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# Pentadienyl-Metal-Phosphine Chemistry. 5.[1] The Reaction Chemistry of ($\eta^5$-2,4-Dimethylpentadienyl)Co[P($C_2H_5$)$_3$]$_2$

John R. Bleeke* and Wei-Jun Peng

Department of Chemistry, Washington University, St. Louis, Missouri 63130

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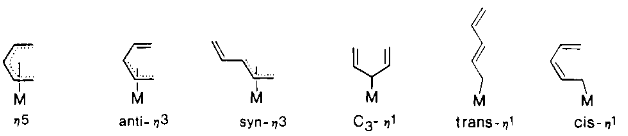
($\eta^5$-2,4-Dimethylpentadienyl)Co[P($C_2H_5$)$_3$]$_2$ (1) reacts with small phosphine and phosphite ligands, L, to produce ($\eta^3$-2,4-dimethylpentadienyl)Co$L_3$ (2, L = P($CH_3$)$_3$, and 3, L = P($OCH_3$)$_3$) and with bulky ligands to produce ($\eta^5$-2,4-dimethylpentadienyl)Co$L_2$ (4, L = P($n$-$C_3H_7$)$_3$). 1 is readily oxidized to ($\eta^5$-2,4-dimethylpentadienyl)Co[P($C_2H_5$)$_3$]$_2{}^+$ by $Ag^+$ and acids. The crystal structure of ($\eta^5$-2,4-dimethylpentadienyl)Co[P($C_2H_5$)$_3$]$_2{}^+BF_4{}^-$ (5) has been determined by X-ray diffraction. The complex crystallizes in the triclinic space group $P1$ with $a$ = 9.284 (2) Å, $b$ = 10.076 (4) Å, $c$ = 8.328 (3) Å, $\alpha$ = 114.31 (2)°, $\beta$ = 116.21 (2)°, $\gamma$ = 91.84 (2)°, and $Z$ = 1. The structure of 5 is similar to that of the neutral parent compound 1 in that the two P($C_2H_5$)$_3$ ligands are oriented with one eclipsing the open edge and one approximately eclipsing the central carbon atom C3 of the pentadienyl ligand. However, in 5 a very pronounced allyl-ene distortion of the pentadienyl ligand is observed. 1 reacts with AgI and with $CH_3I$ to produce ($\eta^5$-2,4-dimethylpentadienyl)Co[P($C_2H_5$)$_3$](I) (7). This complex crystallizes in the monoclinic space group $Cm$ with $a$ = 8.142 (1) Å, $b$ = 12.416 (4) Å, $c$ = 8.479 (2) Å, $\beta$ = 105.23 (1)°, and $Z$ = 2. The molecule resides on a crystallographically imposed mirror plane, which passes through Co, I, P, and the central pentadienyl carbon atom C3. The large P($C_2H_5$)$_3$ ligand sits under the open edge of the pentadienyl ligand, while the smaller iodo ligand resides under pentadienyl carbon atom C3. The reaction of ($\eta^5$-2,4-dimethylpentadienyl)Co[P($C_2H_5$)$_3$]$_2{}^+A^-$ (5, $A^-$ = $BF_4{}^-$, and 6, $A^-$ = $O_3SCF_3{}^-$) with 3 equiv of P($CH_3$)$_3$ produces ($\eta^3$-2,4-dimethylpentadienyl)Co[P($CH_3$)$_3$]$_3{}^+A^-$ (8, $A^-$ = $BF_4{}^-$, and 9, $A^-$ = $O_3SCF_3{}^-$). Both 8 and 9 crystallize in the monoclinic space group $P2_1/c$. The unit cell parameters for 8 are $a$ = 10.565 (2) Å, $b$ = 13.207 (3) Å, $c$ = 17.595 (4) Å, $\beta$ = 97.77 (2)°, and $Z$ = 4, while those for 9 are $a$ = 10.694 (2) Å, $b$ = 14.638 (3) Å, $c$ = 17.171 (3) Å, $\beta$ = 96.52 (1)°, and $Z$ = 4. In both 8 and 9, the $\eta^3$-2,4-dimethylpentadienyl ligand has a W-shaped syn geometry. In contrast, the 2,4-dimethylpentadienyl ligand in the neutral parent compound ($\eta^3$-2,4-dimethylpentadienyl)Co[P($CH_3$)$_3$]$_3$ (2) adopts a U-shaped anti geometry in the solid state. The 17e Co(II) complexes 5, 7, and 8 react cleanly with P($OCH_3$)$_3$ to produce 2,4-dimethylpentadiene and diamagnetic five-coordinate Co(I) complexes Co[P($C_2H_5$)$_3$][P($OCH_3$)$_3$]$_4{}^+BF_4{}^-$ (10), Co[P($OCH_3$)$_3$]$_5{}^+I^-$ (11), and Co[P($CH_3$)$_3$]$_2$[P($OCH_3$)$_3$]$_3{}^+BF_4{}^-$ (12), respectively.

## Introduction

In recent years, there has been a resurgence of interest in the synthesis, physical properties, and reaction chemistry of metal complexes containing the acyclic pentadienyl ligand.[1-3] One intriguing property of the pentadienyl ligand is that it can bond to a metal center in a variety of energetically accessible modes including $\eta^5$, syn-$\eta^3$, anti-$\eta^3$, and $\eta^1$.



We are particularly interested in interconversions between these bonding modes (e.g., $\eta^5 \rightarrow \eta^3$ and $\eta^3 \rightarrow \eta^1$), which can create coordinative unsaturation at the metal center and give rise to novel reaction chemistry. To this end, we have directed our efforts toward synthesizing and studying the chemistry of electron-rich pentadienyl-metal-trialkylphosphine complexes.[1] In these complexes, pentadienyl ligand isomerizations are promoted because the resulting coordinatively unsaturated intermediates are stabilized by the electron-donating phosphine ligands.

In an earlier paper,[1c] we reported the synthesis, structure, and solution dynamics of two pentadienyl-cobalt-trialkylphosphine complexes, ($\eta^5$-2,4-dimethylpentadienyl)Co[P($C_2H_5$)$_3$]$_2$ (1) and ($\eta^3$-2,4-dimethylpentadienyl)Co[P($CH_3$)$_3$]$_3$ (2). Herein, we describe the reaction chemistry of 1 and report the structures of four new pentadienyl-cobalt-phosphine complexes which result from these reactions. Some of the reactions of 1 are similar to those of its $\eta^5$-cyclopentadienyl analogue, ($\eta^5$-cyclopentadienyl)Co[P($C_2H_5$)$_3$]$_2$,[4,5] while others are dramatically different.

## Experimental Section

**A. General Comments.** All manipulations were carried out under inert atmosphere, using either drybox or Schlenk techniques. Benzene, toluene, diethyl ether, and tetrahydrofuran were dried with sodium/benzophenone and distilled before use. Acetone was dried over potassium carbonate and distilled; acetonitrile, chloroform, and dichloromethane were dried over phosphorus(V) oxide and distilled. Trimethylphosphine, triethylphosphine, and tri-$n$-propylphosphine were obtained from

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(1) The previous papers in this series are: (a) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1983**, *2*, 1263. (b) Bleeke, J. R.; Hays, M. K. *Ibid.* **1984**, *3*, 506. (c) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1984**, *3*, 1422. (d) Bleeke, J. R.; Kotyk, J. J. *Ibid.* **1985**, *4*, 194.

(2) Other recent reports of pentadienyl-transition-metal complexes include the following: (a) Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5928. (b) Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *Ibid.* **1982**, *104*, 1120. (c) Liu, J.-Z.; Ernst, R. D. *Ibid.* **1982**, *104*, 3737. (d) Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1982**, *1*, 708. (e) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Ibid.* **1983**, *2*, 1220. (f) Stahl, L.; Ernst, R. D. *Ibid.* **1983**, *2*, 1229. (g) Ernst, R. D.; Liu, J.-Z.; Wilson, D. R. *J. Organomet. Chem.* **1983**, *250*, 257. (h) Campana, C. F.; Ernst, R. D.; Wilson, D. R.; Liu, J.-Z. *Inorg. Chem.* **1984**, *23*, 2732. (i) Wilson, D. R.; Ernst, R. D.; Kralik, M. S. *Organometallics* **1984**, *3*, 1442. (j) Seyferth, D.; Goldman, E. W.; Pornet, J. *J. Organomet. Chem.* **1981**, *208*, 189. (k) Paz-Sandoval, M. A.; Powell, P. *Ibid.* **1981**, *219*, 81. (l) Lehmkuhl, H.; Naydowski, C. *Ibid.* **1982**, *240*, C30. (m) Hegedus, L. S.; Varaprath, S. *Organometallics* **1982**, *1*, 259. (n) Leyendecker, M.; Kreiter, C. G. *J. Organomet. Chem.* **1983**, *249*, C31. (o) Paz-Sandoval, M. A.; Powell, P. *Ibid.* **1983**, *252*, 205. (p) Paz-Sandoval, M. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026.

(3) See also the following review article: Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56.

(4) Werner, H.; Hofmann, W. *Chem. Ber.* **1981**, *114*, 2681.

(5) McKinney, R. J. *Inorg. Chem.* **1982**, *21*, 2051.

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Strem Chemicals or Organometallics; trimethyl phosphite, tetrafluoroboric acid–diethyl ether, trifluoromethanesulfonic acid, silver tetrafluoroborate, and methyl iodide were purchased from Aldrich Chemical Co.; cobalt(II) iodide was obtained from Morton-Thiokol; 2,4-dimethyl-1,3-pentadiene was purchased from Wiley Organics. All were used without further purification. Potassium 2,4-dimethylpentadienide–tetrahydrofuran was prepared by using the procedure of Yasuda et al.[6] The preparation of ($\eta^5$-2,4-dimethylpentadienyl)Co[P($C_2H_5$)$_3$]$_2$ (1) was described in an earlier paper.[1c]

All $^1$H, $^{13}$C, and $^{31}$P NMR experiments were performed on a JEOL FX-100 NMR spectrometer. $^1$H and $^{13}$C spectra were referenced to tetramethylsilane. $^{31}$P spectra were referenced to trialkylphosphine standards as indicated. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer. Gas chromatographic analyses were performed on a Perkin-Elmer Sigma 3B gas chromatograph equipped with a flame ionization detector. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

**B. Reaction of ($\eta^5$-2,4-Dimethylpentadienyl)Co[P($C_2H_5$)$_3$]$_2$ (1) with P($CH_3$)$_3$ To Produce ($\eta^3$-2,4-Dimethylpentadienyl)Co[P($CH_3$)$_3$]$_3$ (2).** At 25 °C, trimethylphosphine (1.1 g, $1.5 \times 10^{-2}$ mol) was added to a stirred solution of 1 (1.9 g, $5.0 \times 10^{-3}$ mol) in 40 mL of diethyl ether. The $^{31}$P{$^1$H} NMR spectrum of the reaction solution was recorded within minutes of the P($CH_3$)$_3$ addition and exhibited peaks due only to ($\eta^3$-2,4-dimethylpentadienyl)Co[P($CH_3$)$_3$]$_3$ (2)[1c] and free P($C_2H_5$)$_3$. Removal of the volatile components of the solution under vacuum produced a red-brown residue, which was dissolved in pentane/diethyl ether (1:3) and cooled to −30 °C. 2 crystallized as red-brown blocks: yield of crude product 1.8 g (95%); yield of crystalline product 1.2 g (65%). The full spectral characterization of 2 has been reported in an earlier paper.[1c]

**C. Reaction of 1 with P($OCH_3$)$_3$. Synthesis of ($\eta^3$-2,4-Dimethylpentadienyl)Co[P($OCH_3$)$_3$]$_3$ (3).** At 25 °C, trimethyl phosphite (5.0 g, $4.0 \times 10^{-2}$ moles) was added to a stirred solution of 1 (1.9 g, $5.0 \times 10^{-3}$ mol) in 40 mL of diethyl ether. The $^{31}$P{$^1$H} NMR spectrum of the reaction solution, recorded within minutes of the P($OCH_3$)$_3$ addition, exhibited peaks due only to ($\eta^3$-2,4-dimethylpentadienyl)Co[P($OCH_3$)$_3$]$_3$ (3, see below), free P($C_2H_5$)$_3$, and free P($OCH_3$)$_3$. The solution was evaporated to dryness leaving a red powder, which was redissolved in pentane and cooled to −30 °C. 3 precipitated as red microcrystals; yield of crystalline product 2.5 g (95%). The NMR spectra of 3 (benzene-$d_6$, 25 °C) exhibited peaks due to an equilibrium mixture of (*syn*-$\eta^3$-2,4-dimethylpentadienyl)- and (*anti*-$\eta^3$-2,4-dimethylpentadienyl)-Co[P($OCH_3$)$_3$]$_3$ isomers. $^{13}$C{$^1$H} NMR: $\delta$ 150.8, 150.1 (C4), 111.2, 105.1 (C5), 85.8, 84.5 (C2), 65.4, 64.5 (C3), 51.0 (P($OCH_3$)$_3$), 43.1, 42.4 (C1), 26.4, 24.3, 23.1, 22.6 (pentadienyl methyl C's). $^1$H NMR (selected peaks): major isomer, $\delta$ 5.41 (s, 1, vinyl H), 5.17 (s, 1, vinyl H), 3.52 (br s, 27, P($OCH_3$)$_3$), 2.51 (d, 3, allyl methyl H's), 2.26 (s, 3, vinyl methyl H's); minor isomer, $\delta$ 5.17 (s, 1, vinyl H), 4.69 (s, 1, vinyl H), 3.52 (br s, 27, P($OCH_3$)$_3$), 3.34 (d, 3, allyl methyl H's), 2.08 (s, 3, allyl vinyl H's). Signals for the allyl H's appear in the $\delta$ 4.2–1.0 region of the spectrum but have not been assigned. $^{31}$P{$^1$H} NMR (referenced to free P($OCH_3$)$_3$): $\delta$ 25.8 (br s). IR (benzene): 3000–2820 (m, pentadienyl/P($OCH_3$)$_3$), 1600 (w, C=C), 1450–1440, 1175 (m, pentadienyl/P($OCH_3$)$_3$), 1090–1000 cm$^{-1}$ (vs, P($OCH_3$)$_3$). Anal. Calcd for $C_{16}H_{38}CoP_3O_9$: C, 36.51; H, 7.29. Found: C, 36.17; H, 6.93.

**D. Reaction of 1 with P($n$-$C_3H_7$)$_3$. Synthesis of ($\eta^5$-2,4-Dimethylpentadienyl)Co[P($n$-$C_3H_7$)$_3$]$_2$ (4). Method 1.** At 25 °C, tri-$n$-propylphosphine (2.0 g, $1.2 \times 10^{-2}$ mol) was added to a stirred solution of 1 (1.9 g, $5.0 \times 10^{-3}$ mol) in 40 mL of toluene. The $^{31}$P{$^1$H} NMR spectrum of the reaction solution exhibited signals due to an equilibrium mixture of ($\eta^5$-2,4-dimethylpentadienyl)Co$L_2$ complexes. Evacuation of the reaction solution resulted in preferential removal of the lower boiling phosphine, P($C_2H_5$)$_3$, and shifted the equilibrium toward ($\eta^5$-2,4-dimethylpentadienyl)Co[P($n$-$C_3H_7$)$_3$]$_2$. The solution was taken to dryness under vacuum, and a second portion of P($n$-$C_3H_7$)$_3$ (0.8 g, $5.0 \times 10^{-3}$ mol) in 20 mL of toluene was added to the residue. The resulting solution was again taken to dryness under vacuum, after which the dark brown residue was dissolved in pentane and cooled to −30 °C. 4 crystallized as dark brown blocks; yield of crystalline product 1.8 g (75%).

**Method 2.** $CoCl_2$ (0.65 g, $5.0 \times 10^{-3}$ mol) and P($n$-$C_3H_7$)$_3$ (1.6 g, $1.0 \times 10^{-2}$ mol) were added to 50 mL of tetrahydrofuran and stirred for 1 h, yielding a dark blue solution. The solution was cooled to 0 °C, and potassium 2,4-dimethylpentadienide–tetrahydrofuran (2.1 g, $1.0 \times 10^{-2}$ mol) in 30 mL of tetrahydrofuran was added dropwise with stirring. The resulting brown solution was warmed to room temperature, stirred for 10 h, filtered, and evaporated to dryness. The brown product was extracted with pentane and crystallized from a saturated pentane solution at −30 °C; yield of crystalline product 1.2 g (50%). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 25 °C): $\delta$ 98.4 (C2, C4), 84.5 (C3), 46.6 (C1, C5), 33.8–33.3 (P$CH_2CH_2CH_3$), 26.4 (pentadienyl methyl C's), 18.4, 17.9 (P$CH_2CH_2CH_3$), 16.8, 16.7 (P$CH_2CH_2CH_3$). $^1$H NMR (benzene-$d_6$, 25 °C): $\delta$ 3.39 (br d, 1, H3), 3.09 (br s, 2, syn H's), 2.01 (s, 6, pentadienyl methyl H's), 1.49 (br s, 12, P($n$-$C_3H_7$)$_3$ methylene H's), 1.32 (br s, 12, P($n$-$C_3H_7$)$_3$ methylene H's), 0.98 (br s, 18, P($n$-$C_3H_7$)$_3$ methyl H's), 0.79 (br s, 2, anti H's). $^{31}$P{$^1$H} NMR (benzene-$d_6$, 25 °C, referenced to free P($n$-$C_3H_7$)$_3$): $\delta$ 74.4, 45.1. IR (benzene): 3010–2860, 1450, 1375 (m, pentadienyl/P($n$-$C_3H_7$)$_3$), 1074, 1020 cm$^{-1}$ (m, P($n$-$C_3H_7$)$_3$). Anal. Calcd for $C_{25}H_{53}CoP_2$: C, 63.26; H, 11.28. Found: C, 63.05; H, 11.02.

**E. Synthesis of ($\eta^5$-2,4-Dimethylpentadienyl)Co[P($C_2H_5$)$_3$]$_2$$^+$$BF_4^-$ (5). Method 1.** At room temperature, a solution of $AgBF_4$ (0.40 g, $2.0 \times 10^{-3}$ mol) in 20 mL of acetonitrile was added to a stirred solution of 1 (0.78 g, $2.0 \times 10^{-3}$ mol) in 15 mL tetrahydrofuran. The reaction solution was filtered through a fine glass frit to remove silver metal, and the solvents were removed under vacuum. The resulting red powder was redissolved in 15 mL of tetrahydrofuran and cooled to −30 °C. 5 crystallized as dark red blocks: yield of powder 0.94 g (99%); yield of crystals 0.70 g (74%).

**Method 2.** Tetrafluoroboric acid–diethyl ether (0.48 g, $3.0 \times 10^{-3}$ mol) was added slowly to a cold (−30 °C), stirred solution of 1 (1.17 g, $3.0 \times 10^{-3}$ mol) in 20 mL of tetrahydrofuran. After several minutes of additional stirring at −30 °C, the volume of tetrahydrofuran solvent was reduced under vacuum and 5 crystallized as dark red blocks; yield of crystalline product 1.10 g (77%). IR (dichloromethane): 2970, 2940 (m, pentadienyl/P($C_2H_5$)$_3$), 1460, 1425, 1380 (m, pentadienyl/P($C_2H_5$)$_3$), 1025–1080 cm$^{-1}$ (vs, $BF_4^-$/P($C_2H_5$)$_3$). Anal. Calcd for $CoP_2C_{19}H_{41}BF_4$: C, 47.81; H, 8.68. Found: C, 47.79; H, 8.62.

**F. Synthesis of ($\eta^5$-2,4-Dimethylpentadienyl)Co[P($C_2H_5$)$_3$]$_2$$^+$$O_3SCF_3^-$ (6).** Trifluoromethanesulfonic acid (0.30 g, $2.0 \times 10^{-3}$ mol) was added dropwise to a cold (−30 °C), stirred solution of 1 (0.78 g, $2.0 \times 10^{-3}$ mol) in 15 mL of tetrahydrofuran. After the addition of $HO_3SCF_3$, the solution was stored in a −30 °C freezer for 24 h. The volume of the tetrahydrofuran solvent was then reduced under vacuum, and the solution was returned to the freezer, where 6 precipitated as red microcrystals; yield of crystalline product 0.21 g (20%). IR (chloroform): 3010, 2980 (m, pentadienyl/P($C_2H_5$)$_3$), 1460, 1430, 1380 (m, pentadienyl/P($C_2H_5$)$_3$), 1275, 1165, 640 (s, $O_3SCF_3^-$), 1035 cm$^{-1}$ (s, P($C_2H_5$)$_3$). Anal. Calcd for $CoP_2C_{20}H_{41}SO_3F_3$: C, 44.52; H, 7.68. Found: C, 44.37; H, 7.67.

**G. Synthesis of ($\eta^5$-2,4-Dimethylpentadienyl)Co[P($C_2H_5$)$_3$](I) (7). Method 1.** At 25 °C, a solution of AgI (0.47 g, $2.0 \times 10^{-3}$ mol) in 15 mL of acetonitrile was added to a stirred solution of 1 (0.78 g, $2.0 \times 10^{-3}$ moles) in 20 mL of tetrahydrofuran. The solution was stirred for 1 h and then filtered to remove silver metal. The acetonitrile/tetrahydrofuran solvent was removed under vacuum, and the resulting red solid was redissolved in diethyl ether. This solution was cooled to −30 °C, yielding 7 as dark red blocks; yield of crystalline product 0.65 g (82%).

**Method 2.** Methyl iodide (0.36 g, $2.5 \times 10^{-3}$ mol) was added dropwise to a cold (−30 °C), stirred solution of 1 (0.98 g, $2.5 \times 10^{-3}$ mol) in 15 mL of diethyl ether. After the addition of methyl iodide, the solution was stored in a −30 °C freezer for 2 h. The volume of diethyl ether solvent was then reduced under vacuum, and the solution was returned to the −30 °C freezer, where 7 crystallized as dark red blocks; yield of crystalline product 0.50 g (50%).

The reactions of 1 with longer/chain alkyl iodides, RI (R = propyl, butyl, pentyl), also produced 7, although in somewhat lower

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[6] Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036.

yields. The volatile organic products of these reactions were analyzed by gas chromatography and, in each case, the coupled dialkyl, R–R (R–R = hexane, octane, decane), was observed. (Gas chromatographic separations were carried out by using a 12 ft × $^1/_8$ in. column of 3% Carbowax K-20M on Gas Chrom-Q at 80 °C).

**Method 3.** At 25 °C, a solution of $NH_4I$ (0.036 g, $2.5 \times 10^{-4}$ mol) in 10 mL of acetonitrile was added to a stirred solution of **5** (0.12 g, $2.5 \times 10^{-4}$ mol) in 10 mL of acetonitrile. After the mixture was stirred for 20 min, the solvent was removed under vacuum. The resulting red solid was extracted with diethyl ether, filtered, and cooled to −30 °C, yielding dark red blocks of **7**; yield of crystalline products 0.080 g (80%).

**Method 4.** A solution of potassium 2,4-dimethylpentadienide–tetrahydrofuran (2.06 g, $1.0 \times 10^{-2}$ mol) in 40 mL of tetrahydrofuran was added dropwise to a cold (0 °C), stirred solution of $CoI_2$ (3.13 g, $1.0 \times 10^{-2}$ mol) and $P(C_2H_5)_3$ (1.18 g, $1.0 \times 10^{-2}$ mol) in 50 mL of tetrahydrofuran. The solution was warmed to room temperature, stirred for 10 h, and filtered. The tetrahydrofuran solvent was removed under vacuum, and the resulting red powder was extracted with diethyl ether. The diethyl ether solution was cooled to −30 °C, and **7** crystallized as dark red blocks; yield of crystalline product 1.2 g (30%). IR (dichloromethane): 2960, 1445, 1415, 1375 (m, pentadienyl/$P(C_2H_5)_3$), 1030 cm$^{-1}$ (m, $P(C_2H_5)_3$). Anal. Calcd for $CoPC_{13}H_{26}I$: C, 39.11; H, 6.58. Found: C, 39.03; H, 6.68.

**H. Reaction of 5 with $P(CH_3)_3$. Synthesis of ($\eta^3$-2,4-Dimethylpentadienyl)Co$[P(CH_3)_3]_3{}^+BF_4{}^-$ (8). Method 1.** At room temperature, $P(CH_3)_3$ (0.41 g, $5.4 \times 10^{-3}$ mol) was added slowly to a stirred solution of **5** (0.85 g, $1.8 \times 10^{-3}$ mol) in tetrahydrofuran/acetone (10 mL/0.5 mL). After completion of the $P(CH_3)_3$ addition, the solution was stirred for 30 min and then slowly cooled to −30 °C. **8** crystallized as red needles; yield of crystalline product 0.62 g (73%).

**Method 2.** At room temperature, a solution of $AgBF_4$ (0.39 g, $2.0 \times 10^{-3}$ moles) in 20 mL of acetonitrile was added to a stirred solution of **2** (0.76 g, $2.0 \times 10^{-3}$ mol) in 15 mL of tetrahydrofuran. After an hour of additional stirring, the solution was filtered through a fine glass frit to remove silver metal and the solvents were removed under vacuum. The residual solid was dissolved in minimal tetrahydrofuran/acetone (20:1) and slowly cooled to −30 °C to yield crystalline **8** (0.5 g, 59%). IR (KBr pellet): 2975, 2910 (m, pentadienyl/$P(CH_3)_3$), 1605 (w, C=C stretch), 1430, 1310, 1290 (m, pentadienyl/$P(CH_3)_3$), 1030–1100 (vs, $P(CH_3)_3/BF_4{}^-$), 950 cm$^{-1}$ (vs, $P(CH_3)_3$). Anal. Calcd for $CoP_3C_{16}H_{38}BF_4$: C, 40.96; H, 8.18. Found: C, 40.80; H, 8.34.

**I. Reaction of 6 with $P(CH_3)_3$. Synthesis of ($\eta^3$-2,4-Dimethylpentadienyl)Co$[P(CH_3)_3]_3{}^+O_3SCF_3{}^-$ (9).** At room temperature, $P(CH_3)_3$ (0.09 g, $1.2 \times 10^{-3}$ mol) was added dropwise to a stirred solution of **6** (0.21 g, $3.9 \times 10^{-4}$ mol) in 15 mL of tetrahydrofuran. The solution was cooled to −30 °C, and **9** crystallized as dark red blocks; yield of crystalline product 0.16 g (77%). IR (KBr pellet): 2975, 2910 (m, pentadienyl/$P(CH_3)_3$), 1605 (w, C=C stretch), 1430, 1305, 1290, 1030 (m, pentadienyl/$P(CH_3)_3$), 1265, 1150, 635 (s, $O_3SCF_3{}^-$), 945 cm$^{-1}$ (s, $P(CH_3)_3$). Anal. Calcd for $CoP_3C_{17}H_{38}SO_3F_3$: C, 38.42; H, 7.22. Found: C, 38.18; H, 7.13.

**J. Reaction of 5 with $P(OCH_3)_3$. Synthesis of Co$[P(C_2H_5)_3][P(OCH_3)_3]_4{}^+BF_4{}^-$ (10).** Trimethyl phosphite (0.25 g, $2.0 \times 10^{-3}$ mol) was added dropwise to a stirred solution of **5** (0.24 g, $5.0 \times 10^{-4}$ mol) in 2 mL of acetonitrile-$d_3$. The solution was stirred for 1 h, during which its color gradually changed from red to orange. The volatile products and acetonitrile-$d_3$ solvent were removed under vacuum, leaving a solid orange residue. The volatile fraction contained approximately equimolar quantities of $P(C_2H_5)_3$ and 2,4-dimethyl-1,3-pentadiene, and *no* $P(OCH_3)_3$, as determined by $^1H$ NMR spectroscopy and gas chromatography. (Gas chromatographic separations were carried out by using a 12 ft × $^1/_8$ in. column of 3% Carbowax K-20M on Gas Chrom-Q at 80 °C.) The orange residue was redissolved in a mixture of tetrahydrofuran and acetone (10:1) and cooled to −30 °C, yielding orange blocks of Co$[P(C_2H_5)_3][P(OCH_3)_3]_4{}^+BF_4{}^-$ (**10**); yield of crystalline product 0.33 g (87%). $^1H$ NMR (acetonitrile-$d_3$, 25 °C) $\delta$ 3.66 (br s, 36, $P(OCH_3)_3$), 1.25–0.90 (m, 15, $P(C_2H_5)_3$). $^{13}C\{^1H\}$ NMR (acetonitrile-$d_3$, 25 °C) $\delta$ 53.4 (s, $P(OCH_3)_3$), 22.8 (d, $J_{P\text{-}C}$ = 15 Hz, $P(C_2H_5)_3$ methylene C's), 10.7 (s, $P(C_2H_5)_3$ methyl C's). $^{31}P\{^1H\}$ NMR (tetrahydrofuran, 25 °C, referenced to free $P(C_2H_5)_3$): $\delta$ 166.1 (s, $P(OCH_3)_3$), 59.3 (s, $P(C_2H_5)_3$). IR (dichloromethane): 2950, 1460, 1175 (m), 1050, 730 cm$^{-1}$ (vs). Anal. Calcd for $CoP_5C_{18}H_{51}O_{12}BF_4$: C, 28.43; H, 6.78. Found: C, 28.23; H, 6.83. Reaction of **5** with excess $P(OCH_3)_3$ (8 mol of $P(OCH_3)_3$/mol of **5**) also led to isolation of **10** in high yield. The volatile fraction of this reaction contained 2,4-dimethyl-1,3-pentadiene, $P(C_2H_5)_3$, and $P(OCH_3)_3$ in an approximate molar ratio of 1:1:4.

**K. Reaction of 7 with $P(OCH_3)_3$. Synthesis of Co$[P(OCH_3)_3]_5{}^+I^-$ (11).** At 25 °C, trimethyl phosphite (0.62 g, $5.0 \times 10^{-3}$ mol) was added dropwise to a stirred solution of **7** (0.40 g, $1.0 \times 10^{-3}$ mol) in 15 mL of tetrahydrofuran. The solution was stirred for 1 h and then cooled to −30 °C, yielding orange needles of Co$[P(OCH_3)_3]_5{}^+I^-$ (**11**); yield of crystalline product 0.69 g (86%). $^1H$ NMR (methanol-$d_4$, 15 °C): $\delta$ 3.70 (m). $^{13}C\{^1H\}$ NMR (acetonitrile, 15 °C): $\delta$ 53.6 (s). $^{31}P\{^1H\}$ NMR (acetonitrile, 15 °C, referenced to free $P(C_2H_5)_3$): $\delta$ 167.7 (s). IR (KBr pellet): 2945, 1450, 1180 (m), 1035, 770, 705 cm$^{-1}$ (vs). Anal. Calcd for $CoP_5C_{15}H_{45}O_{15}I$: C, 22.34; H, 5.64. Found: C, 22.88; H, 5.68.

**L. Reaction of 8 with $P(OCH_3)_3$. Synthesis of Co$[P(CH_3)_3]_2[P(OCH_3)_3]_3{}^+BF_4{}^-$ (12).** Trimethyl phosphite (0.25 g, $2.0 \times 10^{-3}$ mol) was added dropwise to a stirred solution of **8** (0.23 g, $5.0 \times 10^{-4}$ mol) in 2 mL of acetonitrile. The solution was stirred for 1 h, during which its color gradually changed from red to orange. The volatile products and solvent were removed under vacuum, leaving a solid orange residue. This residue was redissolved in a mixture of tetrahydrofuran and acetone (10:1) and cooled to −30 °C, yielding orange blocks of Co$[P(CH_3)_3]_2$$[P(OCH_3)_3]_3{}^+BF_4{}^-$ (**12**); yield of crystalline product 0.27 g (81%). $^1H$ NMR (acetonitrile-$d_3$, 25 °C): $\delta$ 3.70 (m, 27, $P(OCH_3)_3$), 1.31 (m, 18, $P(CH_3)_3$). $^{13}C\{^1H\}$ NMR (acetonitrile, 25 °C): $\delta$ 52.7 (s, $P(OCH_3)_3$), 21.4 (br s, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (acetonitrile, 25 °C, referenced to free $P(CH_3)_3$): $\delta$ 203.82 (br s, $P(OCH_3)_3$), 84.84 (quartet, $J_{PP}$ = 113 Hz, $P(CH_3)_3$). IR (dichloromethane): 2945, 1455, 1175 (m), 1050 (vs, $P(OCH_3)_3/BF_4{}^-$), 955 cm$^{-1}$ (s, $P(CH_3)_3$). Anal. Calcd for $CoP_5C_{15}H_{45}O_9BF_4$: C, 26.88; H, 6.78. Found: C, 26.85; H, 6.84.

**M. X-ray Diffraction Studies of 5, 7, 8, and 9.** Single crystals suitable for X-ray diffraction were grown as indicated above. Data were collected at room temperature on a Nicolet P3 diffractometer, using graphite-monochromated Mo K$\alpha$ radiation. All data reduction and structure refinement were done by using the Enraf-Nonius structure determination package on a VAX 11/780 computer (modified by B.A. Frenz and Associates, Inc., College Station, TX). Crystal data and the details of data collection and structure analysis are summarized in Table I.

All of the structures were solved by standard Fourier techniques, following the location of the cobalt atoms from Patterson maps. In all of the structures, non-hydrogen atoms were refined with anisotropic thermal parameters. Some of the hydrogen atoms were located from difference Fourier maps and refined isotropically. Others were added at idealized positions and included in the structure factor calculations.

## Results and Discussion

A summary of the reaction chemistry of ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3]_2$ (**1**) is shown in Scheme I.

**A. Reaction of ($\eta^5$-2,4-Dimethylpentadienyl)Co$[P(C_2H_5)_3]_2$ (1) with Phosphines and Phosphites, L.** **1** reacts cleanly with 3 equiv of sterically undemanding phosphines and phosphites such as $P(CH_3)_3$ and $P(OCH_3)_3$ to produce ($\eta^3$-2,4-dimethylpentadienyl)CoL$_3$ (**2**, L = $P(CH_3)_3$, and **3**, L = $P(OCH_3)_3$). These reactions proceed very rapidly at room temperature and are irreversible, even in the presence of excess $P(C_2H_5)_3$.

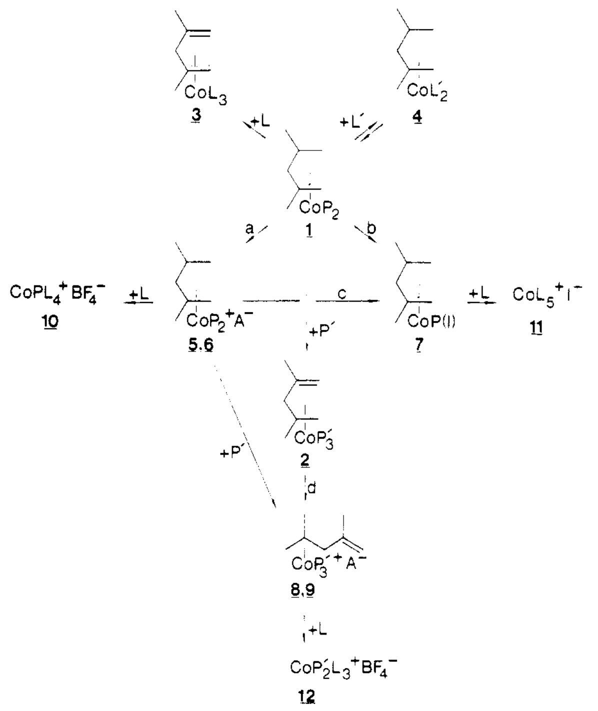
**1** also undergoes substitution reactions with sterically bulky phosphines and phosphites, L, producing ($\eta^5$-2,4-dimethylpentadienyl)Co(P)(L) and ($\eta^5$-2,4-dimethylpentadienyl)CoL$_2$. These are reversible reactions which require excess L to be driven to the fully substituted product. The reaction of **1** with excess $P(n\text{-}C_3H_7)_3$, for example, produces ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(n\text{-}C_3H_7)_3]_2$ (**4**).

**Table I. Crystal and Diffraction Data for 5, 7, 8 and 9**

| | 5 | 7 | 8 | 9 |
|---|---|---|---|---|
| space group | $P\bar{1}$ | $Cm$ | $P2_1/c$ | $P2_1/c$ |
| $a$, Å | 9.284 (2) | 8.142 (1) | 10.565 (2) | 10.694 (2) |
| $b$, Å | 10.076 (4) | 12.416 (4) | 13.207 (3) | 14.638 (3) |
| $c$, Å | 8.328 (3) | 8.479 (2) | 17.595 (4) | 17.171 (3) |
| $\alpha$, deg | 114.31 (2) | 90.0 | 90.0 | 90.0 |
| $\beta$, deg | 116.21 (2) | 105.23 (1) | 97.77 (2) | 96.52 (1) |
| $\gamma$, deg | 91.84 (2) | 90.0 | 90.0 | 90.0 |
| $V$, Å$^3$ | 614.8 (3) | 827.1 (3) | 2432.5 (9) | 2670.6 (9) |
| $Z$ | 1 | 2 | 4 | 4 |
| cryst dimens, mm | 0.5 × 0.4 × 0.2 | 0.6 × 0.5 × 0.4 | 0.6 × 0.4 × 0.3 | 0.6 × 0.5 × 0.4 |
| scan type | $\omega$ | $\omega$ | $\omega$ | $2\theta/\theta$ |
| scan rate, deg/min | variable (2–29) | variable (2–29) | variable (2–29) | variable (2–29) |
| $2\theta$ min, deg | 3 | 3 | 3 | 3 |
| $2\theta$ max, deg | 55 | 65 | 60 | 55 |
| no. of reflcts measd | 5654 | 3301 | 7026 | 6095 |
| no. of reflcts with $I > 3\sigma(I)$ | 2560 | 1478 | 3359 | 3175 |
| abs coeff $\mu$, cm$^{-1}$ | 8.55 | 29.57 | 9.25 | 9.27 |
| abs correctn | none | none | none | none |
| final $R_F$[a] | 0.038 | 0.025 | 0.053 | 0.047 |
| final $R_{wF}$[b] | 0.048 | 0.037 | 0.066 | 0.059 |
| largest peak in final diff Fourier map, e/Å$^3$ | 0.40 | 0.56 | 0.62 | 0.61 |

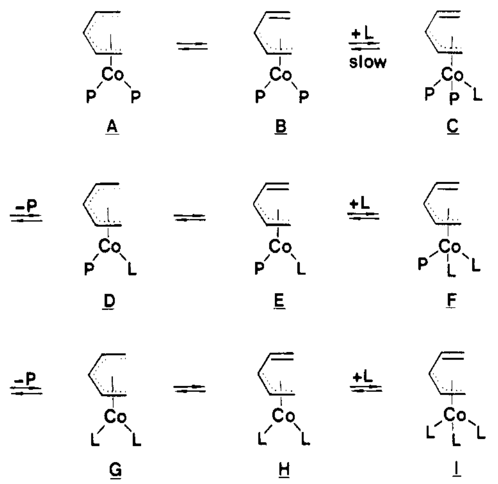
[a] $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|)$.

**Scheme I[a]**



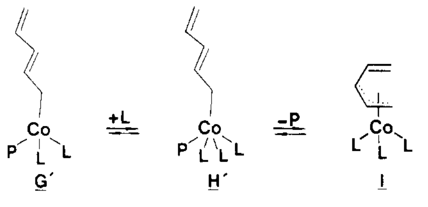
[a] P = P(C$_2$H$_5$)$_3$; P′ = P(CH$_3$)$_3$; L = P(OCH$_3$)$_3$; L′ = P(n-C$_3$H$_7$)$_3$. (a) AgBF$_4$ or HBF$_4$ or HO$_3$SCF$_3$. (b) AgI or alkyl iodides. (c) NH$_4$I. (d) AgBF$_4$.

**Scheme II[a]**



[a] Methyl groups on 2,4-dimethylpentadienyl ligand have been omitted for clarity. P = P(C$_2$H$_5$)$_3$; L = small phosphine or phosphite ligand.

**Scheme III[a]**



[a] Methyl groups on 2,4-dimethylpentadienyl ligand have been omitted for clarity. P = P(C$_2$H$_5$)$_3$; L = small phosphine or phosphite ligand.

We believe that small ligands, L, react with 1 via a series of *associative* steps, which are preceded by $\eta^5 \rightarrow \eta^3$ (and perhaps $\eta^3 \rightarrow \eta^1$) pentadienyl ligand isomerizations (see Scheme II).[7] The first such step (top line, Scheme II) produces sterically crowded C, which relieves steric strain by losing the larger of its phosphine ligands (P), producing D. D can then react with L in a second associative step, producing F. From F, the same series of steps (i.e., loss of P, addition of L) can be repeated, producing G and I. Alternatively, F can undergo an associative attack via 16e $\eta^1$-pentadienyl intermediate G′ (see Scheme III). Loss of P from H′ produces I.

For small ligands, L, the first associative step (B → C) is expected to be the slowest step in the sequence. Later steps involve less sterically congested intermediates and should proceed more readily. Consistent with these expectations is the fact that intermediates such as C, D, F, and G are not observed by NMR, even when the reactions are monitored at low temperature.[8]

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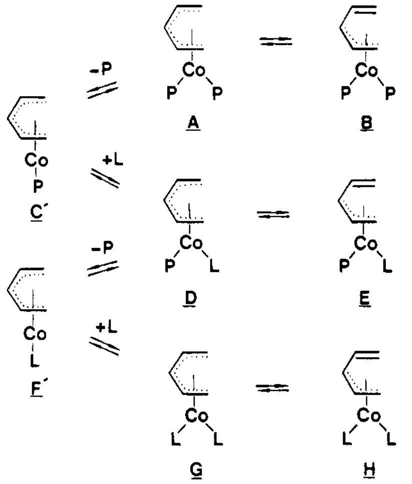
[7] The reaction of ($\eta^5$-pentadienyl)Mn(CO)$_3$ with phosphine has been shown by Powell et al. to proceed by an associative mechanism.[2p] The reactions of ($\eta^5$-cyclopentadienyl)Rh(CO)$_2$[7a] and ($\eta^5$-cyclopentadienyl)-Re(CO)$_3$[7b] with phosphines also involve associative steps which are apparently preceded by $\eta^5 \rightarrow \eta^3$ cyclopentadienyl ring slips. In contrast, ($\eta^5$-cyclopentadienyl)Co-[P(C$_6$H$_5$)$_3$]$_2$ reacts with phosphines by a dissociative mechanism.[7c] (a) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. (b) Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535. (c) Janowicz, A. H.; Bryndza, H. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1516.

**Scheme IV**[a]



[a] Methyl groups on 2,4-dimethylpentadienyl ligand have been omitted for clarity. P = $P(C_2H_5)_3$; L = bulky phosphine or phosphite ligand.

Bulky phosphines and phosphites, L, react with 1 to produce equilibrium mixtures of products A, D, and G (Scheme IV).[7] In these reactions, associative steps are expected to be difficult, because L is large and the 16e intermediates (B, E, and H) are sterically congested. Therefore, we believe that these reactions proceed via a series of *dissociative* steps, i.e., loss of P (cf. intermediates C′ and F′, Scheme IV) followed by addition of L. Kinetic studies have been initiated to probe the mechanisms of these substitution reactions in more detail.

**B. Oxidation of 1 to ($\eta^5$-2,4-Dimethylpentadienyl)Co[$P(C_2H_5)_3$]$_2^+A^-$ (5, $A^- = BF_4^-$, and 6, $A^- = O_3SCF_3^-$).** 1 is readily oxidized to the 17e radical cation by a variety of reagents including $AgBF_4$, $HBF_4{\cdot}O(C_2H_5)_2$, and $HO_3SCF_3$. The reactions involving the Brønsted acids are particularly interesting in that they differ markedly from the analogous reactions of ($\eta^5$-cyclopentadienyl)Co[$P(C_2H_5)_3$]$_2$; the cyclopentadienyl complex is simply protonated by acids, producing isolable ($\eta^5$-cyclopentadienyl)Co[$P(C_2H_5)_3$]$_2(H)^+A^-$ salts.[4]

Several plausible mechanisms for the reactions of 1 with acids can be envisaged, including (a) one-electron outer-sphere electron transfer, (b) one-electron inner-sphere electron transfer, and (c) two-electron inner-sphere electron transfer/comproportionation. Of these possibilities, we

$$\text{(a)}\quad 2(\eta^5\text{-pd})CoP_2 + 2H^+ \rightarrow 2(\eta^5\text{-pd})CoP_2^+ + H_2$$

$$\text{(b)}\quad 2(\eta^5\text{-pd})CoP_2 + 2H^+ \rightarrow 2(\eta^5\text{-pd})CoP_2(H)^+ \rightarrow 2(\eta^5\text{-pd})CoP_2^+ + H_2$$

$$\text{(c)}\quad (\eta^5\text{-pd})CoP_2 + H^+ \rightarrow (\eta^5\text{-pd})CoP_2(H)^+ \xrightarrow{+H^+} (\eta^5\text{-pd})CoP_2(H)_2^{2+} \rightarrow (\eta^5\text{-pd})CoP_2^{2+} + H_2$$

$$(\eta^5\text{-pd})CoP_2^{2+} + (\eta^5\text{-pd})CoP_2 \rightarrow 2(\eta^5\text{-pd})CoP_2^+$$

favor the one-electron inner-sphere mechanism (b), which requires a bimolecular reductive elimination of $H_2$ from two ($\eta^5$-2,4-dimethylpentadienyl)Co[$P(C_2H_5)_3$]$_2(H)^+$ ions. The outer-sphere mechanism (a) involves the intermediacy of free hydrogen radicals and appears to be energetically unfavorable, although we do not yet know the oxidation potential of 1. Cyclic voltammetric experiments are planned to determine this potential. The inner-sphere two-electron transfer mechanism (c) requires attack of a proton on an already protonated cationic intermediate, a process with a large electrostatic barrier.[9] A variant on this mechanism involves loss of hydride from the protonated intermediate ($\eta^5$-2,4-dimethylpentadienyl)Co[$P(C_2H_5)_3$]$_2(H)^+$, followed by reaction of the hydride with a proton from the Brønsted acid.

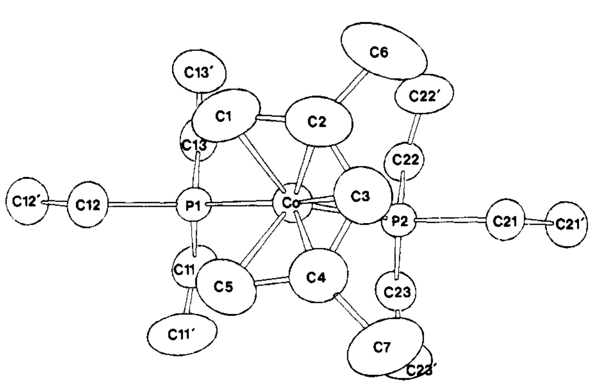


**Figure 1.** ORTEP drawing of the cation of ($\eta^5$-2,4-dimethylpentadienyl)Co[$P(C_2H_5)_3$]$_2^+BF_4^-$ (5). Heavy atoms are represented by thermal ellipsoids drawn to encompass 50% of the electron density.

The contrasting reactivity of 1 and its cyclopentadienyl analogue toward acids (i.e., oxidation vs. protonation) is noteworthy; however, the reason for this reactivity difference is still unclear. It may be due to an intrinsic difference in the tendency for 1 and ($\eta^5$-cyclopentadienyl)Co[$P(C_2H_5)_3$]$_2$ to undergo oxidation,[10] or, alternatively, it may be due to steric and/or electronic differences in the protonated species. Recently, Legzdins reported that [($\eta^5$-cyclopentadienyl)Cr(NO)$_2$]$_2$, [($\eta^5$-cyclopentadienyl)Mn(CO)(NO)]$_2$, and [($\eta^5$-cyclopentadienyl)Co(NO)]$_2$ undergo oxidation when reacted with $HBF_4{\cdot}O(CH_3)_2$.[11] In the chromium and manganese reaction systems, Legzdins proposed initial protonation, followed by unsymmetrical dissociation of the resulting cationic dimer, while in the cobalt system, he proposed protonation and inner-sphere one-electron transfer to account for the observed product [($\eta^5$-cyclopentadienyl)Co(NO)]$_2^+BF_4^-$. Interestingly, reaction of the isoelectronic iron dimer [($\eta^5$-cyclopentadienyl)Fe(CO)$_2$]$_2$ with $HBF_4{\cdot}O(CH_3)_2$ produces an isolable metal hydride complex, [($\eta^5$-cyclopentadienyl)Fe(CO)$_2$]$_2(H)^+BF_4^-$.[11]

**C. Structure of ($\eta^5$-2,4-Dimethylpentadienyl)Co[$P(C_2H_5)_3$]$_2^+BF_4^-$ (5).** An ORTEP drawing of the cation of 5, based on an X-ray structural analysis, is presented in Figure 1. Atomic coordinates for the non-hydrogen atoms are listed in Table II. Important bond distances and angles are reported in Table III. The structure of 5 is very similar to that of the neutral precursor 1, which we described in an earlier paper.[1c] In both structures, the triethylphosphine ligands are oriented so that one phosphine (P2) *approximately* eclipses C3 of the pentadienyl ligand (vide infra), while the other (P1) resides under the open

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(8) Our current data do not allow us to exclude the possibility that the *first* step in the reaction of 1 with small L is dissociative, i.e., loss of P from 1. However, the subsequent steps in the reaction sequence are almost certainly associative; for example, D must react with L by an associative step, because a *dissociative* loss of P from D would be as slow as or slower than loss of P from A. This, in turn, would result in a buildup of D, which is inconsistent with our observations.

(9) However, such as mechanism has been postulated by Werner for the high-temperature reaction of ($\eta^5$-cyclopentadienyl)Co[$P(CH_3)_3$]$_2(H)^+$ with excess aqueous $HBF_4$ in propionic anhydride. See: Werner, H.; Hofmann, W. *Chem. Ber.* **1977**, *110*, 3481.

(10) Ernst has reported that ($\eta^5$-2,4-dimethylpentadienyl)$_2$Fe is more readily oxidized than ($\eta^5$-cyclopentadienyl)$_2$Fe.[3]

(11) Legzdins, P.; Martin, D. T.; Nurse, C. R.; Wassink, B. *Organometallics* **1983**, *2*, 1238.

**Table II. Positional Parameters with Estimated Standard Deviation for Non-Hydrogen Atoms in ($\eta^5$-2,4-Dimethylpentadienyl)Co[P($C_2H_5$)$_3$]$_2$$^+$$BF_4^-$ (5)**

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Co | 0.000 | 0.000 | 0.000 |
| P1 | −0.1543 (1) | −0.1840 (1) | −0.3139 (1) |
| P2 | 0.0561 (1) | 0.20102 (9) | −0.0454 (1) |
| C1 | −0.1362 (7) | −0.0870 (7) | 0.1066 (6) |
| C2 | −0.0389 (6) | 0.0577 (6) | 0.2477 (5) |
| C3 | 0.1324 (7) | 0.1037 (5) | 0.3190 (6) |
| C4 | 0.2324 (6) | 0.0144 (5) | 0.2476 (6) |
| C5 | 0.1729 (7) | −0.1329 (6) | 0.1022 (8) |
| C6 | −0.1205 (8) | 0.1819 (9) | 0.3126 (7) |
| C7 | 0.4050 (7) | 0.0965 (8) | 0.330 (1) |
| C11 | −0.0848 (6) | −0.2130 (7) | −0.4970 (7) |
| C11′ | 0.0796 (8) | −0.255 (1) | −0.442 (1) |
| C12 | −0.1950 (7) | −0.3707 (5) | −0.3338 (8) |
| C12′ | −0.3087 (8) | −0.5014 (6) | −0.543 (1) |
| C13 | −0.3602 (6) | −0.1600 (5) | −0.4551 (7) |
| C13′ | −0.4643 (7) | −0.1320 (8) | −0.3570 (9) |
| C21 | 0.1784 (5) | 0.3806 (5) | 0.1873 (6) |
| C21′ | 0.2064 (7) | 0.5182 (6) | 0.1642 (8) |
| C22 | −0.1281 (6) | 0.2515 (5) | −0.1875 (6) |
| C22′ | −0.2286 (7) | 0.3068 (8) | −0.0838 (9) |
| C23 | 0.1635 (6) | 0.1852 (5) | −0.1896 (6) |
| C23′ | 0.3373 (7) | 0.1635 (8) | −0.0997 (8) |
| B | 0.4185 (8) | 0.5610 (8) | 0.8377 (9) |
| F1 | 0.4986 (9) | 0.5272 (9) | 0.9952 (9) |
| F2 | 0.4758 (8) | 0.511 (1) | 0.7108 (8) |
| F3 | 0.2569 (7) | 0.5053 (7) | 0.7533 (9) |
| F4 | 0.4460 (8) | 0.7146 (8) | 0.927 (1) |

edge of the pentadienyl ligand. The Co–P bonds are longer in the cation **5** than in the neutral species **1** (Co–P1 = 2.204 (1) Å in **5** vs. 2.149 (1) Å in **1** and Co–P2 = 2.292 (1) Å in **5** vs. 2.180 (1) Å in **1**). This is analogous to the lengthening of Co–P bonds in ($\eta^5$-cyclopentadienyl)Co[P($C_2H_5$)$_3$]$_2$$^+$ vs. ($\eta^5$-cyclopentadienyl)Co[P($C_2H_5$)$_3$]$_2$, which was observed by McKinney et al.[12] McKinney attributed this bond lengthening to a reduction in the back-bonding between a metal d orbital and phosphorus p and/or d orbitals which, in turn, resulted from removal of an electron from the HOMO. Increased electrostatic repulsion between the metal center and the phosphine ligands in the 17e cation may also contribute to bond lengthening. The P1–Co–P2 angle is slightly larger in **5** than in **1** (102.96 (4)° vs. 99.01 (3)°). A similar enlarging of the P–Co–P angle was observed for ($\eta^5$-cyclopentadienyl)Co[P($C_2H_5$)$_3$]$_2$$^+$ vs. ($\eta^5$-cyclopentadienyl)Co[P($C_2H_5$)$_3$]$_2$.[12]

Perhaps the most interesting aspect of the structure of **5** is the very pronounced allyl–ene distortion of the $\eta^5$-2,4-dimethylpentadienyl ligand. Byers and Dahl first observed this type of distortion for the pentamethylcyclopentadienyl ligand in ($\eta^5$-pentamethylcyclopentadienyl)-Co(CO)$_2$.[13] McKinney later found a similar distortion in the cyclopentadienyl ligand of ($\eta^5$-cyclopentadienyl)Co-[P($C_2H_5$)$_3$]$_2$ but *not* in the cyclopentadienyl ligand of the cation ($\eta^5$-cyclopentadienyl)Co[P($C_2H_5$)$_3$]$_2$$^+$.[12] In the Dahl and McKinney structures, the cyclopentadienyl C–C bonds which are eclipsed by the carbonyl or phosphine ligands, C3–C4 and C1–C5 (see A, Figure 2), are lengthened, C4–C5 is shortened ("ene"), and C1–C2 and C2–C3 remain intermediate in length ("allyl"). Dahl explained this distortion on the basis of the symmetry of the cyclopentadienyl component of the HOMO.[13]

The allyl–ene distortion in **5** appears to derive from the fact that P2 does not lie directly beneath C3; that is, when Co and P2 are projected onto the pentadienyl plane, the Co–P2 and Co–C3 vectors are *not* collinear (see B, Figure 2). In fact, the P2–Co–C3 angle in this projection is 9.76°, with P2 lying on the C4 side of C3.[14] This rotation of P2 toward the C4 side of the pentadienyl ligand apparently gives rise to a lengthening of the eclipsed bond, C3–C4, and a shortening of the adjacent terminal bond, C4–C5. Bonds C1–C2 and C2–C3 remain intermediate in length. Interestingly, the Co–$C_{allyl}$ bond distances in **5** are significantly shorter than the corresponding Co–$C_{ene}$ distances (i.e., Co–C1 is shorter than Co–C5 and Co–C2 is shorter than Co–C4).

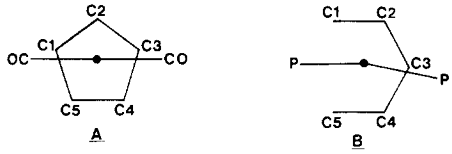

**Figure 2.** (A) Projection of carbonyl ligands onto cyclopentadienyl plane in ($\eta^5$-pentamethylcyclopentadienyl)Co(CO)$_2$ (adapted from Byers and Dahl, *Inorg. Chem.* **1980**, 2, 277). Eclipsed carbon–carbon bonds C1–C5 and C3–C4 are lengthened, while C4–C5 is shortened. (B) Projection of triethylphosphine ligands onto pentadienyl plane in ($\eta^5$-2,4-dimethylpentadienyl)-Co[P($C_2H_5$)$_3$]$_2$$^+$$BF_4^-$ (**5**). Eclipsed bond C3–C4 is lengthened, while C4–C5 is shortened.

A reexamination of the structure of the neutral species **1** shows that it too displays a *small* allyl–ene distortion. In this case, the P2–Co–C3 angle, after projection of P2 and Co into the pentadienyl plane, equals 3.74°. In this case, P2 lies to the C2 side of C3 and the following pentadienyl C–C bond lengths are observed: C1–C2, 1.396 (5) Å ("ene"); C2–C3, 1.428 (5) Å (lengthened bond); C3–C4, 1.404 (5) Å ("allyl"); C4–C5, 1.381 (5) Å ("allyl"). Again, the Co–$C_{ene}$ bond distances are longer than the corresponding Co–$C_{allyl}$ bond distances, although the effect is not as dramatic as in the structure of **5** (Co–C1 = 2.145 (3) Å while Co–C5 = 2.120 (4) Å and Co–C2 = 2.098 (3) Å while Co–C4 = 2.070 (3) Å).

Although the extent of allyl–ene distortion correlates with the extent of rotation of P2, we do not yet understand the reason for this rotation and certainly cannot predict the extent to which it will occur.[15] It is interesting that McKinney observed the allyl–ene distortion only in the structure of neutral ($\eta^5$-cyclopentadienyl)Co[P($C_2H_5$)$_3$]$_2$, not in the structure of the 17e cation ($\eta^5$-cyclopentadienyl)Co[P($C_2H_5$)$_3$]$_2$$^+$.[12] In contrast, we observe a more pronounced distortion in our 17e cation than in our 18e neutral complex. However, there is *no* allyl–ene distrotion in the structure of the 17e neutral complex ($\eta^5$-2,4-dimethylpentadienyl)Co[P($C_2H_5$)$_3$](I) (**7**) (vide infra).

**D. Synthesis of ($\eta^5$-2,4-Dimethylpentadienyl)Co-[P($C_2H_5$)$_3$](I) (7).** ($\eta^5$-2,4-Dimethylpentadienyl)Co[P-($C_2H_5$)$_3$](I) (**7**) can be obtained from **1** by using a variety of iodide-containing reagents including AgI and alkyl iodides. **7** can also be produced by reacting **5** with $NH_4I$ or by reacting $CoI_2$ with 1 equiv of potassium 2,4-dimethylpentadienide and 1 equiv of P($C_2H_5$)$_3$.

The reaction of **1** with AgI probably involves an initial oxidation to produce ($\eta^5$-2,4-dimethylpentadienyl)Co-[P($C_2H_5$)$_3$]$_2$$^+$, which then reacts with $I^-$. This proposal is supported by the observation that **5** reacts cleanly with iodide sources such as $NH_4I$ to produce **7**. The reaction

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[12] Harlow, R. L.; McKinney, R. I.; Whitney, J. F. *Organometallics* **1983**, 2, 1839.

[13] Byers, L. R.; Dahl, L. F. *Inorg. Chem.* 1980, 2, 277.

[14] The rotation of P2 to the C4 side of C3 can be seen quite clearly from the P2–Co–$C_{pentadienyl}$ angles in Table III. P2–Co–C1 is considerably larger than P2–Co–C5 (142.8 (2)° vs. 127.8 (2)°), and P2–Co–C2 is considerably larger than P2–Co–C4 (113.8 (2)° vs. 105.3 (2)°). On the other hand, P1 is only slightly skewed to the C1 side of the open edge of the pentadienyl ligand; angle P1–Co–C1 equals 92.0 (2)° while angle P1–Co–C5 equals 94.8 (2)°, and angle P1–Co–C2 equals 128.2 (2)° while angle P1–Co–C4 equals 130.2(2)°.

[15] The extent of rotation may depend on crystal packing effects.

**Table III. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for ($\eta^5$-2,4-Dimethylpentadienyl)Co$[P(C_2H_5)_3]_2^+BF_4^-$ (5)**

| | | | | | |
|---|---|---|---|---|---|
| | | Bond Distances | | | |
| Co–P1 | 2.204 (1) | P1–C12 | 1.831 (5) | C23–C23′ | 1.517 (9) |
| Co–P2 | 2.292 (1) | C12–C12′ | 1.509 (10) | C1–C2 | 1.375 (9) |
| Co–C1 | 2.171 (5) | P1–C13 | 1.837 (5) | C2–C3 | 1.409 (8) |
| Co–C2 | 2.100 (4) | C13–C13′ | 1.484 (10) | C3–C4 | 1.457 (8) |
| Co–C3 | 2.101 (4) | P2–C21 | 1.833 (4) | C4–C5 | 1.362 (9) |
| Co–C4 | 2.176 (4) | C21–C21′ | 1.506 (8) | C2–C6 | 1.516 (9) |
| Co–C5 | 2.228 (5) | P2–C22 | 1.829 (4) | C4–C7 | 1.484 (9) |
| P1–C11 | 1.828 (5) | C22–C22′ | 1.509 (9) | B–F1 | 1.383 (11) |
| C11–C11′ | 1.516 (12) | P2–C23 | 1.836 (5) | B–F2 | 1.315 (10) |
| | | | | B–F3 | 1.322 (10) |
| | | | | B–F4 | 1.369 (10) |
| | | Bond Angles | | | |
| P1–Co–P2 | 102.96 (4) | C1–Co–C5 | 83.6 (3) | P1–C13–C13′ | 116.6 (4) |
| P1–Co–C1 | 92.0 (2) | C1–C2–C3 | 123.9 (5) | Co–P2–C21 | 115.8 (2) |
| P1–Co–C2 | 128.2 (2) | C2–C3–C4 | 127.3 (5) | P2–C21–C21′ | 117.5 (4) |
| P1–Co–C3 | 157.4 (2) | C3–C4–C5 | 124.1 (5) | Co–P2–C22 | 114.6 (2) |
| P1–Co–C4 | 130.2 (2) | C1–C2–C6 | 119.4 (6) | P2–C22–C22′ | 114.7 (4) |
| P1–Co–C5 | 94.8 (2) | C3–C2–C6 | 116.2 (6) | Co–P2–C23 | 118.5 (2) |
| P2–Co–C1 | 142.8 (2) | C3–C4–C7 | 116.2 (6) | P2–C23–C23′ | 116.1 (4) |
| P2–Co–C2 | 113.8 (2) | C5–C4–C7 | 119.5 (6) | F1–B–F2 | 110.5 (8) |
| P2–Co–C3 | 99.6 (2) | Co–P1–C11 | 118.7 (2) | F1–B–F3 | 107.4 (8) |
| P2–Co–C4 | 105.3 (2) | P1–C11–C11′ | 113.9 (6) | F1–B–F4 | 106 (1) |
| P2–Co–C5 | 127.8 (2) | Co–P1–C12 | 114.3 (2) | F2–B–F3 | 114.0 (9) |
| C1–Co–C3 | 70.2 (2) | P1–C12–C12′ | 117.6 (5) | F2–B–F4 | 112.3 (8) |
| C3–Co–C5 | 70.2 (2) | Co–P1–C13 | 114.5 (2) | F3–B–F4 | 106.2 (8) |

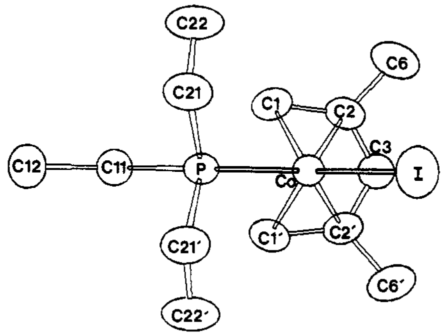

**Figure 3.** ORTEP drawing of ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3](I)$ (7). Heavy atoms are represented by 50% probability thermal ellipsoids.

**Table IV. Positional Parameters with Estimated Standard Deviations for Non-Hydrogen Atoms in ($\eta^5$-2,4-Dimethylpentadienyl)Co$[P(C_2H_5)_3](I)$ (7)**

| atom | *x* | *y* | *z* |
|---|---|---|---|
| I | 0.000 | 0.000 | 0.000 |
| Co | –0.31201 (7) | 0.000 | 0.01628 (7) |
| P | –0.4268 (2) | 0.000 | –0.2439 (1) |
| C1 | –0.4791 (5) | 0.1174 (3) | 0.0771 (5) |
| C2 | –0.3351 (5) | 0.1033 (3) | 0.2067 (4) |
| C3 | –0.2750 (7) | 0.000 | 0.2696 (6) |
| C6 | –0.2210 (8) | 0.1986 (4) | 0.2662 (6) |
| C11 | –0.6587 (8) | 0.000 | –0.3026 (8) |
| C12 | –0.748 (1) | 0.000 | –0.486 (1) |
| C21 | –0.3668 (6) | 0.1134 (3) | –0.3553 (5) |
| C22 | –0.4050 (8) | 0.2230 (4) | –0.2959 (7) |

**Table V. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for ($\eta^5$-2,4-Dimethylpentadienyl)Co$[P(C_2H_5)_3](I)$ (7)**

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Co–I | 2.580 (1) | P–C11 | 1.822 (7) |
| Co–P | 2.158 (1) | C11–C12 | 1.532 (11) |
| Co–C1 | 2.147 (4) | P–C21 | 1.832 (4) |
| Co–C2 | 2.109 (4) | C21–C22 | 1.512 (7) |
| Co–C3 | 2.089 (5) | C1–C2 | 1.392 (6) |
| | | C2–C3 | 1.425 (5) |
| | | C2–C6 | 1.507 (7) |
| | Bond Angles | | |
| I–Co–P | 96.52 (4) | Co–P–C11 | 114.8 (3) |
| I–Co–C1 | 135.0 (1) | Co–P–C21 | 115.1 (2) |
| I–Co–C2 | 109.1 (1) | P–C11–C12 | 117.3 (7) |
| I–Co–C3 | 100.2 (2) | P–C21–C22 | 114.5 (3) |
| P–Co–C1 | 96.5 (1) | C1–C2–C3 | 123.0 (4) |
| P–Co–C2 | 132.9 (1) | C1–C2–C6 | 118.8 (5) |
| P–Co–C3 | 163.3 (2) | C3–C2–C6 | 117.4 (5) |
| C1–Co–C3 | 71.5 (2) | C2–C3–C2′ | 128.3 (6) |
| C1–Co–C1′ | 85.6 (3) | | |

of ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3]_2^+$ with $I^-$ probably proceeds via an associative mechanism (see eq 1) similar to the one described earlier (Scheme II) for the

$$(\eta^5\text{-pd})CoP_2^+ \rightleftarrows (\eta^3\text{-pd})CoP_2^+ \xrightarrow{+I^-} (\eta^3\text{-pd})CoP_2(I) \xrightarrow{-P} (\eta^5\text{-pd})CoP(I) \quad (1)$$

reaction of 1 with small ligands, L. However, other mechanisms are possible for this reaction, including an associative mechanism which does *not* involve an initial $\eta^5 \rightarrow \eta^3$ pentadienyl ligand isomerization[16] (see eq 2).

$$(\eta^5\text{-pd})CoP_2^+ \xrightarrow{+I^-} (\eta^5\text{-pd})CoP_2I \xrightarrow{-P} (\eta^5\text{-pd})CoP(I) \quad (2)$$

The reaction of 1 with alkyl iodides, RI, to produce 7 is particularly intriguing. We favor a mechanism involving initial alkylation of the cobalt center to produce ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3]_2R^+I^-$. Inner-sphere electron transfer then yields ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3]_2^+I^-$ (which reacts as described above to produce 7) and the coupled dialkyl species, R–R (cf. section B in Results and Discussion). These organic products have been detected by gas chromatography in the cases where R = propyl, butyl, and pentyl. Outer-sphere electron-transfer mechanisms and inner-sphere mechanisms which involve an initial interaction between the metal center and the *iodine* end of the $CH_3I$ reagent can also be envisaged. Interestingly, ($\eta^5$-cyclopentadienyl)Co$[P(C_2H_5)_3]_2$ reacts cleanly with $CH_3I$ to produce ($\eta^5$-

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[16] Two reports of nucleophilic attacks on 17e species Mn(CO)$_3$-$[P(i\text{-}C_4H_9)_3]_2$[16a] and V(CO)$_6$[16b] have recently appeared. (a) McCullen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007. (b) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *Ibid.* **1982**, *104*, 4032.

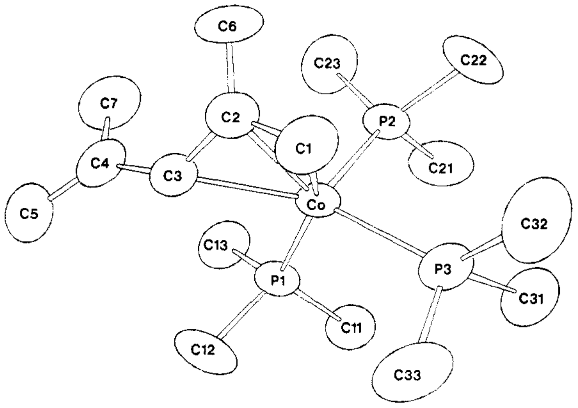

**Figure 4.** ORTEP drawing of the cation of ($\eta^3$-2,4-dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$$^+$O$_3$SCF$_3$$^-$ (**9**). Heavy atoms are represented by 50% probability thermal ellipsoids.

cyclopentadienyl)Co[P(C$_2$H$_5$)$_3$]$_2$(CH$_3$)$^+$I$^-$.[4]

**E. Structure of ($\eta^5$-2,4-Dimethylpentadienyl)Co[P(C$_2$H$_5$)$_3$]I (7).** An ORTEP drawing of 7, based on an X-ray structural analysis, is presented in Figure 3. Atomic coordinates for the non-hydrogen atoms are listed in Table IV. Important bond distances and angles are reported in Table V. The molecule resides on a crystallographically imposed mirror plane, which contains atoms Co, C3, I, P, C11, and C12. The large triethylphosphine ligand sits under the open edge of the pentadienyl ligand, while the smaller iodo ligand eclipses pentadienyl carbon atom C3. As a consequence of the crystallographically imposed mirror plane, the projection of the Co–I vector onto the pentadienyl plane is collinear with the projection of the Co–C3 vector, and an allyl–ene distortion of the pentadienyl ligand is not observed.

The five metal-bound pentadienyl carbon atoms are coplanar to within 0.028 Å. The pentadienyl methyl carbon atoms (C6 and C6′) are bent 0.338 Å out of the pentadienyl plane *toward* the cobalt atom. Similar displacements toward the cobalt atom are observed for the pentadienyl methyl groups of 1 and 5.[17]

**F. Synthesis of ($\eta^3$-2,4-Dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$$^+$A$^-$ (8, A$^-$ = BF$_4$$^-$, and 9, A$^-$ = O$_3$SCF$_3$$^-$).** ($\eta^3$-2,4-Dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$$^+$A$^-$ (8, A$^-$ = BF$_4$$^-$, and 9, A$^-$ = O$_3$SCF$_3$$^-$) can be synthesized by reaction of ($\eta^5$-2,4-dimethylpentadienyl)Co[P(C$_2$H$_5$)$_3$]$_2$$^+$A$^-$ (5, A$^-$ = BF$_4$$^-$, and 6, A$^-$ = O$_3$SCF$_3$$^-$) with 3 equiv of trimethylphosphine. We believe that these reactions proceed by an associative mechanism similar to the one described earlier for the reactions of 1 with P(CH$_3$)$_3$ (Scheme II).[18] 8 can also be produced in a more straightforward fashion from the reaction of ($\eta^3$-2,4-dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$ (2) with AgBF$_4$. The infrared spectra of 8 and 9 both exhibit a weak C=C stretch at 1610 cm$^{-1}$, which is characteristic of ($\eta^3$-pentadienyl)metal complexes.[1b-d] Interestingly, the simple $\eta^3$-allyl analogue of ($\eta^3$-2,4-dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$$^+$ has not been reported.

**G. Structure of ($\eta^3$-2,4-Dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$$^+$A$^-$ (8, A$^-$ = BF$_4$$^-$, and 9, A$^-$ = O$_3$SCF$_3$$^-$).** We have determined the structures of both the tetrafluoroborate and trifluoromethanesulfonate salts of ($\eta^3$-2,4-dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$$^+$ (8 and 9, respectively). An ORTEP drawing of the cation in 9 is shown in Figure 4. Atomic coordinates for the non-hydrogen atoms in 8 and 9 are listed in Tables VI and VII, respectively. Bond distance and bond angle information for both compounds is reported in Table VIII. The tetrafluoroborate anion in 8 was found to be disordered. However, we were able to model the disorder by including two sets of fluorine atoms with occupancies of 0.6 and 0.4. Only the higher occupancy set is included in Tables VI and VIII. Information on the fluorine atoms in the lower occupancy sites is included in supplementary material.

**Table VI. Positional Parameters with Estimated Standard Deviations for Non-Hydrogen Atoms in ($\eta^3$-2,4-Dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$$^+$BF$_4$$^-$ (8)**

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Co | 0.22379 (6) | 0.20446 (5) | 0.34303 (4) |
| P1 | 0.2304 (2) | 0.0368 (1) | 0.36005 (8) |
| P2 | 0.4116 (1) | 0.2501 (1) | 0.41756 (9) |
| P3 | 0.0854 (2) | 0.2449 (1) | 0.42465 (9) |
| C1 | 0.1527 (7) | 0.3298 (5) | 0.2818 (4) |
| C2 | 0.2475 (6) | 0.2880 (4) | 0.2442 (3) |
| C3 | 0.2291 (5) | 0.1860 (4) | 0.2214 (3) |
| C4 | 0.3064 (6) | 0.1199 (5) | 0.1783 (3) |
| C5 | 0.2451 (9) | 0.0510 (6) | 0.1309 (4) |
| C6 | 0.3628 (8) | 0.3520 (5) | 0.2321 (4) |
| C7 | 0.4482 (7) | 0.1306 (6) | 0.1859 (4) |
| C11 | 0.2144 (7) | −0.0215 (5) | 0.4527 (4) |
| C12 | 0.1004 (7) | −0.0269 (5) | 0.2998 (4) |
| C13 | 0.3694 (6) | −0.0309 (4) | 0.3372 (4) |
| C21 | 0.4484 (7) | 0.1821 (6) | 0.5078 (4) |
| C22 | 0.4175 (8) | 0.3816 (5) | 0.4513 (5) |
| C23 | 0.5672 (7) | 0.2385 (9) | 0.3856 (5) |
| C31 | 0.1082 (8) | 0.2069 (6) | 0.5254 (4) |
| C32 | 0.0451 (8) | 0.3769 (6) | 0.4352 (5) |
| C33 | −0.0711 (7) | 0.1897 (9) | 0.3932 (5) |
| B | 0.1945 (9) | 0.6580 (7) | 0.3644 (6) |
| F1 | 0.2628 (9) | 0.5775 (7) | 0.3655 (7) |
| F2 | 0.0804 (8) | 0.629 (1) | 0.3619 (8) |
| F3 | 0.239 (1) | 0.7273 (5) | 0.3121 (5) |
| F4 | 0.211 (2) | 0.7220 (9) | 0.4249 (8) |

**Table VII. Positional Parameters with Estimated Standard Deviations for Non-Hydrogen Atoms in ($\eta^3$-2,4-Dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$$^+$O$_3$SCF$_3$$^-$ (9)**

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Co | 0.22332 (5) | 0.17860 (4) | 0.32868 (3) |
| P1 | 0.2247 (1) | 0.02729 (9) | 0.34553 (7) |
| P2 | 0.4127 (1) | 0.21303 (9) | 0.40179 (7) |
| P3 | 0.0871 (1) | 0.21613 (9) | 0.41492 (7) |
| C1 | 0.1680 (5) | 0.2982 (3) | 0.2712 (3) |
| C2 | 0.2531 (5) | 0.2534 (3) | 0.2276 (3) |
| C3 | 0.2193 (5) | 0.1657 (4) | 0.2020 (3) |
| C4 | 0.2825 (5) | 0.1014 (4) | 0.1537 (3) |
| C5 | 0.2131 (6) | 0.0451 (5) | 0.1055 (3) |
| C6 | 0.3746 (6) | 0.3031 (4) | 0.2133 (3) |
| C7 | 0.4233 (6) | 0.0991 (5) | 0.1567 (4) |
| C11 | 0.2063 (6) | −0.0216 (4) | 0.4412 (3) |
| C12 | 0.0943 (6) | −0.0302 (4) | 0.2859 (3) |
| C13 | 0.3609 (6) | −0.0354 (4) | 0.3216 (4) |
| C21 | 0.4295 (7) | 0.3312 (4) | 0.4355 (4) |
| C22 | 0.4482 (6) | 0.1521 (5) | 0.4951 (3) |
| C23 | 0.5647 (6) | 0.1951 (6) | 0.3663 (4) |
| C31 | 0.1160 (6) | 0.1922 (5) | 0.5189 (3) |
| C32 | 0.0429 (7) | 0.3357 (4) | 0.4225 (4) |
| C33 | −0.0646 (6) | 0.1628 (6) | 0.3896 (4) |
| S | 0.2152 (1) | 0.7068 (1) | 0.3727 (1) |
| C | 0.2212 (6) | 0.5862 (4) | 0.3757 (5) |
| O1 | 0.3271 (5) | 0.7328 (3) | 0.3468 (4) |
| O2 | 0.2070 (8) | 0.7292 (5) | 0.4509 (4) |
| O3 | 0.1054 (5) | 0.7277 (4) | 0.3294 (4) |
| F1 | 0.3163 (4) | 0.5532 (3) | 0.4210 (3) |
| F2 | 0.1228 (4) | 0.5512 (3) | 0.4026 (4) |
| F3 | 0.2388 (8) | 0.5517 (3) | 0.3101 (3) |

The structures of the two cations are virtually identical. In each case, the $\eta^3$-2,4-dimethylpentadienyl ligand is bonded in a syn (W-shaped) fashion. This is in contrast to the 18e neutral parent compound 2 which crystallizes

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[17] The methyl carbon displacements are 0.141 Å (C6) and 0.240 Å (C7) in 1 and 0.324 Å (C6) and 0.158 Å (C7) in 5.

[18] However, other mechanisms can be envisaged, including an associative mechanism, which does not involve an initial $\eta^5 \rightarrow \eta^3$ pentadienyl ligand isomerization.[16]

**Table VIII. Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for ($\eta^3$-2,4-Dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$$^+$A$^-$ (8, A$^-$ = BF$_4$$^-$; 9, A$^-$ = O$_3$SCF$_3$$^-$)**

| bond distances | | | bond angles | | |
|---|---|---|---|---|---|
| | 8 | 9 | | 8 | 9 |
| Co-P1 | 2.235 (1) | 2.233 (1) | P1-Co-P2 | 99.99 (5) | 98.81 (5) |
| Co-P2 | 2.306 (1) | 2.314 (1) | P2-Co-P3 | 99.29 (5) | 98.71 (5) |
| Co-P3 | 2.248 (1) | 2.260 (1) | P2-Co-P3 | 99.17 (5) | 100.44 (5) |
| Co-C1 | 2.057 (5) | 2.063 (4) | P1-Co-C1 | 150.7 (2) | 154.3 (2) |
| Co-C2 | 2.103 (4) | 2.107 (4) | P1-Co-C2 | 128.7 (1) | 128.5 (1) |
| Co-C3 | 2.159 (4) | 2.178 (4) | P1-Co-C3 | 90.8 (1) | 92.5 (1) |
| P1-C11 | 1.836 (5) | 1.822 (5) | P2-Co-C1 | 107.9 (2) | 105.1 (2) |
| P1-C12 | 1.821 (5) | 1.838 (5) | P2-Co-C2 | 98.2 (1) | 97.4 (1) |
| P1-C13 | 1.820 (5) | 1.808 (6) | P2-Co-C3 | 117.1 (1) | 118.5 (1) |
| P2-C21 | 1.835 (5) | 1.826 (6) | P3-Co-C1 | 85.4 (2) | 86.3 (2) |
| P2-C22 | 1.852 (7) | 1.836 (6) | P3-Co-C2 | 124.4 (1) | 125.6 (1) |
| P2-C23 | 1.832 (6) | 1.819 (5) | P3-Co-C3 | 140.0 (1) | 137.2 (1) |
| P3-C31 | 1.855 (6) | 1.812 (6) | C1-Co-C2 | 39.0 (2) | 39.4 (2) |
| P3-C32 | 1.811 (6) | 1.822 (6) | C1-Co-C3 | 68.6 (2) | 67.9 (2) |
| P3-C33 | 1.838 (7) | 1.808 (6) | C2-Co-C3 | 38.7 (2) | 37.8 (2) |
| C1-C2 | 1.388 (7) | 1.405 (7) | C1-C2-C6 | 117.5 (5) | 118.5 (5) |
| C2-C3 | 1.412 (6) | 1.391 (6) | C1-C2-C3 | 116.1 (5) | 115.9 (4) |
| C3-C4 | 1.477 (7) | 1.407 (6) | C3-C2-C6 | 126.4 (5) | 125.6 (5) |
| C4-C5 | 1.321 (8) | 1.332 (7) | C2-C3-C4 | 130.0 (4) | 130.5 (4) |
| C2-C6 | 1.512 (7) | 1.533 (7) | C3-C4-C7 | 123.0 (5) | 121.3 (5) |
| C4-C7 | 1.470 (8) | 1.501 (8) | C3-C4-C5 | 119.1 (6) | 119.2 (5) |
| B-F1 | 1.293 (10) | | C5-C4-C7 | 117.9 (6) | 119.5 (6) |
| B-F2 | 1.275 (11) | | F-B-F | 110 (1)[a] | |
| B-F3 | 1.432 (11) | | O-S-O | | 114.1 (5)[b] |
| B-F4 | 1.361 (12) | | O-S-C | | 104.2 (3)[b] |
| S-C | | 1.768 (6) | S-C-F | | 112.9 (5)[b] |
| S-O1 | | 1.378 (4) | F-C-F | | 105.8 (7)[b] |
| S-O2 | | 1.393 (6) | | | |
| S-O3 | | 1.352 (5) | | | |
| C-F1 | | 1.301 (7) | | | |
| C-F2 | | 1.301 (8) | | | |
| C-F3 | | 1.267 (9) | | | |

[a] Average of six angles. [b] Average of three angles.

with the $\eta^3$-2,4-dimethylpentadienyl ligand in an anti (U-shaped) geometry.[1c] The parent compound 2 exists *in solution* as an equilibrium mixture of the syn and anti isomers,[1c] but it is the anti isomer which crystallizes from nonpolar solvents such as pentane. Because the 17e cationic complex is paramagnetic, we are unable to study its solution state behavior by NMR, but we expect that it too exists in solution as an equilibrium mixture of syn and anti isomers. In this case, however, it is the syn isomer which crystallizes from the polar solvent mixture of tetrahydrofuran and acetone.

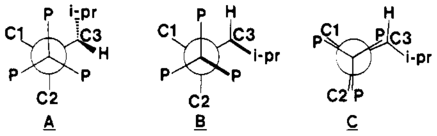

**Figure 5.** (A) Newman projection of trimethylphosphine ligands onto the pentadienyl ligand in (*anti*-$\eta^3$-2,4-dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$ (**2**). The phosphine phosphorus atoms and the allylic carbon atoms (C1, C2, C3) adopt a staggered orientation. Rotation about C2–C3 pushes the anti isopropenyl group on C3 away from the CoP$_3$ moiety, minimizing steric contacts. (B) Hypothetical staggered conformation for (*syn*-$\eta^3$-2,4-dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$$^+$. There is an unfavorable steric contact (shown in dark lines on drawing) involving the isopropenyl group on C3 and one of trimethylphosphine ligands, which *cannot* be relieved by a rotation about C2–C3 (see text). (C) Observed eclipsed conformation for (*syn*-$\eta^3$-2,4-dimethylpentadienyl)Co[P(CH$_3$)$_3$]$_3$$^+$ in **8** and **9**. The steric contact shown in (b) has been relieved by a 60° rotation of the CoP$_3$ moiety with respect to the pentadienyl ligand.

Another interesting contrast between the structure of the 17e cation and that of 2 is the following. In the 17e cation, the allylic moiety of the pentadienyl ligand (C1, C2, C3) has an eclipsed orientation with respect to the phosphorus atoms P1, P2, and P3 (see C, Figure 5), while in 2, a staggered orientation is observed (see A, Figure 5).[1c] The staggered geometry is, in general, the more favorable one,[19] and with the pentadienyl ligand in the anti geometry (as in 2), there are no unfavorable steric contacts between the isopropenyl group and the phosphine ligands. In this case, steric contact is avoided by a rotation about C2–C3, which pushes the isopropenyl group *away* from the CoP$_3$ moiety *and* at the same time improves overlap between the p$_z$ orbital on C3 and appropriate metal orbitals (see A, Figure 5). However, with the pentadienyl ligand in the *syn* geometry, an unfavorable steric contact develops between the isopropenyl group and one of the phosphine ligands (see B, Figure 5). In this case, rotation about C2–C3 to relieve isopropenyl/phosphine steric contact would *reduce* overlap between the p$_z$ orbital on C3 and the metal orbitals. As a result, rotation about C2–C3 does *not* occur (C1, C2, C3, C4, and C6 are coplanar to within 0.024 Å in the structures of both 8 and 9).[20] Instead, the unfavorable steric interaction is relieved by rotating the CoP$_3$

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[19] A similar orientation has been observed for the $\eta^3$-allyl ligand in ($\eta^3$-allyl)Co(CO)$_2$[P(C$_6$H$_5$)$_3$][19a] and for the $\eta^3$-cyclooctenyl ligand in ($\eta^3$-cyclooctenyl)Co[P(OCH$_3$)$_3$]$_3$.[19b] Extended Hückel molecular orbital calculations have shown it to be the most stable orientation for 18e $\eta^3$-allyl-ML$_3$ systems in general.[19c,d] (a) Rinze, P. V.; Muller, U. *Chem. Ber.* **1979**, *112*, 1973. (b) Thompson, M. R.; Day, V. W.; Tau, K. D.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 1237. (c) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (d) Harlow, R. L.; McKinney, R. J.; Ittel, S. D. *Ibid.* **1979**, *101*, 7496.

[20] There is, however, a rotation about C3–C4, which pushes C5 away from the cobalt atom and C7 toward it. In 8 the dihedral angle between planes C1-C2-C3-C4-C6 and C3-C4-C5-C7 is 30.7°; in 9, the same angle is 30.2°. Similar rotations are observed for the *syn*-$\eta^3$-pentadienyl ligands in ($\eta^3$-pentadienyl)$_2$Fe[P(CH$_3$)$_3$]$_2$[1b] and ($\eta^3$-pentadienyl)Mn-[(CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$]$_2$.[1d]

fragment by 60° with respect to the allyl fragment, generating the observed staggered conformation (see C, Figure 5).

As in the structure of **2**, the geometry about the cobalt atom in **8** and **9** approximates a square pyramid with C1, C3, P1, and P3 occupying the four basal positions and P2 residing in the axial position. The four basal atoms are coplanar to within 0.10 Å in **8** and 0.18 Å in **9**.

Cobalt–phosphorus and cobalt–carbon bonds are somewhat longer in the 17e cation than in the 18e neutral compound. (The average Co–P bond lengths are 2.263 (1) Å in **8**, 2.269 (1) Å in **9**, and 2.183 (1) Å in **2**. The average Co–C bond lengths for **8**, **9**, and **2** are 2.106 (4), 2.116 (4), and 2.052 (4) Å, respectively.) Pentadienyl carbon–carbon bond distances are very similar in **2**, **8**, and **9**. The *average* C–C bond distances for **8** and **9** are as follows: C1–C2 = 1.396 (7) Å, C2–C3 = 1.402 (6) Å, C3–C4 = 1.474 (7) Å, and C4–C5 = 1.326 (8) Å. The corresponding bond distances in neutral **2** are 1.385 (7) Å, 1.404 (6) Å, 1.477 (6) Å, and 1.344 (7) Å, respectively.

**H. Reaction of Radical Species 5, 7, and 8 with $P(OCH_3)_3$.** Each of the three 17e radical species discussed above (**5**, **7**, and **8**) reacts rapidly and cleanly with $P(OCH_3)_3$ to produce 2,4-dimethylpentadiene and the diamagnetic salt of a five-coordinate cobalt cation. For example, the reaction of ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3]_2{}^+BF_4{}^-$ (**5**) with four equivalents of $P(OCH_3)_3$ produces $Co[P(C_2H_5)_3][P(OCH_3)_3]_4{}^+BF_4{}^-$ (**10**) in essentially quantitative yield. One equivalent of $P(C_2H_5)_3$ and one equivalent of 2,4-dimethylpentadiene are released in this reaction, as determined by $^1H$ NMR spectroscopy and gas chromatography. **10** is also obtained if *more* than 4 equiv of $P(OCH_3)_3$ are added to **5**. Similarly, the reaction of ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3]$(I) (**7**) with $P(OCH_3)_3$ produces $Co[P(OCH_3)_3]_5{}^+I^-$ (**11**)[21] and the reaction of ($\eta^3$-2,4-dimethylpentadienyl)Co$[P(CH_3)_3]_3{}^+BF_4{}^-$ (**8**) with $P(OCH_3)_3$ produces $Co[P(CH_3)_3]_2[P(OCH_3)_3]_3{}^+BF_4{}^-$ (**12**) in high yields. Compounds **10** and **12** have not been previously reported.

These reactions appear to involve release of a pentadienyl *radical*,[22,23] which then scavenges a hydrogen atom from tetrahydrofuran solvent or trimethyl phosphite to form the observed organic product 2,4-dimethylpentadiene. Interestingly, the pentadienyl radical is *not* released when neutral ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3]_2$ (**1**) is reacted with $P(OCH_3)_3$ or when ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3]_2{}^+BF_4{}^-$ (**5**) is reacted with $P(CH_3)_3$; in these reactions, pentadienyl-containing complexes **4** and **8**, respectively, are produced. Only when the cationic complex **5** is reacted with trimethyl phosphite is the pentadienyl radical lost, suggesting that it is a *combination* of the formal positive charge on the metal complex and the π-accepting ability of the $P(OCH_3)_3$ ligands which weakens the cobalt–pentadienyl bond and causes the observed bond rupture.

The detailed mechanisms of these trimethyl phosphite reactions are not known. It is quite likely that they proceed via a series of associative steps which are preceded by $\eta^5 \rightarrow \eta^3$ and $\eta^3 \rightarrow \eta^1$ pentadienyl ligand isomerizations. The pentadienyl radical is probably lost from an $\eta^1$-pentadienyl–metal intermediate. The reaction of **5** with $P(OCH_3)_3$, for example, could proceed via intermediates analogous to A through F in Scheme II and G′ → H′ in Scheme III. For the reasons described above, the cobalt–pentadienyl bond in H′ would be weakened and rupture would occur.

In the reaction of ($\eta^5$-*cyclopentadienyl*)Co$[P(C_2H_5)_3]_2{}^+$ with $P(OCH_3)_3$, the cyclopentadienyl ligand is *not* released.[5]

## Conclusions

From this study, three salient characteristics of the reactivity of ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3]_2$ (**1**) have emerged. First, **1** is readily oxidized to 17e Co(II) species such as ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3]_2{}^+BF_4{}^-$ (**5**) and ($\eta^5$-2,4-dimethylpentadienyl)Co$[P(C_2H_5)_3]$(I) (**7**). Oxidations can be carried out with traditional oxidizing agents such as $Ag^+$ or with untraditional reagents such as acids and alkyl halides. Second, pentadienyl ligand isomerizations ($\eta^5 \rightleftarrows \eta^3$ and $\eta^3 \rightleftarrows \eta^1$) are facile. These isomerizations create unsaturation at the metal center and allow ligand addition and substitution to occur readily. Third, under certain conditions, the pentadienyl ligand is cleanly expelled as a radical causing a formal one-electron reduction of the metal center.

These three fundamental reactivity features give rise to an overall reaction chemistry for **1** which differs substantially from that of ($\eta^5$-cyclopentadienyl)Co$[P(C_2H_5)_3]_2$. Further studies to ascertain the generality of these features among electron-rich pentadienyl–metal–phosphine complexes are under way in our laboratories.

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**Registry No.** **1**, 90991-09-6; **2**, 91050-45-2; **3** (isomer 1), 100190-50-9; **3** (isomer 2), 100190-61-2; **4**, 100190-51-0; **5**, 100190-53-2; **6**, 100190-54-3; **7**, 100190-55-4; **8**, 100190-57-6; **9**, 100295-53-2; **10**, 100205-41-2; **11**, 100190-58-7; **12**, 100190-60-1; $CoCl_2$, 7646-79-9; $CoI_2$, 15238-00-3; $HO_3SCF_3$, 1493-13-6; (2,4-dimethylpentadienyl)potassium, 74205-98-4.

**Supplementary Material Available:** Listings of final atomic coordinates, thermal parameters, bond length, bond angles, observed and calculated structure factor amplitudes, and significant least-squares planes including subtended dihedral angles (77 pages). Ordering information is given on any current masthead page.

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(21) (a) Verkade, J. G.; Piper, T. S. *Inorg. Chem.* **1963**, *2*, 944. (b) Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 5751.

(22) The reaction of $CoCl_2$, 2 equiv of $P(C_2H_5)_3$, and 2 equiv of potassium 2,4-dimethylpentadienide to produce **1** involves a similar loss of pentadienyl radical.[1c]

(23) The electron-rich sandwich compounds ($\eta^5$-cyclopentadienyl)$_2$Co and ($\eta^5$-cyclopentadienyl)$_2$Mn react with $P(OCH_3)_3$ to produce ($\eta^5$-cyclopentadienyl)Co$[P(OCH_3)_3]_2$[23a] and ($\eta^5$-cyclopentadienyl)Mn$[P(OCH_3)_3]_3$,[23b] respectively. These reactions involve loss of cyclopentadienyl radical. (a) Harder, V.; Müller, J.; Werner, H. *Helv. Chim. Acta* **1971**, *54*, 1. (b) Werner, H.; Juthani, B. *J. Organomet. Chem.* **1977**, *129*, C39.