H, 3.10. ^1H NMR (THF-d_8): δ 6.15–6.09 (br s, cyclopentadienyl), 7.15–7.30 (br m, Ph). ^{31}P NMR (CD_3CN): δ −22.21 (s).

$Co^{II}(C_5H_4PPh_2)_2$. THF (250 mL) was added to 14.0 g (30.9 mmol, 10% excess) of $TlC_5H_4Ph_2$ in a 500-mL Schlenk flask. The flask was immersed in an ice bath, and 1.80 g of finely ground anhydrous $CoCl_2$ (13.9 mmol) was added via a solid addition tube. The pale blue suspension quickly became red-brown. The cold bath was removed after 15 min and the reaction stirred at room temperature for 1 h. The reaction mixture was then refluxed overnight under Ar. Filtration of the reaction mixture yielded a deep red-brown filtrate and a blue solid. Removal of the THF from the filtrate left a red-brown solid, which was extracted with toluene and filtered. Cooling to −25 °C overnight yielded a brown crystalline solid. Successive crystallizations from toluene or THF yielded a total of 6.26 g of $Co(C_5H_4PPh_2)_2$ (72% based on $CoCl_2$). This material is moderately air stable as a solid. Anal. Calcd for $C_{34}H_{28}CoP$: C, 73.25; H, 5.06; P, 11.11; Co, 10.57. Found: C, 73.17; H, 5.07; P, 11.06; Co, 10.49. ^1H NMR (THF-d_8): δ 6.39 (br s, ~35 Hz), 7.36 (br t), 8.02 (br d).

$[Co^{III}(C_5H_4PPh_2)_2]PF_6$.[1] A clear solution of $Co^{II}(C_5H_4PPh_2)_2$ was prepared in 250 mL of THF from $TlC_5H_4PPh_2$ (3.18 g, 7 mmol) and $CoCl_2$ (0.45 g, 3.5 mmol) using the above procedure. The solution was chilled to −78 °C, and O_2 gas was admitted via syringe. Next, 4 mL of 25% acetic acid in H_2O was added dropwise over about 5 min. The reaction was stirred at −78 °C for 15 min and then allowed to warm gradually to room temperature. After 30 min at room temperature the reaction was filtered in air. A solution of 2.7 g (16 mmol) NH_4PF_6 in the minimum volume of H_2O was added to the red-brown filtrate, resulting in a slightly cloudy solution. To this solution was added about 250 mL of 95:5 ethanol/2-propanol, and the resultant solution was filtered through Celite to yield a clear red-brown solution. The volume was reduced by two-thirds on a rotary evaporator, whereupon orange crystals precipitated. These crystals were collected on a frit and washed with ethanol and diethyl ether. The yield was 1.19 g of reasonably pure $[Co^{III}(C_5H_4PPh_2)_2]PF_6$ (61.1% based on $CoCl_2$). Removal of trace impurities was accomplished by passage of a CH_2Cl_2 solution through a short bed of silica. ^1H NMR (CD_3CN): δ 5.36 (t), 5.68 (t, cyclopentadienyl), 7.42 (br s, Ph). ^{31}P NMR (CD_3CN): δ −23.09.

$[Co^{II}(C_5H_4PPh_2)_2][Mo(CO)_4]$. A solution of 0.38 g (1.25 mmol) of $Mo(CO)_4$(norbornadiene)[17] in THF (30 mL) was added rapidly to a solution of 0.70 g (1.25 mmol) of $Co(C_5H_4PPh_2)_2$ in THF (20 mL). The resultant red solution was stirred at room temperature for 2 h. The solvent was removed in vacuo to give a red solid which was dissolved in 50 mL of toluene. This solution was filtered and then cooled to −25 °C overnight. The resulting red crystals were collected by filtration and dried in vacuo at 40 °C for 3 h to yield 0.270 g (28%). Removal of the solvent from the filtrate in vacuo yielded an additional 0.62 g which were pure by infrared spectroscopy and cyclic voltammetry. The total yield was 93%. Anal. Calcd for $C_{38}H_{28}CoMoO_4P_2$: C, 59.62; H, 3.69; P, 8.09; Co, 7.70. Found: C, 59.44; H, 3.62; P, 7.97; Co, 7.70.

Table I. Crystal Data and Summary of Intensity Data and Refinement

	$C_{34}H_{28}CoP_2$ (1)	$C_{44}H_{28}CoMo_2O_{20}P_2{\cdot}2C_7H_8$ (3)
M_r, g/mol	557.48	1213.64
space group	$P2_1/c$	$C2/c$
a, Å	8.5966 (16)	16.651 (5)
b, Å	18.765 (4)	12.669 (6)
c, Å	8.8137 (15)	26.322 (9)
β, deg	99.702 (14)	99.42 (2)
Z	2	4
μ, cm^{-1}	7.43	8.51
ρ_{obsd}, g/cm^3	~1.50	1.58
ρ_{calcd}, g/cm^3	1.32	1.47
no. of observns	1735	1474
no. of variables	169	254
R	0.033	0.048
R_w	0.041	0.060

$[Co^{III}(C_5H_4PPh_2)_2][Mo(CO)_4]PF_6$.[1] Ferrocenium hexafluorophosphate (0.130 g, 0.39 mmol) was added to a THF solution of $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ (0.30 g, 0.39 mmol in 50 mL of THF). The reaction mixture was stirred at room temperature for 2 h to give a red-brown solution. The reaction mixture was filtered, and 50 mL of toluene was added to the filtrate. The volume of the solution was reduced to 20 mL, and a red-brown precipitate formed. The solid was collected by filtration, washed with hexanes, and dried in vacuo. The yield was 0.16 g (45%). ^{31}P NMR (CD_3CN): δ +31.84 (s). Infrared and ^1H NMR data were consistent with literature values.[1]

$[Co^{II}(C_5H_4PPh_2)_2][Mo(CO)_5]_2$. A suspension of 2.64 g (10 mmol) of $Mo(CO)_6$ and 0.56 g (1 mmol) of $Co(C_5H_4PPh_2)_2$ in 200 mL of THF in a 250-mL Schlenk flask was refluxed for 25 h. The solvent was removed under vacuum, and excess $Mo(CO)_6$ was removed by sublimation. The resulting brown solid was dissolved in 50 mL of toluene, and the resultant solution was filtered and cooled to −20 °C overnight. The red-brown crystals that formed were collected by filtration. Drying the crystals under vacuum effectively removed the toluene of crystallization. The yield was 0.220 g (25%). Anal. Calcd for $C_{44}H_{28}CoMo_2O_{20}P_2$: C, 51.33; H, 2.75; P, 6.02; Co, 5.72. Found: C, 51.42; H, 2.99; P, 6.32; Co, 4.82.

X-ray Structure of $Co(C_5H_4PPh_2)_2$. A brown crystal (parallelopiped, approximately 0.3 × 0.3 × 0.5 mm grown from a THF solution at −20 °C) was glued to a glass fiber, coated with epoxy, and mounted on a Nicolet P3F four-circle automatic diffractometer with molybdenum X-ray tube (Mo Kα, 0.71069 Å) and graphite monochromator. Accurate cell parameters were determined by a least-squares refinement of 25 automatically centered reflections ($29.9° \le 2\theta \le 34.2°$). A short preliminary data collection confirmed the monoclinic symmetry and revealed the systematic absences $0k0$, $k = 2n$, and $h0l$, $l = 2n$, characteristic of space group $P2_1/c$ (no. 14). A total of 2699 $-h,+k,\pm l$ data were collected ($2.0° \le 2\theta \le 50.0°$). The data were corrected for Lorentz and polarization effects and for absorption by using an empirical correction based on 10 psi scans. The maximum and minimum transmission coefficients were 0.691 and 0.676. The resulting 1735 structure factor amplitudes greater than $6\sigma(F)$[18] were used for the final refinement.[19] Further crystal and intensity data are given in Table I.

---

(13) The construction of the Faraday magnetic balance was similar to that described by: Lindoy, L. F.; Katović, V.; Busch, D. H. *J. Chem. Educ.* **1972**, *49*, 117.

(14) All diamagnetic corrections were taken from: Figgis, B. N.; Lewis, J. In *Modern Coordination Chemistry*; Lewis, J., Wikins, R. G., Eds.; Interscience Publishers; New York, 1960; p 403. Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: New York, 1968; pp 5–7.

(15) $TlC_5H_4PPh_2$ has been prepared previously by Rausch and coworkers.[8] However, our experimental procedure is sufficiently different that complete experimental details are included here.

(16) Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1977**, *16*, 1788.

(17) Bennett, M. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 2037.

(18) $\sigma^2(F_o) = \sigma_c^2 + 0.0004F_o^2$ where σ_c^2 is from counting statistics.

(19) Programs used for the data reduction and refinement of 1 are contained in the Nicolet SHELXTL program package. SHELXTL, Revision 4, Aug 1983, Nicolet Analytical Instruments, Madison, WI.

Table II. Final Positional and Thermal Parameters for 1,1′-Bis(diphenylphosphino)cobaltocene (1)

atom	x	y	z	U,[a] Å^2
Co1	0	0	0	0.062 (1)
P1	−0.1276 (1)	0.1336 (1)	−0.2722 (1)	0.060 (1)
C1	−0.1234 (3)	0.0421 (2)	−0.2088 (3)	0.059 (1)
C2	−0.0259 (4)	−0.0168 (1)	−0.2352 (3)	0.066 (1)
C3	−0.0770 (4)	−0.0791 (2)	−0.1666 (3)	0.082 (1)
C4	−0.2003 (4)	−0.0596 (2)	−0.0937 (4)	0.096 (1)
C5	−0.2290 (3)	0.0150 (2)	−0.1144 (3)	0.079 (1)
C6	−0.2229 (3)	0.1242 (1)	−0.4732 (3)	0.052 (1)
C7	0.2193 (3)	0.1811 (2)	−0.5746 (3)	0.070 (1)
C8	−0.2987 (4)	0.1776 (2)	−0.7230 (4)	0.078 (1)
C9	−0.3853 (3)	0.1188 (2)	−0.7750 (3)	0.077 (1)
C10	−0.3926 (3)	0.0624 (2)	−0.6764 (3)	0.071 (1)
C11	−0.3117 (3)	0.0649 (1)	−0.5277 (3)	0.059 (1)
C12	0.0776 (3)	0.1513 (1)	−0.2938 (3)	0.056 (1)
C13	0.1502 (3)	0.1205 (1)	−0.4067 (3)	0.063 (1)
C14	0.3058 (3)	0.1344 (2)	−0.4142 (4)	0.076 (1)
C15	0.3916 (4)	0.1790 (2)	−0.3097 (4)	0.086 (1)
C16	0.3214 (4)	0.2117 (2)	−0.2000 (4)	0.095 (1)
C17	0.1649 (3)	0.1983 (2)	−0.1921 (3)	0.075 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

An initial Patterson map using a preliminary data set confirmed $Z = 2$, thus requiring Co atoms at 0, 0, 0 and 0, $^1/_2$, $^1/_2$. The program DIRDIF,[20] using only the Co atom at the origin, located all the remaining heavy atoms. Least-squares refinement using the complete data set described above and scattering factors for neutral atoms[21] converged with $R = 0.054$. For the final refinement the hydrogen atoms, clearly visible in the resulting difference electron density map, were included in calculated positions.[22] The thermal parameters of all non-hydrogen atoms were treated anisotropically. This refinement converged with $R = 0.033$ and $R_w = 0.041$.[24] In the final difference Fourier, the largest residual peak was 0.32 electron/Å^3. Final thermal and positional parameters are found in Table II.

X-ray Structure of $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$. An irregularly shaped brown crystal (approximately 0.2 × 0.2 × 0.3 mm, grown from toluene/hexane at 4 °C) was placed in a argon-flushed glass capillary and mounted on a Syntex P$\bar{1}$ four-circle automatic diffractometer with molybdenum X-ray tube and graphite monochromator. Accurate cell parameters were determined by a least-squares refinement of 15 automatically centered reflections $18° \leq 2\theta \leq 25°$. A short preliminary data collection confirmed the monoclinic symmetry and revealed the systematic absences hkl, $h + k = 2n$, and $h0l$, $l = 2n$, characteristic of space groups Cc and $C2/c$ (no. 9 and 15, respectively). A total of 6020 $\pm h,\pm k,\pm l$ data were collected ($3° \leq 2\theta \leq 37.5°$), which after averaging ($R = 2.4\%$) yielded 1474 reflections greater than $6\sigma(F)$[18] used in the final refinement.[25,26] Further crystal and intensity data are given in Table I.

Table III. Final Positional and Thermal Parameters for $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$[a] (3)

atom	x	y	z	B_{eq}, Å^2
Co1	0.500000 (0)	0.5658 (2)	0.750000 (0)	3.55 (8)
Mo1	0.58795 (7)	0.3415 (1)	0.90698 (5)	4.15 (4)
P1	0.6051 (2)	0.5314 (3)	0.8779 (1)	3.56 (11)
C1	0.6024 (7)	0.554 (1)	0.8098 (5)	3.44 (43)
C2	0.6046 (7)	0.476 (1)	0.7713 (6)	4.27 (47)
C3	0.6100 (7)	0.528 (2)	0.7251 (6)	4.59 (57)
C4	0.6057 (8)	0.633 (1)	0.7323 (5)	4.75 (57)
C5	0.5992 (7)	0.651 (1)	0.7842 (5)	4.26 (49)
C6	0.7072 (9)	0.5733 (7)	0.9041 (3)	3.33 (44)
C7	0.7694 (9)	0.5604 (7)	0.8749 (3)	4.65 (47)
C8	0.8499 (9)	0.5814 (7)	0.8968 (3)	6.18 (68)
C9	0.8683 (9)	0.6152 (7)	0.9478 (3)	6.50 (66)
C10	0.8061 (9)	0.6280 (7)	0.9770 (3)	5.95 (55)
C11	0.7256 (9)	0.6071 (7)	0.9551 (3)	4.80 (55)
C12	0.5405 (9)	0.6369 (8)	0.8943 (3)	3.66 (51)
C13	0.4607 (9)	0.6129 (8)	0.9001 (3)	4.77 (52)
C14	0.4086 (9)	0.6929 (8)	0.9109 (3)	5.76 (58)
C15	0.4362 (9)	0.7970 (8)	0.9160 (3)	7.37 (78)
C16	0.5159 (9)	0.8210 (8)	0.9102 (3)	6.88 (65)
C17	0.5681 (9)	0.7409 (8)	0.8993 (3)	5.18 (52)
C18	0.4985 (9)	0.375 (1)	0.9482 (6)	5.40 (56)
C19	0.673 (1)	0.366 (1)	0.9694 (7)	6.38 (62)
C20	0.5814 (9)	0.190 (1)	0.9295 (6)	5.47 (56)
C21	0.5046 (9)	0.302 (1)	0.8435 (6)	5.23 (53)
C22	0.680 (1)	0.305 (1)	0.8658 (6)	5.20 (55)
O1	0.4483 (7)	0.3892 (9)	0.9723 (4)	6.90 (41)
O2	0.7219 (7)	0.376 (1)	0.0055 (5)	8.60 (48)
O3	0.5782 (7)	0.1062 (9)	0.9435 (5)	8.09 (45)
O4	0.4586 (7)	0.2726 (9)	0.8095 (4)	7.28 (40)
O5	0.7309 (7)	0.283 (1)	0.8451 (5)	8.46 (48)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = 8\pi^2(U_{22} \sin^2 \beta + 2U_{13} \cos \beta)/3(1 - \cos^2 \beta)$.

The initial Patterson map confirmed space group $C2/c$ and was solved for a molybdenum atom in a general position. The largest peak in the subsequent difference Fourier map was found at 0, y, $^3/_4$, indicating the cobalt atom lies on a twofold axis and $Z = 4$. All remaining heavy atoms were located in subsequent difference Fourier maps, including one molecule of toluene per asymmetric unit ($\rho_{calcd} = 1.47$ g/cm^3, $\rho_{obsd} = 1.58$ g/cm^3, flotation). The model converged with $R = 0.048$ and $R_w = 0.060$, respectively. Scattering factors were those for neutral atoms.[21] The thermal parameters of all non-hydrogen atoms, except those of the toluene molecule, were treated anisotropically. A common isotropic thermal parameter was refined for the ring carbon atoms of the toluene molecule, and an independent isotropic thermal parameter was refined for the methyl carbon atom. The phenyl rings (including the toluene molecule) were treated as rigid groups. Hydrogen atoms were included in calculated positions assuming sp^2 hybridization ($d_{C-H} = 0.95$ Å[23]) with fixed isotropic thermal parameters. They were not included for the toluene molecule. In the final difference Fourier map, the largest residual peak was 0.6 electron/Å^3, near the disordered toluene molecule. Final positional and thermal parameters are found in Table III.

Results and Discussion

Syntheses. 1-(Diphenylphosphino)cyclopentadiene was prepared by reaction of sodium cyclopentadienide with chlorodiphenylphosphine in diethyl ether as described by Davison and co-workers.[1] Reaction of $C_5H_5PPh_2$ with thallium ethoxide results in the formation of $TlC_5H_4PPh_2$ which has been isolated and characterized by elemental analysis and ^{1}H and ^{31}P NMR spectroscopy.[15] This reagent and $Li(C_5H_4PPh_2)$ offer synthetic chemists a choice of $(C_5H_4PPh_2)^-$ starting materials. By analogy with various derivatives of $C_5H_5^-$ one can expect these reagents to have slightly different reactivities toward various transition metal halides.

Reaction of $TlC_5H_4PPh_2$ with anhydrous $CoCl_2$ in THF results in the formation of $Co(C_5H_4PPh_2)_2$ in reasonable yields. The effective magnetic moment for this complex is 1.73 μ_B, which is consistent with the presence of one unpaired electron. This value is similar to the values of 1.75 and 1.45 μ_B observed for cobaltocene[27] and bis(pen-

---

[20] Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; vandenHark, Th. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V. "DIRDIF81, Technical Report 1982"; Crystallography Laboratory: Toernooiveld, 6525 ED, Nijmegen, The Netherlands.

[21] The scattering factors used for all atoms were taken from the *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974.

[22] Hydrogen atom positions were calculated by assuming sp^2 hybridization with $d_{C-H} = 0.95$ Å.[23] The thermal parameters used for the hydrogen atoms were 1.2 times the thermal parameter of the carbon atom to which they were attached.

[23] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

[24] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. The weighting scheme used for all refinements was based on counting statistics where $w = 1/\sigma^2(F_o)$.

[25] Programs were contained in or derived from Syntex (Nicolet) data reduction routines, the Northwestern University Crystallographic Computing Package of Dr. J. A. Ibers, and the SHELX-76 package.

[26] Sheldrick, G. M., 1976, Program for Crystal Structure Determination, University of Cambridge, England.

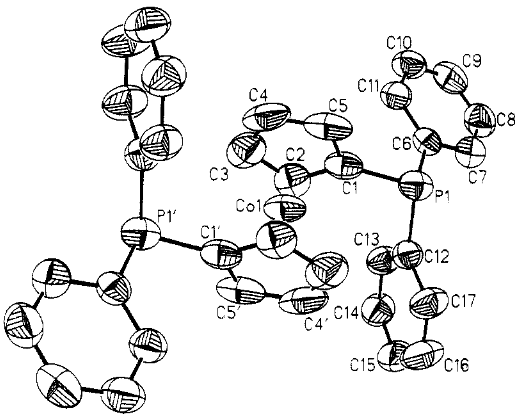


Figure 1. A diagram showing thermal ellipsoids and the atomic numbering scheme for $Co(C_5H_4PPh_2)_2$ (1).

tamethylcyclopentadienyl)cobalt,[28] respectively. We were unable to observe any signal in the EPR spectrum of a 10^{-3} M toluene solution of $Co(C_5H_4PPh_2)_2$ at room temperature due to rapid relaxation of the unpaired electron. Again, this behavior is similar to that of cobaltocene[27] and permethylcobaltocene.[28] Aerial oxidation of $Co(C_5H_4PPh_2)_2$ results in the isolation of the previously characterized $[Co(C_5H_4PPh_2)_2]PF_6$ salt[1] in good yield and further supports the formulation of this complex.

$[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ can be prepared by the reaction of $Mo(CO)_4$(norbornadiene), with $Co(C_5H_4PPh_2)_2$ in THF. The infrared spectrum of $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ in CH_2Cl_2 has four bands at 2019, 1920 (sh), 1905, and 1890 (sh) cm^{-1} compared with $[Fe(C_5H_4PPh_2)_2][Mo(CO)_4]$[1] with four bands at 2018, 1920 (sh), 1905, and 1885 (sh) cm^{-1}. The infrared spectra of both of these complexes in the solid state (Nujol mull) are more complicated but are remarkably similar. $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ has bands at 2017, 1917, 1908, 1899, 1885, and 1878 cm^{-1}; and $[Fe(C_5H_4PPh_2)_2][Mo(CO)_4]$[1] has bands at 2018, 1918, 1910, 1899, 1887, and 1880 cm^{-1}. The similarity of the carbonyl stretching frequencies for $[Fe(C_5H_4PPh_2)_2][Mo(CO)_4]$ and $[Co(C_5H_4PPh_2)_2)][Mo(CO)_4]$ in both the solid state and solution indicates that $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ must have a structure quite similar to $[Fe(C_5H_4PPh_2)_2][Mo(CO)_4]$, whose crystal structure has been determined.[6] The infrared spectra also indicate that the $M(C_5H_4PPh_2)_2$ ligands have similar abilities to donate electrons to the $Mo(CO)_4$ fragment. The magnetic moment of $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ of 1.55 μ_B is consistent with the presence of one unpaired electron. Oxidation of $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ with ferrocenium ion yields $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]PF_6$ which has been previously characterized.[1]

Reaction of $Co(C_5H_4PPh_2)_2$ with a tenfold excess of $Mo(CO)_6$ in THF yields the trinuclear complex $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$. The infrared spectrum of this complex in CH_2Cl_2 has carbonyl stretching frequencies at 2032, 1995, 1975, 1947, and 1895 cm^{-1} consistent with a molecule of low symmetry. The magnetic moment of 1.78 μ_B indicates the presence of one unpaired electron.

Structural Studies. The crystal structure of $Co(C_5H_4PPh_2)_2$ consists of discrete molecular units at centers of inversion. The closest intermolecular contact (excluding H–H contacts) is 2.82 Å between H13 and C2. The molecular structure consists of a Co(II) ion coordinated by two inversion related η^5-$C_5H_4P(C_6H_5)_2$ ligands (Figure 1). The substituted cyclopentadienyl rings deviate slightly from planarity. As can be seen from Table IV, the Co–C(ring) distances can be divided into two groups: bonds between Co and C1, C3, and C4 and bonds between Co and C2 and C5. The intervals dividing the groups are greater than 5σ. The angle between the plane defined by carbon atoms C1, C2, and C5 and the least-squares plane of C2, C3, C4, C5 is 3.4°. This puckering of the ring at C2 and C5 is believed to be due to the preferential occupation of one of the **e** molecular orbitals of $Co(C_5H_4PPh_2)_2$ as discussed below. Similar distortions have been observed for $C_5Me_5Rh(CO)_2$[29] and $C_5Me_5Co(CO)_2$[30] although the electronic origins are somewhat different.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for $Co(C_5H_4PPh_2)_2$ (1)

Co1–C1	2.116 (2)	Co1–C1–P1	127.3 (1)
Co1–C3	2.114 (3)	C1–P1–C12	103.6 (1)
Co1–C4	2.101 (4)	P1–C1–C2	131.9 (2)
Co1–C2	2.072 (2)	P1–C1–C5	122.6 (2)
Co1–C5	2.075 (2)	P1–C6–C6	119.4 (2)
C1–C2	1.431 (4)	P1–C6–C11	122.9 (2)
C1–C5	1.425 (4)	C1–C2–C3	109.6 (3)
C2–C3	1.419 (4)	C1–C5–C4	108.1 (3)
C4–C5	1.428 (5)	C2–C3–C4	107.3 (3)
C3–C4	1.378 (5)	C3–C4–C5	109.4 (3)
P1–C1	1.804 (3)	C2–C1–C5	105.5 (3)
P1–C6	1.831 (2)	P1–C12–C13	123.7 (2)
P1–C12	1.836 (3)	P1–C12–C17	118.3 (2)

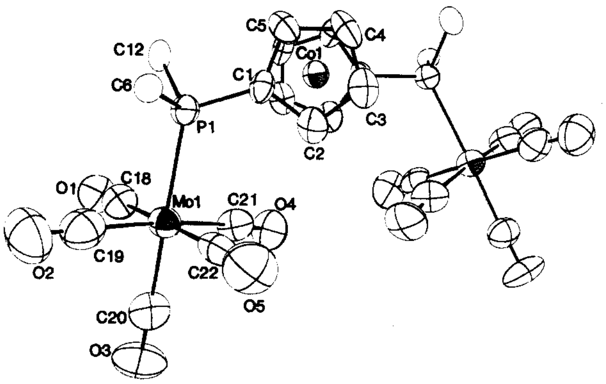


Figure 2. An Ortep diagram and atom numbering scheme for $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$ (3).

The molecules of $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$ are positioned about sites of twofold symmetry. The closest intermolecular contact is 2.728 Å between O3 and H9. There exist three contacts between the toluene molecule and H atoms on the cyclopentadienyl ring of approximately 3.0 Å. Excluding H atoms, the closest intermolecular contact is 3.373 Å, between C14 and O5. Although the quality of this structure determination is limited by the low-angle data set, the basic structural features of this complex are clear. The molecular structure consists of one Co(II) and two $Mo(CO)_5$ moieties bridged by two $C_5H_4PPh_2^-$ ligands such that the Co(II) is coordinated by two substituted cyclopentadienyl rings while the Mo(0) experiences an essentially octahedral coordination sphere supplied by five CO groups and the phosphorus atom (Figure 2). The cobalt is located on a twofold rotation axis that takes one $(C_5H_4PPh_2)Mo(CO)_5$ moiety into the other.

Molecular Orbital Calculations. From simple molecular orbital considerations the unpaired electron in

---

[27] Gordon, K. R.; Warren, K. P. *Inorg. Chem.* **1978**, *13*, 1317. Fritz, H. D.; Schwarzhaus, K. E. *J. Organomet. Chem.* **1964**, *1*, 208. Ammeter, J. H. *J. Magn. Reson.* **1978**, *30*, 299.

[28] Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882.

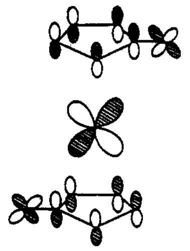
[29] Lichtenberger, D. L.; Blevins, C. H., II; Ortega, R. B. *Organometallics* **1984**, *3*, 1614.

[30] Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277.

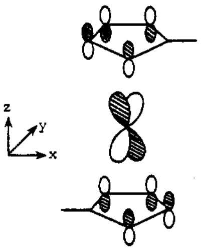
Table V. Selected Bond Lengths (Å) and Angles (deg) for $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2 \bullet 2MeC_6H_5$ (3)

Co1–C1	2.13 (1)	C1–C1	1.42 (2)	P1–C1	1.81 (1)
Co1–C2	2.08 (1)	C2–C3	1.40 (2)	P1–C6	1.81 (1)
Co1–C3	2.10 (1)	C3–C4	1.35 (2)	P1–C12	1.81 (1)
Co1–C4	2.07 (1)	C4–C5	1.40 (2)	P1–Mo1	2.555 (4)
Co1–C5	2.05 (1)	C5–C1	1.40 (2)		
Mo1–C18	2.03 (2)	C18–O1	1.14 (1)		
Mo1–C19	2.01 (2)	C19–O2	1.15 (1)		
Mo1–C20	2.02 (2)	C20–O3	1.13 (1)		
Mo1–C21	2.05 (2)	C21–O4	1.14 (1)		
Mo1–C22	2.07 (2)	C22–O5	1.12 (1)		
C1–C2–C3	108 (1)	C1–P1–C6	101.7 (5)	P1–Mo1–C18	95.3 (4)
C2–C3–C4	109 (1)	C1–P1–C12	101.7 (6)	P1–Mo1–C19	90.1 (5)
C3–C4–C5	108 (1)	C6–P1–C12	104.5 (5)	P1–Mo1–C20	176.6 (4)
C4–C5–C1	109 (1)	C1–P1–Mo1	117.2 (5)	P1–Mo1–C21	94.5 (4)
C5–C1–C2	106 (1)	C6–P1–Mo1	107.8 (3)	P1–Mo1–C22	85.9 (4)
		C12–P1–Mo1	121.6 (3)		
C18–Mo1–C19	90.8 (6)	C19–Mo1–C20	88.3 (6)		
C18–Mo1–C20	87.8 (6)	C19–Mo1–C21	174.5 (6)		
C18–Mo1–C21	91.6 (6)	C19–Mo1–C22	88.7 (6)		
C18–Mo1–C22	178.7 (6)	C20–Mo1–C21	86.9 (6)		
C21–Mo1–C22	88.8 (6)	C20–Mo1–C22	91.0 (6)		

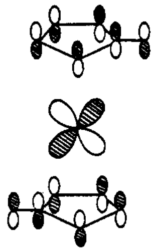
cobaltocene would be expected to reside in the e orbitals which are metal-to-ligand antibonding orbitals. For substituted cobaltocenes the degeneracy of the e set is removed. The question to be answered is which of the two e orbitals will be lower in energy. The results of extended Hückel calculations indicate that the highest occupied molecular orbital of $Co(C_5H_4PH_2)_2$, arises from an e orbital that is stabilized by a bonding interaction between the d_{xz} orbital on phosphorus and the pz orbital of C1, orbital I.[31] That substitution of H by the diphenylphosphino group on the cyclopentadienyl ring is slightly stabilizing is consistent with our electrochemical results. The Co(II)/Co(III) couple for $Co(C_5H_4PPh_2)_2$ is ~200 mV positive of that for cobaltocene. If the d_{xz} orbital, I, is lower in energy than the d_{yz} orbital, II, then the reason for the slight puckering of the ring observed in the crystal structure becomes apparent. The metal d_{xz} orbital interacts in an antibonding fashion with C1, C3, and C4 with the strongest interaction being with C1. This is consistent with the longer metal-to-ring carbon distances observed for C1, C3, and C4 compared to C2 and C5 (see Table IV). The predicted order is C1 > C3, C4 > C2, C5. This argument does not depend on exclusive occupation of the d_{xz} orbital by the unpaired electron, only preferential occupation. Our calculations place the d_{xz} orbital only 0.16 eV below d_{yz}. A further argument that d_{xz} orbital, I, is the HOMO can be made as follows. If the orbital occupancy of the HOMO and LUMO were equal, the C–C bond distances would be expected to be equal since the e set of the ligand would be equally occupied. However, occupying the d_{xz} orbital preferentially should lead to a stronger bonding interaction and a shorter bond distance between C3 and C4 than between the remaining carbons while the reverse should be true if the d_{yz} orbital were occupied preferentially. The calculated reduced overlap populations are C3–C4 (1.05), C2–C3 (1.02), and C1–C2 (0.97). The observed bond distance ordering is C3–C4 < C2–C3 = C4–C5 = C1–C2 = C1–C5 (see Table IV).[32]



I



II



III

If the π acceptor ability of phosphorus is increased by substituting alkoxy for phenyl groups, the d_{xz} is stabilized even more, and an enhancement in the distortions already observed for $Co(C_5H_4Ph_2)_2$ is expected. If, on the other hand, the diphenylphosphino group is replaced with a dimethylamino substituent, then the d_{xz} orbital is destabilized by the substitution and appears as shown in orbital III. (These conclusions are based on calculations carried out on $Co(C_5H_4NH_2)_2$.) The nitrogen has no readily accessible d orbitals, and the nitrogen p_z orbital interacts in an antibonding fashion with the p_z orbital of C1. As a result the d_{yz} orbital, II, is the HOMO for $Co(C_5H_4NMe_2)_2$ and leads to the prediction that the ring puckering would occur along the plane containing the substituent atom C1 and cobalt with C1 being closer to cobalt than the remaining atoms. In addition the calculated reduced overlap populations for the carbon ring C3–C4 (1.00), C1–C2 (1.03), and C3–C2 (1.05) leads to the prediction that the ring C–C bond distances will vary in the following order C3–C4 > C1–C2 > C3–C2. A molecular structure determination of the recently synthesized $Co(C_5H_4NMe_2)_2$[34] would be interesting in light of these predictions.

The staggered conformation of $Co(C_5H_4PPh_2)_2$ is felt to arise from a reduction of the nonbonding repulsions between the two phosphorus atoms. The d_{xz} orbital of $Co(C_5H_4PH_2)_2$ is destabilized by 0.16 eV upon rotating from the staggered position in which the two phosphorus atoms are related by an inversion center to an eclipsed position in which the two phosphorus atoms are related by mirror

---

[31] It is also possible for σ^* orbitals of phosphorus to act as π acceptor orbitals; however, the basic arguments remain the same. Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 4064–4065.

[32] Using the crystallographic coordinates, librational analysis of rigid-body motion[33] on the entire molecule and on the five atoms C1–C5 of the cyclopentadienyl ring showed no change in the relative lengths of the bonds of the cyclopentadienyl ring.

[33] Schomaker, V.; Trueblood, K. N. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 63.

[34] Stahl, K.-P.; Boche, G.; Massa, W. *J. Organomet. Chem.* **1984**, *277*, 113.

[35] Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

[36] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 701. See also: Koepp, H. M.; Wendt, H.; Strehlow, H. *Z. Elektrochem.* **1960**, *64*, 483.

Table VI. Electrochemical Parameters of $Co(C_5H_4PPh_2)_2$ and $Fe(C_5H_4PPh_2)_2$ and Some Related Complexes[a]

compd	$E_{1/2}$-(II/III)	i_{p_a}/i_{p_c}	$E_{1/2}$(I/II)	i_{p_a}/i_{p_c}
$Co(C_5H_5)_2$[b]	−1.33	1.0		
$Co(C_5H_4PPh_2)_2$[b]	−1.11	1.02	−2.02	0.0
$Fe(C_5H_4PPh_2)_2$[b]	+0.20	0.43		
$[Co(C_5H_4PPh_2)_2]Mo(CO)_4$[c]	−0.98	1.00	−1.98	0.99
$[Fe(C_5H_4PPh_2)_2]Mo(CO)_4$[c]	+0.42[d]	0.0		
$[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$[c]	−0.75	1.0	−1.92	0.71

[a] The potentials are referenced to a ferrocene internal standard and can be related to a SCE reference electrode by using a value of +0.31 V vs. SCE for the ferrocene/ferrocenium couple.[35,36] A glassy carbon electrode was used as a working electrode, Ag wire as a pseudoreference electrode, and platinum wire as a counter electrode. The scan rate in all cases was 50 mV/s. [b] The supporting electrolyte solution was 0.3 M NEt_4BF_4 in CH_3CN. [c] The supporting electrolyte solution was 0.3 M NBu_4BF_4 in THF. [d] Potential given is that corresponding to the potential for the peak anodic current.

symmetry. The majority of this destabilization can be traced to an antibonding interaction between the two nonbonding phosphorus atoms in the eclipsed conformation.

Electrochemical Studies. As discussed above the ligands $Co(C_5H_4PPh_2)_2$ and $Fe(C_5H_4PPh_2)_2$ are of interest because of their potential to act as redox mediators and electron-storage ligands. Cyclic voltammetry measurements have been carried out on all metal complexes whose syntheses have been described in this papeer as well as $Fe(C_5H_4PPh_2)_2$ and $[Fe(C_5H_4PPh_2)_2][Mo(CO)_4]$.[1] The data for these complexes are compiled in Table VI. As can be seen from Table VI, $Co(C_5H_4PPh_2)_2$ undergoes a chemically reversible one-electron oxidation to $Co(C_5H_4PPh_2)_2^+$ at −1.11 V and an irreversible reduction at −2.02 V vs. the ferrocene/ferrocenium couple. In contrast, the oxidation of $Fe(C_5H_4PPh_2)_2$ is only quasi-reversible with the oxidation apparently being followed by an irreversible chemical reaction. For $Co(C_5H_5)_2$ and $Fe(C_5H_5)_2$ the redox couple is shifted +0.22 and +0.20 V upon substituting hydrogen with the diphenylphosphino group, indicating that it is an electron-withdrawing group with respect to hydrogen. In contrast, for $Co(C_5H_4NMe_2)_2$ the Co(III/II) couple is 0.37 V more negative than cobaltocene.[34]

$[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ undergoes a chemically reversible oxidation at a potential approximately 0.13 V positive of $Co(C_5H_4PPh_2)_2$, consistent with transfer of electron density from cobalt to the $Mo(CO)_4$ fragment as expected. Since $Co(C_5H_4PPh_2)_2$ undergoes an irreversible reduction, it is surprising that $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ undergoes a reversible reduction. This change in the nature of this reduction from irreversible to reversible upon coordination to molybdenum probably reflects a template effect in which molybdenum prevents dissociation of a cyclopentadienyl ring from cobalt(I).[37] In contrast, $[Fe(C_5H_4PPh_2)_2][Mo(CO)_4]$ undergoes an irreversible oxidation that is shifted approximately 0.2 V in a positive direction from $Fe(C_5H_4PPh_2)_2$. The template effect of molybdenum does not seem to be capable of preventing subsequent reaction of the oxidized ferrocenium ligand.

The cyclic voltammogram of $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$ reveals a chemically reversible oxidation wave approximately 0.6 V positive of the parent cobaltocene complex and indicates that substitution of the cyclopentadienyl ring can have dramatic effects on the potential of the Co(II)/Co(III) couple. The reduction of $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$ appears to be only quasi-reversible, having lost the stabilizing template effect present in $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$.

Table VII. Extended Hückel Parameters

atom	orbital	H_{ij}, eV	ζ_1	ζ_2
Co	4s	−8.54	2.00	
	4p	−4.76	2.00	
	3d	−12.11	5.55 (0.5679)[a]	2.10 (0.6059)[a]
P	3s	−18.60	1.60	
	3p	−14.00	1.60	
	3d	−7.00	1.40	
C	2s	−21.40	1.625	
	2p	−11.4	1.625	
H	1s	−13.6	1.30	
N	2s	−26.00	1.95	
	2p	−13.4	1.95	

[a] Coefficient used in double-ζ expansion of d orbitals.

Table VIII. Geometrical Parameters Used for Calculations on $Co(C_5H_4PH_2)_2$ and $Co(C_5H_4NH_2)_2$

atoms	bond dist, Å	atoms	bond angle, deg
Co–C	2.08	C–C–C(ring)	108
C–C	1.41	C–P–H	109.5
C–P	1.80	C–N–H	109.5
C–H	1.10		
P–H	1.40		
C–N	1.45		
N–H	1.00		

Summary

In this paper we have described the synthesis of $Co(C_5H_4PPh_2)_2$ and two of its complexes, $[Co(C_5H_4PPh_2)_2][Mo(CO)_4]$ and $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$. Molecular structure determinations have been carried out on $Co(C_5H_4PPh_2)_2$ and $[Co(C_5H_4PPh_2)_2][Mo(CO)_5]_2$. Molecular orbital calculations were performed on $Co(C_5H_4PH_2)_2$ to aid in the interpretation of the puckering and differences in the C–C bond distances observed for the cyclopentadienyl ring of $Co(C_5H_4PPh_2)_2$. Electrochemical studies of $M(C_5H_4PPh_2)_2$ (where M = Fe, Co) and their molybdenum complexes have resulted in three significant findings. First the potential for the Co(II)/(III) couple can vary over a range of 1.0 V depending on the nature of the ring subtituent. Second the Co(I)/(II) couple becomes reversible when complexed to the $Mo(CO)_4$ fragment. This reversibility has been attributed to a template effect exerted by $Mo(CO)_4$ on the ligand. Finally, the Co(II)/(III) couple of $Co(C_5H_4PPh_2)_2$ and its complexes is much more reversible than the Fe(II)/(III) couple of $Fe(C_5H_4PPh_2)_2$ and its complexes. This latter observation suggests that $Co(C_5H_4PPh_2)_2$ would be a better redox mediator and electron storage ligand than $Fe(C_5H_4PPh_2)_2$.

Acknowledgment. This research was supported by the Office of Energy Research of the U.S. Department of Energy under Contract EG-77-C-01-4042.

Appendix

Extended Hückel calculations[38] were performed by using the weighted H_{ij} formula.[39] The atomic parameters used are listed in Table VII with the cobalt parameters taken from ref 40. A double-ζ expansion was used for the d orbitals of cobalt. Geometrical parameters used to model

---

(37) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295.

(38) Hoffmann, R. J. *Phys. Chem.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 3179.

(39) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. Hoffmann, R.; Hofmann, P. *Ibid.* **1976**, *98*, 598.

(40) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

Organometallics 1986, *5*, 1411–1417 1411

$Co(C_5H_4PPh_2)_2$ are given in Table VIII.

Registry No. 1, 67292-47-1; $1^+ \cdot PF_6^-$, 67292-48-2; 2, 99920-72-6; $2^+ \cdot PF_6^-$, 67292-27-7; 3, 101835-52-3; $TlC_5H_4PPh_2$, 85320-10-1; TlOEt, 20398-06-5; $Mo(CO)_4$(norbornadiene), 12146-37-1; $Co(:C_5H_5)_2$, 1277-43-6; $Fe(C_5H_4PPh_2)_2$, 12150-46-8; $[Fe(C_5H_4PPh_2)_2][Mo(Co)_4]$, 95408-43-8; NaC_5H_5, 4984-82-1; $ClPPh_2$, 1079-66-9; $CoCl_2$, 7646-79-9; $[Fe(C_5H_5)_2]PF_6$, 11077-24-0; $Mo(Co)_6$, 13939-06-5.

Supplementary Material Available: Tables of hydrogen coordinates and temperature factors, anisotropic temperature factors, least-squares planes, and observed and calculated structure factors for 1 (25 pages). Ordering information is given on any current masthead page.

Formation of Tungstenacyclobutadiene Complexes Containing a Proton in the Ring and Their Conversion to "Deprotio" Tungstenacyclobutadiene Complexes[1]

John H. Freudenberger and Richard R. Schrock*

Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received October 17, 1985

The reaction between $W(C\text{-}t\text{-}Bu)[OCH(CF_3)_2]_3(dme)$ (dme = 1,2-dimethoxyethane) and *tert*-butylacetylene or phenylacetylene yields the tungstenacyclobutadiene complexes $W(C\text{-}t\text{-}BuCHCR)(HFIP)_3$ (R = *t*-Bu or Ph; HFIP = hexafluoroisopropoxide). In the presence of triethylamine and dme the R = Ph species is converted into a "deprotio" tungstenacyclobutadiene complex, $W(C_3\text{-}t\text{-}BuPh)(HFIP)_2(dme)$. Addition of dme to $W(C\text{-}t\text{-}BuCHCR)(HFIP)_3$ results in formation of $W(C_3\text{-}t\text{-}BuR)(HFIP)_2(dme)$ in equilibrium with $W(C\text{-}t\text{-}BuCHCR)(HFIP)_3$. Addition of phenylacetylene to $W(CPh)(HFIP)_3(dme)$ yields only $W(C_3Ph_2)(HFIP)_2(dme)$. Addition of *tert*-butylacetylene to $W(C\text{-}t\text{-}Bu)(DIPP)_3$ (DIPP = 2,6-diisopropylphenoxide) yields isolable red $W(C\text{-}t\text{-}BuCHC\text{-}t\text{-}Bu)(DIPP)_3$ that slowly and irreverisbly is converted in solution into $W(C_3\text{-}t\text{-}Bu_2)(DIPP)_2$. The reaction is greatly accelerated by addition of triethylamine or LiDIPP; it is believed that the base removes the ring proton directly. The pyridine adduct $W(C_3\text{-}t\text{-}Bu_2)(DIPP)_2(py)$ has been fully characterized. $W(C_3\text{-}t\text{-}Bu_2)(DIPP)_2$ reacts with excess *tert*-butylacetylene to give a compound with the formula $W(C_5H\text{-}t\text{-}Bu_3)(DIPP)_2$ that can be isolated as its monopyridine adduct. The planar $C_5H\text{-}t\text{-}Bu_3$ ligand system is formed (it is proposed) by regiospecific reaction of *tert*-butylacetylene with the $W\text{–}C_\alpha$ bond in the "deprotio" tungstenacyclobutadiene complex. The alkylidene-like carbon atom in $W(C_5H\text{-}t\text{-}Bu_3)(DIPP)_2$ can be protonated by CF_3CO_2H or $PhCO_2H$ to give complexes of the type $W(C_5H_2\text{-}t\text{-}Bu_3)(DIPP)_2(RCO_2)$. The chemistry of the analogous DMP complexes (DMP = 2,6-dimethylphenoxide) is analogous to that of the DIPP complexes. Isolated characterized complexes include $W(C\text{-}t\text{-}BuCHC\text{-}t\text{-}Bu)(DMP)_3$, $W(C_3\text{-}t\text{-}Bu_2)(DMP)_2(py)$, $W(C_5H\text{-}t\text{-}Bu_3)(DMP)_2(py)$, $W(C\text{-}t\text{-}BuCHC\text{-}t\text{-}Bu)(DMP)_2Cl$, and $W(C_3\text{-}t\text{-}Bu_2)(DMP)_2$.

Introduction

The metathesis of internal acetylenes is now reasonably well understood.[2] The key requirement of a practical metathesis catalyst is a crowded alkoxide coordination sphere that, first, sterically prevents further reaction of the metallacyclobutadiene complex with an acetylene and, second, sterically and electronically destabilizes the metallacycle toward loss of an acetylene from the ring to reform an alkylidyne complex. It is also now clear that the metal center must be reasonably electrophilic, a property that can be controlled by the nature of the alkoxide ligand (e.g., $OCMe_3$ vs. $OCMe_2(CF_3)$ vs. $OCMe(CF_3)_2$).

Terminal acetylenes, on the other hand, have never been metathesized successfully. The first hint that a proton can be lost from a presumed intermediate metallacyclobutadiene ring was the formation of $W(\eta^5\text{-}C_5H_5)(C_3\text{-}t\text{-}Bu_2)Cl$ upon addition of $t\text{-}BuC{\equiv}CH$ to $W(\eta^5\text{-}C_5H_5)(C\text{-}t\text{-}Bu)Cl_2$.[3] More recently, alkoxy molybdenum alkylidyne complexes have been found to react with terminal acetylenes to give other examples of isolable "deprotiometallacyclobutadiene" complexes.[2e] We then turned to analogous alkoxy tungsten alkylidyne complexes. We felt that we would more likely observe intermediate metallacyclobutadiene complexes since tungstenacyclobutadiene complexes[2b,c] are more stable than their molybdenum analogues[2e] toward loss of an acetylene from the ring. Secondly, the proton in a tungstenacycle should be less acidic than that in an analogous molybdenacycle on the basis of the fact that tungsten alkylidyne complexes appear to be more easily protonated to give alkylidene complexes than molybdenum alkylidyne complexes.[4] The results of this investigation are reported here.

Results

Studies Involving Hexafluoroisopropoxide Complexes. Yellow, crystalline $W(C\text{-}t\text{-}Bu)(HFIP)_3(dme)$ (dme

---

(1) Multiple Metal–Carbon Bonds. 42. For part 41 see: Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1986**, *5*, 398.

(2) (a) Schrock, R. R.; Freudenberger, J. H.; Listemann, M. L.; McCullough, L. G. *J. Mol. Catal.* **1985**, *28*, 1. (b) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (c) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; and Ziller, J. W. *Organometallics* **1984**, *3*, 1563. (d) McCullough, L. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 4067. (e) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. S. *J. Am. Chem. Soc.* **1985**, *107*, 5987.

(3) McCullough, L. G.; Listemann, M. L.; Schrock, R. R.; Churchill, M. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6729.

(4) Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 1937.

(5) Churchill, M. R.; Ziller, J. W. *J. Organomet. Chem.* **1985**, *286*, 27.

0276-7333/86/2305-1411$01.50/0 © 1986 American Chemical Society