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Synthesis and Characterization of (Cyclopentadienyl)(2,4-dimethylpentadienyl)cobalt(III) Fluoroborate and of the Dimeric Product Resulting from Its Reduction

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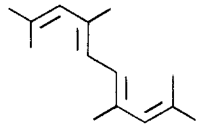
The synthesis and solid-state structure of the "half-open" cobalticinium complex $Co(C_5H_5)(2,4\text{-}C_7H_{11})^+BF_4^-$ are reported (C_7H_{11} = dimethylpentadienyl). This air-stable compound is one of few trivalent metal–pentadienyl compounds known and was prepared by hydride abstraction from $Co(C_5H_5)(\eta^4\text{-}2,4\text{-dimethyl-}1,3\text{-pentadiene})$. An X-ray structural study of the cationic compound was undertaken, revealing an "eclipsed" orientation of the two organic ligands. The compound crystallizes in space group C_s^3—Cm (No. 8) with a = 12.059 (2) Å, b = 9.724 (1) Å, c = 7.072 (1) Å, and β = 125.70 (1)°, for Z = 2. Least-squares refinement led to agreement indices of R = 0.044 and R_w = 0.040 for the 616 independent reflections judged to be above background ($I > 2.5\sigma(I)$). The average Co–C bond distances to the C_5H_5 and C_7H_{11} ligands are essentially identical at 2.047 (9) and 2.056 (7) Å, respectively. Reduction of this cation with sodium amalgam leads to a dimeric compound, $(\mu\text{-}\eta^4,\eta^4\text{-}2,4,7,9\text{-}(CH_3)_4\text{-}1,3,7,9\text{-}C_{10}H_{10})[Co(C_5H_5)]_2$, where $C_{10}H_{10}$ = decatetraene. Unlike the product formed from the dimerization of $Co(2,4\text{-}C_7H_{11})_2$, which contained a 2,4,6,8-decatetraene, this species was found spectroscopically and crystallographically not to have undergone such an isomerization. The compound crystallizes in space group C_{2h}^5—$P2_1/a$ (No. 14), with a = 7.779 (4) Å, b = 10.955 (6) Å, c = 12.239 (7) Å, and β = 94.93 (2)°, for Z = 2 dimeric units. Least-squares refinement led to agreement indices of R = 0.058 and R_w = 0.048 for the 1412 independent reflections judged to be above background. That isomerization occurs only when an unaltered 2,4-dimethylpentadienyl ligand is present on the cobalt atom clearly implicates an η^5–η^3 pentadienyl transformation in the decatetraene isomerization process observed for the "open cobaltocene" dimer.

In coupling reactions occurring between two coordinated pentadienyl ligands, the observed products have almost invariably contained 1,3,7,9-decatetraene moieties, which may or may not remain bound to the original metal atoms.[2] Recently, the dimerization of bis(2,4-dimethylpentadienyl)cobalt, $Co(2,4\text{-}C_7H_{11})_2$, led instead to a coordinated 2,4,6,8-decatetraene, I, rather than the expected 1,3,7,9 isomer II apparently via an isomerization initiated by an η^5–η^3 transformation of the remaining unchanged[3] 2,4-dimethylpentadienyl ligand on each cobalt atom. However, an alternative mechanism involving an η^4–η^2 transformation of coupled bis(pentadienyl) fragments could not be completely dismissed. In order to better evaluate the viability of this latter possibility, we have therefore synthesized the "half-open" cobalticinium complex $Co(C_5H_5)(2,4\text{-}C_7H_{11})^+BF_4^-$ and the dimeric product resulting from formal reduction of the cation to $Co(C_5H_5)(2,4\text{-}C_7H_{11})$. This dimeric product should be quite analogous to the "open cobaltocene" dimer, except that the remaining unaltered 2,4-dimethylpentadienyl ligand on each cobalt atom is replaced by a cyclopentadienyl ligand. Thus, if the isomerization in the "open cobaltocene" dimer did require an η^5–η^3 transformation of the pentadienyl ligand, this should now be greatly retarded for the cyclopentadienyl ligand, while if the isomerization depended on an η^4–η^2 transformation of the bridging unit, one would not expect to observe a large difference between the two systems, so that the isomerization should be observed.



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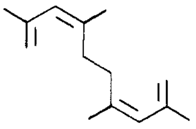

II

Experimental Section

All operations involving organometallics were carried out under a nitrogen atmosphere in prepurified Schlenk apparatus or in a glovebox. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled immediately before use. Elemental analyses were performed by Micanal Laboratories (Tucson, AZ).

Spectroscopic Studies. ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on Varian EM-390 and SC-300 spectrometers. Infrared spectra were recorded with a Perkin-Elmer 298 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol.

(Cyclopentadienyl)(2,4-dimethylpentadiene)cobalt. This compound was prepared by a variation of a general literature procedure.[4] Thus, 2.4 g of magnesium (100 mmol, particle size = 40–80 mesh) was treated under a nitrogen atmosphere with 0.37 g of anthracene (2.06 mmol), 100 mL of THF, and ca. 0.1 mL of methyl iodide. On stirring at room temerature, a yellow-green solution was formed, from which orange-colored (anthracene)magnesium separated in ca. 1 h. The mixture was heated with stirring to 65 °C and subjected to ultrasonic treatment for 3 h.

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[1] (a) University of Utah. (b) Universität Heidelberg.

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After addition of 8.02 g of 2,4-dimethyl-1,3-pentadiene (83.3 mmol) and 2.43 g of monomeric cyclopentadiene (37.0 mmol), the source of heat was removed and 11.87 g of cobalt(III) acetylacetonate[5] (33.33 mol) was added in portions to the continually stirred solution over a period of 15 min, whereby the solution vigorously boiled. After cooling to room temperature and filtration through Celite, the filtrate was evaporated to dryness in vacuo. The residue was extracted with four 50-mL portions of pentane and filtered a second time. After removal of the solvent, 3.0 g of a dark red oil was obtained (41%), which underwent slow decomposition on standing. Infrared data (Nujol mull): 3080 (sh), 1254 (w), 1103 (ms), 1060 (ms), 992 (s), 798 (s), 778 (vs) cm^{-1}. ^{1}H NMR (toluene-d_8): δ 4.43 (s, 1 H, CH), 4.36 (s, 5 H, C_5H_5), 1.92 (s, 3 H, CH_3), 1.61 (s, br, 1 H, CH), 0.96 (s, 3 H, CH_3), 0.76 (s, br, 1 H, CH), 0.57 (s, 3 H, CH_3).

(Methylcyclopentadienyl)(η^4-2,4-dimethylpentadiene)cobalt. This thermally sensitive compound was prepared by the same procedure using the identical molar quantities. ^{1}H NMR (toluene-d_8): δ 4.60 (br, 2 H), 4.40 (s, 1 H), 4.20 (br, 1 H), 4.08 (br, 1 H) 1.96 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 1.44 (s, br, 1 H, CH), 1.02 (s, 3 H, CH_3), 0.80 (s, br, 1 H, CH), 0.60 (s, 3 H, CH_3).

(Cyclopentadienyl)(2,4-dimethylpentadienyl)cobalt Tetrafluoroborate. To (cyclopentadienyl)(2,4-dimethylpentadiene)cobalt (1.17 g, 5.27 mmol) in 20 mL of dichloromethane at −78 °C was added dropwise triphenylmethyl tetrafluoroborate (1.77 g, 5.30 mmol) in 25 mL of the same solvent. The mixture was slowly warmed to room temperature, and an excess of ether was added, leading to precipitation of 1.23 g of the brick red product (75.5%). While this material could be used in subsequent reactions, very pure material was obtained by crystallization from nitromethane–ether mixtures. Infrared data (Nujol mull): 3119 (sh), 1283 (w), 1099 (s), 1055 (s), 1041 (vs), 1030 (vs), 990 (s), 950 (ms), 853 (s), 829 (w), 718 (w) cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.00 (s, 1 H), 5.63 (s, 5 H), 4.13 (d, J = 4 Hz, 2 H), 2.20 (s, 6 H), 1.58 (d, J = 4 Hz, 2 H). ^{13}C NMR (CD_3NO_2): δ 113.8 (s), 101.2 (d, J = 166.9 Hz), 89.3 (d, J = 188.8 Hz, Cp), 60.6 (t, J = 168.6 Hz), 25.9 (q, J = 130.1 Hz). Anal. Calcd for $C_{12}H_{16}BCoF_4$: C, 47.10; H, 5.27. Found: C, 46.67; H, 5.30.

(Methylcyclopentadienyl)(2,4-dimethylpentadienyl)cobalt Tetrafluoroborate. This was prepared by using the above method by simply substituting the identical molar quantities. ^{1}H NMR (CD_2Cl_2): δ 6.92 (s, 1 H, CH), 5.50 (s, 4 H, Cp), 3.95 (d, J = 4 Hz, 2 H), 2.30 (s, 6 H), 2.04 (s, 3 H), 1.57 (d, J = 4 Hz, 2 H). ^{13}C NMR (CD_2Cl_2): δ 112.6 (s), 106.2 (s, Cp), 99.2 (d, J = 170.2 Hz), 87.7 (d, J = 182.7 Hz), 87.2 (d, J = 182.8 Hz), 60.6 (t, J = 162.5 Hz), 25.0 (q, J = 130.7 Hz), 12.7 (q, J = 130.1 Hz). Anal. Calcd for $C_{13}H_{18}BCoF_4$: C, 48.79; H, 5.67. Found: C, 49.12; H, 5.18.

(μ-η^4,η^4-2,4,7,9-Tetramethyl-1,3,7,9-decatetraene)bis[(cyclopentadienyl)cobalt]. A suspension of 0.40 g of (cyclopentadienyl)(2,4-dimethylpentadienyl)cobalt tetrafluoroborate (1.33 mmol) and 15 g of sodium amalgam (1%, 65 mmol) in 30 mL of THF was stirred at room temperature for 4 h. The mixture was filtered through Celite and the solvent removed in vacuo. The residual solid was extracted with pentane (3 × 15 mL) and filtered through Celite. After the filtrate volume was reduced, 0.17 g of dark red crystals (59%) was isolated by cooling to −78 °C. The solid compound is reasonably stable at room temperature, but solutions do decompose on standing. Infrared data (Nujol mull): 3060 (sh), 1160 (w), 1103 (ms), 1074 (w), 1019 (w), 1000 (s), 988 (w), 890 (sh), 850 (ms), 828 (w), 794 (vs), 785 (s), 744 (w), 719 (s), 692 (vs) cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.58 (s, 2 H, 2CH), 4.35 (s, 10 H, 2Cp), 1.95 (s, 6 H), 1.71 (br, 2 H), 0.94 (s, 6 H), 0.87 (br, 4 H), 0.55 (br, 2 H). ^{13}C NMR (toluene-d_8): δ 95.7 (s), 85.5 (d, J = 158 Hz), 81.5 (d, J = 174 Hz, Cp), 58.9 (s), 34.1 (t, J = 132 Hz), 33.0 (t, J = 156 Hz), 31.5 (q, J = 126 Hz), 24.8 (q, J = 127 Hz). Anal. Calcd for $C_{24}H_{32}Co$: C, 65.75; H, 7.36. Found: C, 65.57; H, 7.52.

X-ray Diffraction Studies of $Co(C_5H_5)(2,4\text{-}C_7H_{11})BF_4$ and (μ,η^4,η^4-2,4,7,9-$(CH_3)_4$-1,3,7,9-$C_{10}H_{10}$)[$Co(C_5H_5)$]$_2$. Single crystals of these compounds were obtained by cooling concentrated solutions in nitromethane/ether and toluene/hexane mixtures, respectively, to −20 °C. Unit-cell constants and their standard deviations were determined from least-squares refinements of 25 reflections each, leading to a = 12.059 (2) Å, b = 9.724 (1) Å, c = 7.072 (1) Å, β = 125.70 (1)°, V = 673.45 Å^3, and Z = 2 for the first compound. From characteristic systematic absences the space group could be either C_2—$C2$ (No. 5), C_s^3—Cm (No. 8), or C_{2h}^3—$C2/m$ (No. 12). Data were collected on a Nicolet R3 diffractometer using a red crystal of approximate dimensions 0.30 × 0.19 × 0.08 mm. Scans were carried out in the θ–2θ mode out to 60° in 2θ by using Mo Kα radiation (λ = 0.71073 Å), leading to 652 reflections, of which 616 were judged to be observed ($I > 2.5\sigma(I)$). All crystallographic calculations employed the SHELXTL program package 4.1 (August 1983). An empirical absorption correction was applied, on the basis of four reflections in the 2θ range of 14.6–32.1°. The relative range of transmission factors was 0.828–1.000, while the value for the linear absorption coefficient is 12.94 cm^{-1}. The function minimized in least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. As space groups $C2$ or $C2/m$ would lead to a disordered structure, a solution was first attempted in space group Cm. A satisfactory structure did result in this space group with crystallographically imposed mirror symmetry for both the cation and the anion. The cobalt atom position was suggested by a Patterson map, after which the remaining non-hydrogen atoms were located from a Fourier map. Most of the hydrogen atoms were located from a difference Fourier map and subjected to isotropic refinement. However, H(5) and H(7) were poorly behaved and therefore were placed in calculated positions with C–H distances fixed at 0.96 Å. The endo hydrogen atom on C(1) could not be located. Final refinement led to agreement indices of R = 0.044 and R_w = 0.040. A final difference Fourier map revealed no peaks greater than 0.41 e/Å^3. The positional parameters for the non-hydrogen atoms are listed in Table I, and anisotropic thermal parameters are included in Table II.[6] Positional and thermal parameters for the hydrogen atoms may be found in Table III,[6] while pertinent bonding parameters and least-squares plane information may be found in Tables IV and V, respectively. The final values of $|F_o|$ and $|F_c|$ are also available.[6]

Table I. Positional Parameters for the Non-Hydrogen Atoms of $Co(C_5H_5)(2,4\text{-}C_7H_{11})^+BF_4^-$

atom	x	y	z
Co	0.0000 (0)	0.0000 (0)	0.0000 (0)
C(1)	−0.1338 (10)	0.1407 (11)	−0.0052 (17)
C(2)	−0.0113 (12)	0.1305 (10)	0.2147 (20)
C(3)	0.0343 (17)	0.0000 (0)	0.3120 (29)
C(4)	0.0790 (13)	0.2530 (11)	0.3340 (21)
C(5)	0.1843 (14)	0.0000 (0)	0.0351 (26)
C(6)	0.1035 (15)	0.1151 (16)	−0.0906 (25)
C(7)	−0.0206 (16)	0.0742 (13)	−0.2884 (25)
B	−0.0409 (15)	0.5000 (0)	−0.2611 (33)
F(1)	0.3780 (10)	0.0000 (0)	0.8042 (19)
F(2)	0.0845 (8)	0.5000 (0)	−0.0813 (20)
F(3)	0.4194 (9)	−0.1100 (9)	0.6015 (16)

For (μ-η^4,η^4-2,4,7,9-$(CH_3)_4$-1,3,7,9-$C_{10}H_{10}$)[$Co(C_5H_5)$]$_2$, the unit-cell constants were found to be a = 7.779 (4) Å, b = 10.955 (6) Å, and c = 12.239 (7) Å, with β = 94.93 (2)° for Z = 2 dimeric units. Systematic absences indicated the space group to be C_{2h}^5–$P2_1/a$ (No. 14). Data were collected out to 2θ = 60° on a purplish crystal of approximate dimensions 0.2 × 0.2 × 0.4 mm using Mo Kα radiation (λ = 0.71073 Å) and θ–2θ scans. A total of 1522 reflections were processed, leading to 1412 which were judged to be above background ($I > 3\sigma(I)$) An empirical absorption correction was applied, on the basis of reflections in the 2θ range of 5–20°. The relative range of transmission factors was 0.75–1.000, while the linear absorption coefficient is 16 cm^{-1}. Refinements were weighted as before. The cobalt atom position was determined from a Patterson map, after which the non-hydrogen atoms were located by using a Fourier map. Hydrogen atoms were placed in positions suggested by a difference Fourier map, and for the methyl groups, these were idealized by assuming tetrahedral geometry with d(C–H) = 0.96 Å. Thermal parameters for the hydrogen atoms were set to be 10% larger than those for their carbon atoms. Final refinement led to agreement indices of R = 0.058 and R_w = 0.048. A final difference Fourier map revealed no peaks greater than 0.36 e/Å^3. The positional pa-

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[6] Supplementary material.

Table IV. Pertinent Bond Distances (Å) and Angles (deg) for $Co(C_5H_5)(2,4-C_7H_{11})^+BF_4^-$

		Bond Distances			
Co–C(1)	2.099 (13)	Co–C(7)	2.038 (19)	C(6)–C(7)	1.382 (17)
Co–C(2)	2.044 (14)	C(1)–C(2)	1.389 (12)	C(7)–C(7′)	1.444 (24)
Co–C(3)	1.994 (22)	C(2)–C(3)	1.394 (11)	B–F(1)	1.302 (30)
Co–C(5)	2.087 (19)	C(2)–C(4)	1.498 (14)	B–F(2)	1.288 (15)
Co–C(6)	2.037 (21)	C(5)–C(6)	1.407 (16)	B–F(3)	1.332 (15)
		Bond Angles			
C(1)–C(2)–C(3)	118.2 (10)	C(6)–C(5)–C(6′)	105.3 (13)	F(1)–B–F(2)	110.0 (18)
C(1)–C(2)–C(4)	121.5 (9)	C(5)–C(6)–C(7)	110.7 (12)	F(1)–B–F(3)	103.6 (12)
C(3)–C(2)–C(4)	119.9 (9)	C(6)–C(7)–C(7′)	106.7 (8)	F(2)–B–F(3)	115.8 (10)
C(2)–C(3)–C(2′)	131.0 (13)			F(3)–B–F(3′)	106.8 (16)

Table V. Pertinent Least-Squares Plane Information for $Co(C_5H_5)(2,4-C_7H_{11})^+$

atom	dev	atom	dev
Plane Defined by Cyclopentadienyl Ligand[a]			
*C(5)	−0.008	C(1)	3.007
*C(6)	0.006	C(1′)	3.007
*C(7)	−0.003	C(2)	3.177
*C(6′)	0.006	C(2′)	3.177
*C(7′)	−0.003	C(3)	3.340
Co	1.663	C(4)	3.023
		C(4′)	3.023
Plane Defined by Pentadienyl Ligand[b]			
*C(1)	0.009	C(5)	−3.290
*C(2)	−0.032	C(6)	−3.147
*C(3)	0.045	C(6′)	−3.147
*C(1′)	0.009	C(7)	−2.955
*C(2′)	−0.032	C(7′)	−2.955
C(4)	−0.320	H(1A)	−0.236
C(4′)	−0.320	H(3)	−0.075
Co	−1.449		

[a] Equation (monoclinic coordinates): $-0.854x + 0.520z = 1.663$. [b] Equation (monoclinic coordinates): $-0.923x + 0.384z = -1.449$.

Table VI. Positional Parameters for the Non-Hydrogen Atoms of $(\mu-\eta^4,\eta^4-2,4,7,9-(CH_3)_4-1,3,7,9-C_{10}H_{10})[Co(C_5H_5)]_2$

atom	x	y	z
Co	0.19203 (11)	−0.01007 (8)	0.24702 (6)
C(1)	−0.0602 (7)	−0.0003 (6)	0.2622 (4)
C(2)	0.0257 (8)	0.1146 (6)	0.2857 (5)
C(3)	0.1305 (8)	0.1581 (5)	0.2059 (5)
C(4)	0.1480 (8)	0.0954 (5)	0.1072 (5)
C(5)	−0.0035 (9)	0.0635 (4)	0.0254 (4)
C(6)	0.0272 (9)	0.1760 (6)	0.3966 (5)
C(7)	0.3100 (8)	0.1256 (6)	0.0495 (5)
C(8)	0.4510 (11)	−0.0314 (8)	0.3005 (12)
C(9)	0.3994 (12)	−0.1077 (9)	0.2103 (8)
C(10)	0.2750 (11)	−0.1862 (6)	0.2384 (7)
C(11)	0.2428 (10)	−0.1602 (8)	0.3412 (8)
C(12)	0.3489 (14)	−0.0703 (9)	0.3828 (7)

rameters for the non-hydrogen atoms are listed in Table VI, and anisotropic thermal parameters are given in Table VII.[6] Atomic parameters for the hydrogen atoms are included in Table VIII,[6] while pertinent bonding and least-squares plane data are contained in Tables IX and X,[6] respectively. The final values of $|F_o|$ and $|F_c|$ are also available.[6]

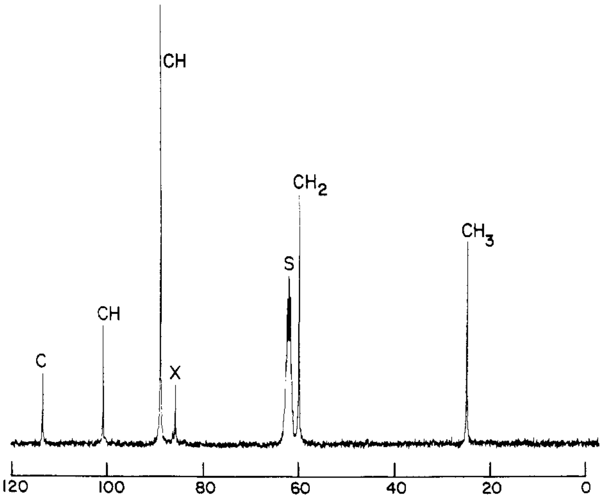

Figure 1. Proton-decoupled ^{13}C NMR spectrum of $Co(C_5H_5)(2,4-C_7H_{11})^+BF_4^-$ in CD_3NO_2. The impurity resonance designated "X" at ca. 86 ppm is due to a 5% $Co(C_5H_5)_2^+$ content.

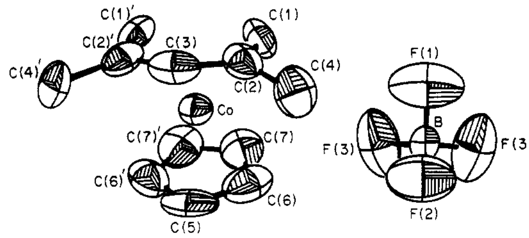

Figure 2. Perspective view of the "half-open cobalticinium" complex $Co(C_5H_5)(2,4-C_7H_{11})^+BF_4^-$. Both the cation and the anion reside on crystallographic mirror planes.

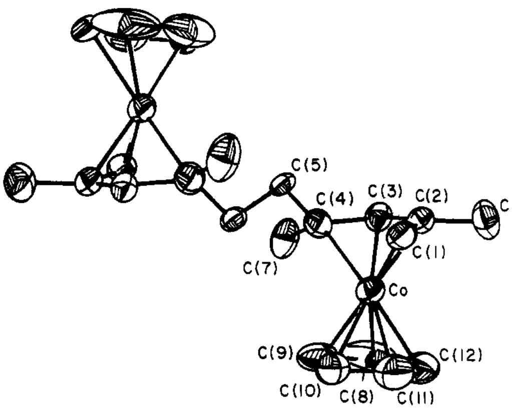

Figure 3. Perspective view of $(\mu-\eta^4,\eta^4-2,4,7,9$-tetramethyl-1,3,7,9-decatetraene)bis[(cyclopentadienyl)cobalt]. The dimer is situated on an inversion center.

Results

The reaction of the somewhat thermally unstable (cyclopentadienyl)(η^4-2,4-dimethyl-1,3-pentadiene)cobalt with triphenylmethyl tetrafluoroborate led to the formation of the very stable "half-open" cobalticinium complex $Co(C_5H_5)(2,4-C_7H_{11})^+BF_4^-$ (1). Similar complexes of cobalt and rhodium have, in fact, been previously prepared by entirely different routes by Powell et al.[7] Straightforward characterization was achieved through routine analytical and spectroscopic methods. The ^1H and ^{13}C NMR resonances (Figure 1) were observed to be shifted substantially downfield from those of the isoelectronic $Fe(C_5H_5)(2,4-$

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Table IX. Pertinent Bond Distances (Å) and Angles (deg) for $(\mu\text{-}\eta^4,\eta^4\text{-}2,4,7,9\text{-}(CH_3)_4\text{-}1,3,7,9\text{-}C_{10}H_{10})[Co(C_5H_5)]_2$

Bond Distances

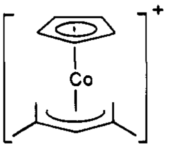
Co–C(1)	1.990 (6)	Co–C(8)	2.077 (8)	C(8)–C(9)	1.414 (17)	C(1)–C(2)	1.442 (10)		
Co–C(2)	1.967 (6)	Co–C(9)	2.018 (7)	C(8)–C(12)	1.402 (18)	C(2)–C(3)	1.408 (10)		
Co–C(3)	1.958 (6)	Co–C(10)	2.041 (6)	C(9)–C(10)	1.360 (14)	C(2)–C(6)	1.515 (8)		
Co–C(4)	2.069 (6)	Co–C(11)	2.028 (7)	C(10)–C(11)	1.335 (13)	C(3)–C(4)	1.405 (8)		
C(5)–C(5′)	1.526 (7)	Co–C(12)	2.083 (7)	C(11)–C(12)	1.356 (14)	C(4)–C(5)	1.521 (8)		
						C(4)–C(7)	1.533 (9)		

Bond Angles

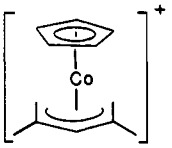
C(1)–C(2)–C(3)	116.3 (7)	C(3)–C(4)–C(5)	123.5 (6)	C(9)–C(8)–C(12)	104.0 (9)
C(1)–C(2)–C(6)	122.3 (7)	C(3)–C(4)–C(7)	115.8 (7)	C(8)–C(9)–C(10)	109.7 (9)
C(3)–C(2)–C(6)	120.7 (7)	C(5)–C(4)–C(7)	111.5 (6)	C(9)–C(10)–C(11)	107.4 (9)
C(2)–C(3)–C(4)	122.4 (8)	C(4)–C(5)–C(5′)	115.1 (5)	C(10)–C(11)–C(12)	110.6 (8)
				C(8)–C(12)–C(11)	108.3 (9)

C_7H_{11}), and the pentadienyl resonances are actually much more similar to those of $Fe(2,4\text{-}C_7H_{11})(CO)_3^+BF_4^-$.[8]

The trivalent cobalt complexes are of particular interest due to the fact that metal complexes of pentadienyl ligands almost always involve lower oxidation states. In order to learn more about metal–pentadienyl bonding in higher oxidation state complexes, a single-crystal X-ray diffraction study was carried out on 1. The result may be seen in Figure 2, along with the atom numbering scheme. Atomic coordinates for the non-hydrogen atoms are listed in Table I, while the thermal parameters and hydrogen atom parameters are listed in Tables II and III, respectively.[6] Table IV contains pertinent bonding parameters, while Table V contains least-squares plane information. It can be seen in Figure 2 that both the cation and the anion reside on crystallographic mirror planes, which relate the nonprimed atoms to their primed counterparts. Also apparent is the cation's conformation which is crystallographically perfectly eclipsed (III), as opposed to the staggered conformation (IV), 36° away. Of course, the large thermal motion of the cyclopentadienyl ligand renders this distinction somewhat ambiguous, as the adoption of two equivalent slightly staggered conformations would lead to large apparent thermal parameters for the carbon atoms and an apparent eclipsed conformation. However, it is interesting to note that "half-open" metallocenes, $M(C_5H_5)(2,4\text{-}C_7H_{11})$ (M = Fe, Ru), and some related molecules seem to adopt this same conformation,[8,9] although some rhodium, iridium, and vanadium complexes have been found to be staggered.[10,11]



III



IV

The cobalt–carbon bond distances are similar to those in the isoelectronic $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$, which averaged 2.06 Å to each ligand.[8b] In $Co(C_5H_5)(2,4\text{-}C_7H_{11})^+$, the Co–C ($C_5H_5$) bond distances average 2.047 (9) Å, while the Co–C bond distances for the pentadienyl ligand average 2.056 (7) Å. As has been observed for pentadienyl complexes of chromium,[12] iron,[8,13] ruthenium,[14] and osmium,[9a] the metal–pentadienyl and metal–cyclopentadienyl bond distances are very similar. This is not the case, however, for vanadium[11,12] or, presumably, titanium.

However, the individual metal-pentadienyl bond distances are not actually equivalent. It can be seen from Table IV that the Co–C(3) distance appears to be the shortest at 1.994 (22) Å, with the Co–C(2) value being intermediate at 2.044 (14) Å and the Co–C(1) value longest at 2.099 (13) Å. Thus in this complex the metal atom appears to have slipped to the C(3) end of the pentadienyl ligand. Possibly this difference occurs as a result of the charge or relatively high oxidation state of the cobalt complex. It can be noted that in "U"-shaped pentadienyl anions, negative charge tends to build up in the 3-position,[15] and in the rather ionic $Nd(2,4\text{-}C_7H_{11})_3$ complex, the shortest bond distances did involve C(3).[16] However, in that structure the longest bonds involved the formally uncharged C(2,4) positions. The present pattern might represent something intermediate between the Nd(III) and divalent transition-metal extremes,[16] although some lower valent cobalt phosphine complexes also have shown a related pattern.[17]

The carbon–carbon bond distances appear normal. Those for the cyclopentadienyl ligand average 1.404 (12) Å, compared to a value of 1.392 (8) Å for the delocalized C–C bonds in the pentadienyl ligand. Concerning the pentadienyl backbone, the C–C–C bond angles follow the usual pattern; i.e., when a methyl group is present on the central carbon atom, a smaller angle is observed.[16b] Thus, the C(1)–C(2)–C(3) angle is much smaller than the C(2)–C(3)–C(4) angle (118.2 (10)° vs. 131.0 (13)°, respectively). However, the difference of ca. 13° is much larger than the more normal differences of 4–6°. Whether this is due to the oxidation state, formal charge, or some other feature of the complex is not yet known. Both ligands are reasonably planar, and the angle formed between the two ligand planes is 8.7°. As is normally observed,[16b] the methyl groups on the pentadienyl ligand bend toward the metal atom by 12.3°, and a similar bending of 7.0° is ob-

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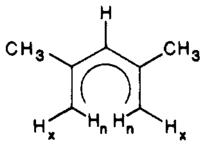
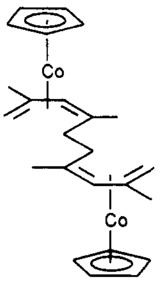
[17] Bleeke, J. R.; Peng, W.-J. *Organometallics* **1984**, *3*, 1422; **1986**, *5*, 635.

served for the hydrogen atom on C(3). The bending of the "exo" hydrogen atom (see V) on C(1) is larger at 16.7°. The "endo" hydrogen atom could not be located.

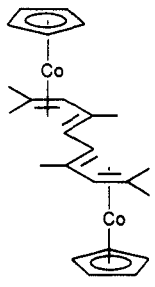


V

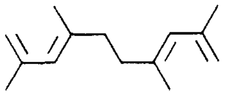
Reduction of the above cation was first attempted with zinc dust, as had been done for $Fe(2,4\text{-}C_7H_{11})(CO)_3BF_4$.[8c] However, the reduction was slow, and only very low yields (ca. 1–2%) of product could be isolated. As $Co(C_5H_5)(\eta^4$-2,4-dimethyl-1,3-pentadiene) itself was found to decompose at room temperature, it was believed that the expected product VIa or VIb might also be subject to decomposition in solution and that this rate was relatively rapid compared to the rate of product formation. Hence, the reaction was attempted with a more reactive reducing agent, sodium amalgam, which did then allow for isolation of the product in reasonably yield (59%). Once the dimer was isolated, it was indeed observed that it did decompose slowly in solution, although it was more stable in the solid state and could be characterized analytically and spectroscopically. ^1H and ^{13}C NMR spectra clearly indicated that the bridging bis(pentadienyl) unit was a 2,4,7,9-tetramethyl-1,3,7,9-decatetraene, as in VIa, rather than the isomerized 2,4,6,8-decatetraene form (VIb). However, this data did not exclude the possibility of the bridging unit containing two "S" (as in VII), rather than the expected "U", pentadienyl fragments, even though previous dimer analogues involve two "U" fragments.[3,8c]



VIa



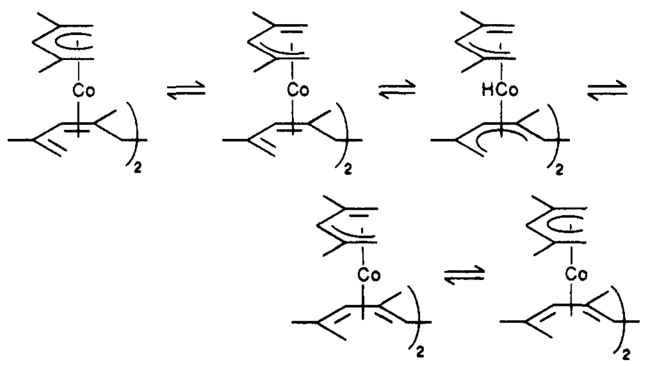
VIb



VII

To determine the actual conformation of the dimerized pentadienyl unit, an X-ray structural determination was carried out. Atomic positional and thermal parameters are presented in Tables VI, VII,[6] and VIII,[6] while pertinent bonding parameters and least-squares plane information are contained in Tables IX and X,[6] respectively. As can be seen in Figure 2, the complex does indeed exist in form VIa, involving two coupled "U" pentadienyl fragments. As the geometry of the bridging group is analogous to that of the observed I, formed by the dimerization of $Co(2,4\text{-}C_7H_{11})_2$,[3] it is clear that no geometric barrier is preventing the isomerization of VIa to VIb. Hence, it can be concluded that a significant electronic barrier to isomerization exists for the cyclopentadienyl complex VIa.

Scheme I



The dimeric complex lies on a crystallographic inversion center.[18] The cyclopentadienyl ligands are very nearly planar, with the carbon–carbon bond distances averaging 1.373 (7) Å. The average cobalt–carbon (Cp) bond distance of 2.049 (3) Å compares well with those for related compounds.[19] The butadiene fragment is oriented so that its central carbon–carbon bond is nearly eclipsing one of the cyclopentadienyl bonds (C8–C12). The Co–C(1), Co–C(2), Co–C(3), and Co–C(4) bond distances are 1.990 (6), 1.967 (6), 1.958 (6), and 2.069 (6) Å, respectively, so that the longer bonds clearly involve the terminal carbon atoms, as had also been found for the "open cobaltocene" dimer.[3] Particularly noticeable, however, is the Co–C(4) bond, which is perhaps so long due to the two attached carbon atoms C(5) and C(7).

The carbon–carbon bond distances in the coordinated butadiene are not unusual. The butadiene fragment is essentially planar, with none of the four bound carbon atoms deviating from it by more than 0.007 Å. C(5) lies 1.091 Å out of this plane in a direction away from the cobalt atom, while C(6) and C(7) are 0.178 and 0.517 Å out of the plane, respectively, in a direction toward the cobalt atom. These values correspond to angles of 45.8, 6.8, and 19.7° between the appropriate C–C vectors and the butadiene best plane. As in the case of pentadienyl complexes,[16b] attachment of a methyl group to an interior carbon atom brings about a contraction in the C–C–C bond angle. Thus, the C(1)–C(2)–C(3) angle is markedly smaller than the C(2)–C(3)–C(4) angle, 116.3 (7)° vs. 122.4 (8)°. The C(3)–C(4)–C(5) and C(4)–C(5)–C(5′) angles appear unusually large at 123.5 (6)° and 115.1 (7)°, respectively. It is not clear whether this is due to mutual repulsions between the two dimers, intermolecular packing forces, or some other influence. An angle of 13.1° is observed between the best planes for the two ligands.

Discussion

The formal dimerization of $Fe(2,4\text{-}C_7H_{11})(CO)_3$, $Co(C_5H_5)(2,4\text{-}C_7H_{11})$, or $Co(2,4\text{-}C_7H_{11})_2$ leads to 2,4,7,9-tetramethyldecatetraenes whose opposite diene fragments are each η^4-coordinated to $Fe(CO)_3$, $Co(C_5H_5)$, or $Co(2,4\text{-}C_7H_{11})$ units, respectively. For the first two dimers, the bridging units are present in the expected 1,3,7,9-decatetraene form. However, the last dimer was observed to contain a highly conjugated 2,4,6,8-decatetraene.[3] Since the latter two dimers differ only in the replacement of a

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[18] As was observed for the dimeric product which resulted from the reduction of $Fe(2,4\text{-}C_7H_{11})(CO)_3^+$, it must be expected that two dimeric cobalt isomers should exist, one being the less soluble "trans" form, the other having the two metal groups on the same side of the bridging unit (at least when the bridging unit is in the configuration depicted for VIa). The fact that no "cis" isomer was isolated might be attributed to a combination of its's expected higher solubility and the low stability of these complexes in solution.

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cyclopentadienyl group by the 2,4-dimethylpentadienyl ligand, it seems that the presence of the 2,4-dimethylpentadienyl ligand must be responsible for the observed isomerization of a 1,3,7,9-decatetraene to a 2,4,6,8-decatetraene. Since the major difference between these ligands in such complexes should involve the greater facility of the pentadienyl group to undergo η^5–η^3 transformations,[20] the isomerization mechanism depicted in Scheme I is clearly implicated for this process.[21] In fact, there are many reasons to expect η^5–η^3 transformations to be facile in this and in other complexes. Not only is the loss in π-delocalization energy for the η^5–η^3 transformation much less for a pentadienyl ligand than for a cyclopentadienyl ligand (0.64 vs. 1.64 β),[22] but it has also been demonstrated that the very large size of a pentadienyl ligand gives rise to a loss in metal–ligand overlap, which could therefore be improved upon its conversion to an η^3-bound form.[16b] In fact, for essentially isoelectronic (cyclohexadienyl)platinum bis(phosphine) cations,[23] the ground state has been observed to involve η^3-pentadienyl coordination for a 16-electron complex, and calculations indicate that such a form has enhanced overlap for an important bonding interaction, while the η^5-alternative (an 18-electron complex) is destabilized due to enhanced overlap for an antibonding interaction.[24] Not surprisingly, therefore, facile reversibility of the η^5-η^3 transformation has been demonstrated for this platinum system, as well as for some manganese[25] complexes. η^3-Cycloheptadienyl[26] and -pentadienyl[17] complexes of cobalt are also known.

In accord with earlier expectations, the open nature of the pentadienyl ligand does indeed impart high reactivity to its metal complexes.[20,22] Not only are reversible η^5–η^3 (and perhaps η^3–η^1) transformations readily attainable, but also these complexes readily become involved in other useful reactions, both catalytic and stoichiometric, often involving the coupling of pentadienyl ligands to other unsaturated species. Interestingly, even in cases in which the pentadienyl ligand is more strongly bound that the cyclopentadienyl ligand, it is the former that is still the more active center. Clearly, pentadienyl ligands are superb ligands for imparting not only thermal stability but also high reactivity.

Acknowledgment. R.D.E. expresses his gratitude for support of this research through grants from the National Science Foundation (CHE-8120683 and CHE-8419271) and from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We would also like to acknowledge the National Science Foundation (Grant CHE-8100424) and the University of Utah Institutional Funds Committee for providing funds for the departmental purchase of the mass spectrometer system. The 300-MHz NMR instruments were acquired via NSF and DOD instrumentation grants.

Registry No. 16, 106212-39-9; VIa, 106212-34-4; (cyclopentadienyl)(2,4-dimethylpentadiene)cobalt, 106212-37-7; 2,4-dimethyl-1,3-pentadiene, 1000-86-8; cobalt(III) acetylacetonate, 21679-46-9; (methylcyclopentadienyl)(η^4-2,4-dimethylpentadiene)cobalt, 106212-40-2; (methylcyclopentadienyl)(2,4-dimethylpentadienyl)cobalt tetrafluoroborate, 106212-36-6.

Supplementary Material Available: Listings of the anisotropic thermal parameters for the non-hydrogen atoms and of the positional and thermal parameters for the hydrogen atoms (Tables II, III, VII, VIII, and X) (5 pages); listings of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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(21) (a) One might question why no transfer of the hydrogen atom to the η^3-2,4-dimethylpentadienyl ligand in Scheme I takes place. It could be that the transfer is a concerted process, so that a true metal hydride intermediate does not actually exist.[21b–d] Alternatively, it could be that some hydride is transferred to the η^3 ligand but that the process is reversible. In such an event, an equilibrium of species could result, which might favor the highly conjugated, observed product of Scheme I. A cycloheptadienyl-derived dimer related to VIa has also recently been reported.[21e] (b) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 63. (c) Lamanna, W.; Brookhart, M. *Ibid.* **1980**, *102*, 3490. (d) Karel, K. J.; Brookhart, M.; Aumann, R. *Ibid.* **1981**, *103*, 2695. (e) Geiger, W. E.; Gennett, G. A.; Lane, A.; Salzer, A.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1352.

(22) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56.

(23) Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 1058.

(24) (a) Mingos, D. M. P.; Nurse, C. R. *J. Organomet. Chem.* **1980**, *184*, 281. (b) Hoffmann, R.; Tse, Y.-C.; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812. (c) Silvestre, J.; Albright, T. A. *Ibid.* **1985**, *107*, 6829.

(25) Paz-Sandoval, M. d. l. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026.

(26) Rinze, P. V. *J. Organomet. Chem.* **1974**, *77*, 259.