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Transition Metal Arene Chemistry. 4.[1] Structural Studies of Cobalt Group Complexes

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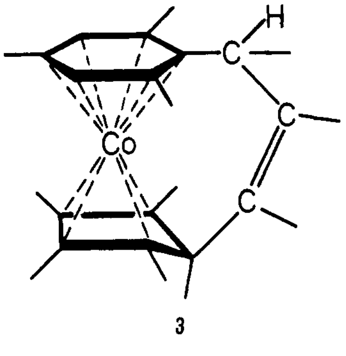
Abstract: The molecular and crystal structures of $[\eta^6\text{-}C_6(CH_3)_6]_2Co^+PF_6^-$ (**1**) and of $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+PF_6^-$ (**2**) are described from an analysis of three-dimensional X-ray diffraction data. The cobalt salt, **1**, is orthorhombic, space group $Pnnm\text{-}D_{2h}^{12}$ (no. 58), with a = 8.137 (3) Å, b = 10.738 (4) Å, c = 13.777 (4) Å, and Z = 2. For the cationic cobalt complex, there is near D_{6h} symmetry with an eclipsed arrangement of the two hexahapto arene rings. Because all methyl substituents are bent away from the cobalt center there is no significant inter-ring nonbonded interaction. Consistent with the 20-electron character of this complex with the last two electrons residing in a degenerate metal-carbon antibonding orbital, the complex is paramagnetic and has relatively long cobalt-carbon bonds. The rhodium complex which was produced by Zn-HCl reduction of $[C_6(CH_3)_6]_2Rh^{2+}$ and previously described as a bis(hexamethylbenzene)rhodium$^+$ complex is shown to be $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+$. The PF_6^- salt of the rhodium complex, **2**, is orthorhombic, space group $Pnna\text{-}D_{2h}^{16}$ (no. 62), with a = 21.831 (3) Å, b = 13.401 (2) Å, c = 8.446 (2) Å, and Z = 4. Partial hydrogenation of the one ring in the rhodium complex did not proceed through H_2 or H^+ addition to the metal center of the precursor rhodium(II) bis(arene) complex because the two added hydrogen atoms are at exo ring positions. Presumably, the hydrogenation was effected by a heterogeneous process, i.e., at the zinc surface. This is the first crystallographic determination of an arene-rhodium complex and the structure exhibits several features of general significance in arene-metal chemistry.

Introduction

In a general study of transition metal arene complex chemistry, we seek structural and stereochemical definition of the mechanism by which transition metal bonds to aromatic hydrocarbons are formed and broken,[2] and of the mechanistic features of molecular transition metal complex catalysis of arene hydrogenation.[2b,3] A tetrahapto bonding of arene to metal has been suggested as a critical feature of the catalysis of arene hydrogenation by the d^8 complex, $\eta^3\text{-}C_3H_5Co[P(OCH_3)_3]_3$.[3-5] For this reason, we have sought precise structural information about d^8-metal arene complexes.

Literature reports posed interesting electronic and structural questions about d^8 cobalt(I) bis(arene) complexes. A paramagnetic $[C_6(CH_3)_6]_2Co^+$ ion had been synthesized by the Fischer-Hafner procedure[6] and a diamagnetic $[C_6(CH_3)_6]_2Co^+$ ion reportedly[7] had been prepared from (mesityl)$_2$Co and 2-butyne. This apparent anomaly has been resolved. Here we describe the crystal structure of the PF_6^- salt of the paramagnetic cation. In other studies, we have found that the (mesityl)$_2$Co and 2-butyne reactions produce no detectable bis(hexamethylbenzene)cobalt complex but rather a set of at least three cobalt(I) complexes. One has structure **3** with one hexahapto arene ligand and a tetrahapto pentamethylcyclopentadiene ligand. Preliminary X-ray diffraction results for another of these complexes indicate a solid-state structure in which a nonclassical carbonium ion has apparently been stabilized by interaction with a novel neutral (η^6-hexamethylbenzene)cobalt(η^3-pentamethylcyclopentadienyl) complex **4**. (In structures **3** and **4**, methyl groups are denoted by vectors from the contiguous carbon atoms.) However, the structural details have not yet been fully resolved for this system; complete structural descriptions of these relatively bizarre cobalt(I) complexes will be reported separately.[8]



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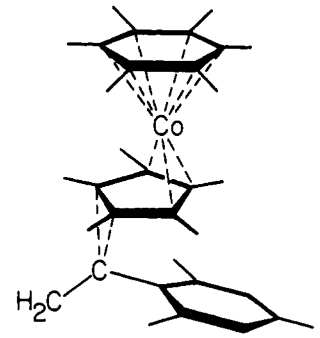

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There has been a single report[6] of the preparation of the rhodium ion analogue, bis(hexamethylbenzene)rhodium$^+$. This ion, found to be diagmagnetic, was of particular interest to us because the ruthenium analogue $[\eta^6\text{-}C_6(CH_3)_6]Ru[\eta^4\text{-}C_6(CH_3)_6]$,[9] has exhibited unusual fluxional[10] and catalytic[10,11] chemistry. Described here are the crystal structure and the chemistry of the diamagnetic rhodium complex which was found not to have the reported composition but rather has one η^4 partially hydrogenated arene ligand (hexamethylcyclohexadiene) and one η^6-arene ligand: $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+PF_6^-$.

Experimental Section

Reagents and General Procedures. Cobalt(II) chloride, rhodium(III) chloride hydrate, and hexamethylbenzene were commercial samples and were not purified prior to use. All solvents were dried by standard procedures and were vacuum transferred before use. Commercial samples of aluminum halides were vacuum sublimed, and dimethylaluminum chloride was used without purification. Analytical procedures for identification of arene hydrogenation reactions have been described previously.[5] All reactions and product isolation and purification procedures were initially effected with a Vacuum Atmospheres Dribox, with modified Schlenk technique, vacuum line procedure, or a combination of these procedures. These precautions proved unnecessary for the isolation and purification of the cobalt(I) and rhodium(I) complexes.

The PF_6^- salt of $[C_6(CH_3)_6]_2Co^+$ was prepared by the procedure of Fischer and Lindner[6] and recrystallized from a CH_2Cl_2-ether mixture to give yellow single crystals.

Preparation of $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+PF_6^-$. The precursor of this complex, $[C_6(CH_3)_6]_2Rh^{2+}[PF_6^-]_2$, was prepared precisely by, and with various modifications (including the addition of $[(CH_3)_2AlCl]_2$) of, the procedure described by Fischer and Lindner.[6] The results were essentially invariant. For the reduction of the rhodium(II) complex, the zinc-HCl procedure[6] reported for the synthesis of $[C_6(CH_3)_6]_2Rh^+PF_6^-$ was employed to obtain yellow crystals of $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+[PF_6]^-$. Single crystals were obtained by perfusion of a 20% aqueous acetone solution to an acetone solution of ~200 mg of the complex to which about 8 drops of water had been added. Large crystals began to form after about 5 days. Anal. Calcd for $C_{24}H_{38}RhPF_6$: C, 50.17; H, 6.62; Rh, 17.94; P, 5.40; F, 19.86. Found: C, 50.18; H, 6.62; Rh, 16.82; P, 5.44; F, 19.92. This complex, dissolved in tetrahydrofuran, slowly decomposed at 74 °C—green coloration in 3–5 h and a dark precipitate in 2 days.

NMR data, ^1H (acetone-d_6 solution, $(CH_3)_4Si$ internal reference), temperature invariant −50 to +50 °C, δ values (ppm):

δ 90 MHz	δ 200 MHz	δ 360 MHz	J, Hz
2.33 (20) s	2.33 (24) d	2.34 s	0.24
2.29 (2) s	2.29 (2.5) d	2.32 s	0.24
1.94 (7) d	1.94 (6.3) d	1.95 d	0.73
1.32 (5) broad	1.32 (6.5) d	1.38 d	0.61

Doublets of low intensity (and other minor peaks) were also observed at δ 1.33, 0.97, 0.93, and 0.84. $^{13}C\{^1H\}$ ($CDCl_3$ solution), $(CH_3)_4Si$ reference, 20 MHz, 30 °C) (see Figure 2 for labeling scheme): δ 113.70, d (J = 3.9 Hz), 6 (C_a); 96.13, d (J = 7.8 Hz), 2 (C_{b1} or C_{b2}); 81.99, d (J = 16.4 Hz), 2 (C_{b2} or C_{b1}); 37.83, d (J = 1.7 Hz), 2 (C_{b3}); 20.24, s, 2 (C_{bm1}); 15.86, d (J = 1.7 Hz, 6 (C_{am}); 14.39, s, 2 (C_{bm3}); 12.90, s, 2 (C_{bm2}). ^{13}C ($CDCl_3$): δ 113.70, broad, 6 (C_a); 96.13, broad, 2 (C_{b1} or C_{b2}); 81.99, broad, 2 (C_{b2} or C_{b1}); 37.83, br d of q (J = 127, 5 Hz), 2 (C_{b3}); 20.24, q (J = 126 Hz), 2 (C_{bm1}); 15.86 q (J = 128 Hz), 6 (C_{am}); 14.39, br q of d (J = 126, 5 Hz), 2 (C_{bm3}); 12.90, br q of d (J = 127, 3 Hz), 2 (C_{bm2}).

Catalytic Hydrogenation Reactions. The reaction vessel and procedure have been described.[5] Solutions of $[C_6(CH_3)_6]Rh[C_6H_2(CH_3)_6]^+PF_6^-$ (0.02 g, 0.035 mmol) in 5 mL of tetrahydrofuran (or 0.8 mL of acetone) and toluene (0.37 mL, 3.5 mmol) and hydrogen (~720 mm pressure at −196 °C) were heated to 25, 50–55 and 78 °C. Analysis was by gas chromatography on a 10% Carbowax 20M at 70 °C and 20 mL/min flow rate. No reaction occurred at 20 °C (15 h), some discoloration but no methylcyclohexane formation occurred at 50–55 °C (2 h), and rhodium metal formed at 78 °C, after which time methylcyclohexane formation was evident.

The cobalt complex underwent reduction with hydrogen and consequently was not itself a catalyst for arene hydrogenation.

Crystallography. Large well-shaped, single crystals of $[\eta^6\text{-}C_6(CH_3)_6]_2Co^+PF_6^-$ (**1**) and $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+PF_6^-$ (**2**), obtained as described above, were suitable for X-ray diffraction studies. Weissenberg and precession photographs, used to determine preliminary sets of lattice constants and probable space groups, indicated orthorhombic, *mmm*, Laue symmetry for both compounds. The systematically absent reflections were those required by space groups $Pnnm\text{-}D_{2h}^{12}$ (no. 58)[12a] or $Pnn2\text{-}C_{2v}^{10}$ (no. 34)[12b] for **1** and by space groups $Pnma\text{-}D_{2h}^{16}$ (no. 62)[12c] or $Pn2_1a$ [an alternate setting of $Pna2_1\text{-}C_{2v}^{9}$ (no. 33)[12d]] for **2**. The choice of centrosymmetric space groups (*Pnnm* for **1** and *Pnma* for **2**) for both compounds was fully supported by all stages of the subsequent structure determinations and refinements.

Diffraction measurements utilized a nearly cube-shaped specimen of **1** which was ~0.70 mm on an edge and a parallelepiped-shaped sample of **2** which had dimensions of 0.63 × 0.38 × 0.25 mm. These crystals were then each in turn accurately centered on a computer-controlled four-circle Syntex P$\bar{1}$ autodiffractometer and a total of 15 high-angle ($2\theta_{MoK\bar{\alpha}} > 25°$) reflections, chosen to give a good sampling of reciprocal space and diffractometer settings, were used to align them and calculate angular settings for their reflections. Least-squares refinements of the diffraction geometry for each set of 15 reflections, recorded at the ambient laboratory temperature of 20 ± 1 °C with graphite-monochromated Mo K$\bar{\alpha}$ (λ = 0.710 73 Å), gave the lattice constants a = 8.137 (3) Å, b = 10.738 (4) Å, and c = 13.777 (4) Å for **1** and a = 21.831 (3) Å, b = 13.401 (2) Å, and c = 8.446 (2) Å for **2**. Unit-cell contents of two $[\eta^6\text{-}C_6(CH_3)_6]_2Co^+PF_6^-$ and four $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+PF_6^-$ moieties gave calculated densities of 1.458 and 1.540 g cm^{-3} for **1** and **2**, respectively. These are in excellent agreement with the densities of 1.442 and 1.530 g cm^{-3} measured for **1** and **2** by flotation in aqueous KI solutions.

Intensity measurements for both compounds utilized graphite-monochromated Mo K$\bar{\alpha}$ radiation and the ω scanning technique with a 4° takeoff angle and a normal-focus X-ray tube on a computer controlled Syntex P$\bar{1}$ autodiffractometer. Scanning rates of 3°/min were employed with both compounds for reflections having $2\theta_{MoK\bar{\alpha}} < 43°$. Reflections for **1** having $43° < 2\theta_{MoK\bar{\alpha}} < 53.9°$ were scanned at a rate of 2°/min while those having $53.9 < 2\theta_{MoK\bar{\alpha}} < 66.8°$ were scanned at a rate of 1°/min. A scanning rate of 2°/min was used for those reflections of **2** having $43° < 2\theta_{MoK\bar{\alpha}} < 55°C$. The scan for each reflection of both compounds was between ω settings 0.50° above and below the calculated K$\bar{\alpha}$ (λ = 0.710 73 Å) doublet value. Counts were accumulated for 19 equal time intervals during each scan and those 13 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Careful and systematic preliminary studies of peak widths (half-height to half-height) indicated little variation from values of 0.29 and 0.34° in ω for various orientations of the crystals of **1** and **2**, respectively. Background counts for both compounds, each lasting for one-half the total scan time used for the net scan, were measured at ω settings 1.0° above and below the calculated K$\bar{\alpha}$ value for each reflection. Totals of 2474 and 3558 independent reflections having maximum $2\theta_{MoK\bar{\alpha}}$ limits of 66.8 and 55° were measured for **1** and **2**, respectively, in concentric shells of increasing 2θ.

The six standard reflections for each compound, measured every 300 reflections as a monitor for possible disalignment and/or deterioration of the respective crystals, gave no indication of either. The linear absorption coefficients of **1** and **2** for Mo K$\bar{\alpha}$ radiation[13] are 1.03 and 1.10 mm^{-1}, respectively. The intensities for both compounds were reduced without absorption corrections to relative squared amplitudes, $|F_O|^2$, by means of standard Lorentz and polarization corrections.

Of the 2474 reflections examined for **1**, 910 were rejected as objectively unobserved by applying the rejection criterion, $I < 3\sigma(I)$, where $\sigma(I)$ is the standard deviation in the intensity computed from

$$\sigma^2(I) = (C_t + k^2B)$$

C_t being the total count from scanning, k the ratio of scanning time to total background time (in this case, k = 1), and B the total background count. For **2**, 1477 of the 3558 reflections examined had $I < 3\sigma(I)$ and were rejected. The heavy-atom technique, difference Fourier syntheses, and full-matrix least-squares refinement were used with the remaining 1564 observed intensities for **1** and 2081 for **2**, in the determination and refinement of their respective solid-state structures. Wilson plots and sets of normalized structure factors, E_{hkl}, were calculated for both compounds; the various statistical indicators using these sets of normalized structure factors were all in agreement with the choice of the approprriate centrosymmetric space group for each compound.

The atomic coordinates of the cobalt atom of **1** and the rhodium atom of **2** were derived from Patterson syntheses. Cycles of isotropic least-squares refinement for the structural parameters of the metal atom resulted in conventional unweighted residuals

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

of 0.524 for **1** and 0.278 for **2** for those reflections having $2\theta_{\mathrm{Mo}K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. In both cases, the remaining nonhydrogen atoms were located from a series of difference Fourier syntheses using increasingly more complete structural models. Unit-weighted full-matrix least-squares refinement of the fractional atomic coordinates and isotropic thermal parameters for all nonhydrogen atoms resulted in R_1 values of 0.122 for **1** and 0.118 for **2** and 0.118 for **2** and conventional weighted residuals

$$R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$$

of 0.131 and 0.138, respectively, for 616 (**1**) or 1155 (**2**) reflections having $2\theta_{\mathrm{Mo}K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. These and all subsequent structure-factor calculations employed the atomic form factors compiled by Cromer and Mann[14] and anomalous dispersion corrections[15] to the scattering factors of rhodium, cobalt, and phosphorus atoms. Utilization of anisotropic thermal parameters for all atoms in further cycles of least-squares refinement gave $R_1 = 0.059$ and $R_2 = 0.080$ for 616 independent reflections of **1** and $R_1 = 0.050$ and $R_2 = 0.056$ for 1155 independent reflections of **2**.

While a difference Fourier synthesis calculated at this point for **2** failed to reveal hydrogen atom positions, a similar calculation for **1** revealed the nine hydrogen atoms in chemically anticipated positions. All subsequent least-squares refinement cycles for **1** employed anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms; the model for additional refinement cycles of **2** included only anisotropic nonhydrogen atoms. Further unit-weighted full-matrix minimization of the function $\Sigma w(|F_o| - K|F_c|)^2$ (where w is the weight given to each reflection and K is the scale factor) with the low-angle ($2\theta_{\mathrm{Mo}K\bar{\alpha}} < 43°$) data for **1** converged to $R_1 = 0.033$ and $R_2 = 0.033$ for 616 reflections.

At this point the more complete data set ($2\theta_{\mathrm{Mo}K\bar{\alpha}} < 66.8°$ for **1** and $2\theta_{\mathrm{Mo}K\bar{\alpha}} < 55°$ for **2**) was included in both refinements. Unit-weighted cycles converged to $R_1 = 0.038$ and $R_2 = 0.036$ for 1564 reflections of **1** and $R_1 = 0.058$ and $R_2 = 0.060$ for 2081 reflections of **2**. Empirical weights ($w = 1/\sigma^2$) were then calculated from

$$\sigma = \sum_0^2 a_n|F_o|^n = 0.316 + 1.40 \times 10^{-2}|F_o| - 7.25 \times 10^{-5}|F_o|^2$$

for **1** and

$$\sigma = 1.20 + 5.71 \times 10^{-3}|F_o| + 1.74 \times 10^{-4}|F_o|^2 - 2.91 \times 10^{-7}|F_o|^3$$

for **2**, the a_n being coefficients derived from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum a_n|F_o|^n$$

where the F_c values were calculated from the fully refined models using unit weighting and an $I > 3\sigma(I)$ rejection criterion. The final cycles of least-squares refinement for both compounds utilized these weights to refine the atomic parameters together with a scale factor and extinction correction[16] of the form $1/(1 + gI_c)^{1/2}$ (where the extinction coefficient, g, refined to values of 6.76×10^{-7} for **1** and 1.31×10^{-7} for **2**). These cycles gave $R_1 = 0.037$ and $R_2 = 0.047$ for 1564 independent reflections of **1** having $2\theta_{\mathrm{Mo}K\bar{\alpha}} < 66.8°$ and $I > 3\sigma(I)$ and $R_1 = 0.057$ and $R_2 = 0.076$ for 2081 reflections of **2** having $2\theta_{\mathrm{Mo}K\bar{\alpha}} < 55°$ and $I > 3\sigma(I)$.[17]

During the final cycle of refinement for both compounds,[17] no parameter (including those for the hydrogen atoms of **1**) shifted by more than $0.36\sigma_p$ and the average parameter shift was $<0.05\sigma p$, where σp is the estimated standard deviation for the parameter in question. No significant differences were observed in either compound for the final parameters from least-squares refinement cycles utilizing empirical weights or unit weights.

The following computer programs were employed in this work with an IBM 360/65 or 370/158 computer: MAGTAPE, SCALEUP, and SCTFT4, data reduction programs written in this laboratory by V. W. Day; FAME, a Wilson plot and normalized structure factor program by R. Dewar and A. Stone; FORDAP, Fourier and Patterson synthesis program, a modified version of A. Zalkin's program; ORFLSE, full-matrix least-squares refinement program, a highly modified version of Busing, Martin, and Levy's original ORFLS; ORFFE, bond lengths and angles with standard deviations by Busing, Martin, and Levy; ORTEP2, thermal ellipsoid plotting program by Johnson; MPLANE, least-squares mean plane calculation program from L. Dahl's group.

Results and Discussion

Solid-State Structures for the PF_6^- Salts of $[\eta^6\text{-}C_6(CH_3)_6]_2Co^+$ and $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+$. Final atomic coordinates and (equivalent) isotropic thermal parameters for the X-ray structural analyses of $[\eta^6\text{-}C_6(CH_3)_6]_2Co^+PF_6^-$ (**1**) and $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+PF_6^-$ (**2**) are presented in Tables I and II, respectively; corresponding anisotropic thermal parameters for their nonhydrogen atoms are given in Tables III and IV.[17] The numbering scheme used to designate atoms of **1** and **2** is as follows. The atomic symbols for the ring carbon atoms of the hexamethylbenzene (hmb) or hexamethylcyclohexadiene (hmcy) ligands in both compounds carry a numerical subscript which is also used in the subscripts for their methyl substituents. Methyl carbon atoms have an additional subscripted *m* and hydrogens have a second numerical subscript to distinguish between hydrogens of the same methyl. Atoms of the hexamethylbenzene ligand in **2** have a subscripted *a* while those of the hexamethylcyclohexadiene ligand have a subscripted *b*. Unique PF_6^- fluorine atoms in both compounds are distinguished from one another by numerical subscripts. The anions and cations of both compounds are required to possess crystallographic site symmetry: the Co and P atoms of **1** occupy twofold positions of $C_{2h}\text{-}2/m$ symmetry and the Rh and P atoms of **2** occupy fourfold positions of $C_s\text{-}m$ symmetry. Atoms in both compounds labeled with a prime are related to those without by the crystallographic mirror plane which contains the metal and phosphorus atoms. Atoms of **1** labeled with double and triple primes are related to those without primes by the crystallographic C_2 and C_i operations, respectively, which are centered on the Co or P atoms.

Perspective models which illustrate this notation scheme for the cations of **1** and **2** are shown in Figures 1 and 2, respectively. Covalent bond lengths and angles for **1** are listed with their estimated standard deviations in Table V; corresponding data for **2** are given in Table VI. With all hexamethylbenzene ligands in both compounds hexahapto ligands and the hexamethylcyclohexadiene ligand of **2** a tetrahapto ligand, the cation of **1** is nominally a 20-electron species while that of **2** is an 18-electron complex.

The rigorous symmetry of bis(arene) metal complexes has attracted considerable attention in the past with $(\eta^6\text{-}C_6H_6)_2Cr$ representing the most controversial example.[18] Whereas the $[\eta^6\text{-}C_6(CH_3)_6]_2Co^+$ cation is required to possess only C_{2h} site symmetry in **1**, it approaches very closely full D_{6h} symmetry. Major departures from this symmetry comprise methyl group orientations and a ~0.04-Å slippage of each hexamethylbenzene ring center of gravity (Cg) off the idealized C_6 axis in the crystallographic mirror plane. This skewing of the cation produces small, but statistically significant, systematic differences in the Co–C(ring) distances which range from 2.235 (2) Å for C_1 to 2.278 (2) Å for C_3. The 2.257 (2, 14, 22, 3) Å[19] average length for the Co–C(ring) bonds in **1** is ≥0.06 Å longer than those observed for other bis(arene) complexes of first transition series metals[18,20] and ~0.10 Å longer than those in several other monoarene cobalt complexes.[21] This elongation of the Co–C bonds in the cation of **1** is totally consistent with a 20-electron metal complex with 2 electrons in a degenerate antibonding molecular orbital. Ring carbon-to-metal distances

Table I. Atomic Coordinates in Crystalline $\{(\eta^6\text{-}C_6(CH_3)_6)_2Co\}^+\{PF_6\}^-$ (**1**)[a]

atom type[b]	fractional coordinates 10^4x	10^4y	10^4z	isotropic thermal parameter,[c] B, Å^2
		Anion		
P	5000[d]	5000[d]	0[d]	4.1
F_1	3190(3)	5516(3)	0[d]	7.4
F_2	4522(3)	4011(2)	799(2)	7.7
		Cation		
Co	0[d]	0[d]	0[d]	2.5
C_1	2592(3)	−224(2)	509(2)	3.7
C_2	1912(3)	792(3)	1013(2)	3.9
C_3	1213(3)	1792(2)	503(2)	4.2
C_{m1}	3375(6)	−1303(5)	1040(6)	6.9
C_{m2}	1992(9)	804(10)	2116(3)	7.5
C_{m3}	556(6)	2908(5)	1062(7)	7.4
	10^3x	10^4y	10^4z	
H_{11}	300(7)	−95(7)	166(6)	15(3)
H_{12}	416(6)	−127(5)	121(4)	8(2)
H_{13}	297(7)	−200(5)	82(4)	9(2)
H_{21}	113(8)	160(6)	221(4)	10(2)
H_{22}	160(9)	13(6)	243(4)	12(2)
H_{23}	284(8)	101(6)	231(4)	9(2)
H_{31}	129(6)	348(5)	111(4)	8(1)
H_{32}	0(9)	259(7)	182(5)	13(2)
H_{33}	−34(9)	316(6)	60(4)	13(3)

[a] Figures in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] For nonhydrogen atoms which are modeled with anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, this is the equivalent isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$; for hydrogen atoms it is the isotropic temperature factor. [d] This is a symmetry-required value and is listed without an estimated standard deviation.

Table II. Atomic Coordinates in Crystalline $\{(\eta^6\text{-}C_6(CH_3)_6)Rh(\eta^4\text{-}C_6H_2(CH_3)_6)\}^+\{PF_6\}^-$ (**2**)[a]

atom type[b]	10^4x	10^4y	10^4z	equivalent isotropic thermal parameter,[c] B, Å^2
		Anion		
P	3600(2)	2500[d]	6888(5)	6.2
F_1	3341(8)	2500[d]	8563(13)	13.9
F_2	3841(8)	2500[d]	8563(18)	17.1
F_3	4082(3)	1705(5)	6396(13)	11.4
F_4	3120(4)	1718(6)	7360(11)	11.4
		Cation		
C_{a1}	2130(4)	1980(8)	716(10)	6.3
C_{a2}	1627(6)	1474(6)	20(11)	6.4
C_{a3}	1147(4)	2001(8)	−587(9)	6.3
C_{am1}	2682(6)	1399(15)	1377(17)	10.2
C_{am2}	1651(10)	343(9)	−123(21)	11.5
C_{am3}	606(7)	1418(15)	−1345(16)	11.1
C_{b1}	1202(5)	1960(13)	4304(14)	7.9
C_{b2}	749(8)	1560(7)	3574(17)	7.5
C_{b3}	118(6)	1960(11)	3805(18)	10.5
C_{bm1}	1725(8)	1424(24)	5083(24)	14.2
C_{bm2}	870(20)	449(11)	3469(40)	15.7
C_{bm3}	−289(15)	1427(27)	2703(30)	19.0
	10^5x	10^5y	10^5z	
Rh	12 439(3)	25 000[d]	19 786(8)	3.6

[a] Figures in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2. [c] The nonhydrogen atoms were modeled with anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and this is the equivalent isotropic thermal parameter calculated from $B = 4\,[V^2 \det(\beta_{ij})]^{1/3}$. [d] This is a symmetry-required value and is listed without an estimated standard deviation.

in electron-rich nickelcene[22] and one of its derivatives[23] are similarly longer (~0.10 Å) than those in ferrocene.[24] An unanswered question about $[\eta^6\text{-}C_6(CH_3)_6]_2Co^+$ is why this complex does not adopt a diamagnetic $[\eta^6\text{-}C_6(CH_3)_6]Co[\eta^4\text{-}C_6(CH_3)_6]^+$ form analogous to the isoelectronic, neutral ruthenium complex. In fact, there is no evidence for a tetrahapto bonding of an arene ligand to a *first*-row transition metal in bis(arene) metal complexes; this may partially reflect the balance of ligand field stabilization energies and electron pairing energies in d^8 (arene)$_2$M complexes.

Each of the six-membered arene rings in the cation of **1** is coplanar[25] to within 0.003 Å and they are separated by 3.539 Å. Methyl carbon atoms are displaced out of the ring mean plane by 0.04–0.07 Å away from the Co atom. Although the two rings are eclipsed in **1**, there is no interligand C···C, C···H, or H···H contact significantly less than the appropriate van der

Table V. Bond Lengths and Angles in Crystalline $\{(\eta^6\text{-}C_6(CH_3)_6)_2Co\}^+\{PF_6\}^-$ (**1**)[a]

type[b]	value	av[c]	type[b]	value	av[c]
		Bond Lengths (Å)			
$Co\text{-}C_1$	2.235(2)		$P\text{-}F_1$	1.574(3)	1.577(3,3,3)
$Co\text{-}C_2$	2.257(2)	2.257(2,14,22)	$P\text{-}F_2$	1.579(2)	
$Co\text{-}C_3$	2.278(2)				
			$C_{m1}\text{-}H_{11}$	0.99(8)	
$C_1\text{-}C_1'$	1.403(5)		$C_{m1}\text{-}H_{12}$	0.68(5)	
$C_1\text{-}C_2$	1.407(4)	1.398(5,7,13)	$C_{m1}\text{-}H_{13}$	0.87(6)	
$C_2\text{-}C_3$	1.398(4)		$C_{m2}\text{-}H_{21}$	1.11(7)	0.93(7,13,26)
$C_3\text{-}C_3'$	1.385(6)		$C_{m2}\text{-}H_{22}$	0.90(7)	
			$C_{m2}\text{-}H_{23}$	0.78(7)	
$C_1\text{-}C_{m1}$	1.511(4)		$C_{m3}\text{-}H_{31}$	0.86(5)	
$C_2\text{-}C_{m2}$	1.520(5)	1.519(5,5,8)	$C_{m3}\text{-}H_{32}$	1.19(7)	
$C_3\text{-}C_{m3}$	1.526(5)		$C_{m3}\text{-}H_{33}$	1.01(6)	
		Bond Angles (deg)			
C_1CoC_1'	36.6(1)		$C_1'C_1C_2$	119.6(2)	
C_1CoC_2	36.5(1)		$C_1C_2C_3$	120.2(2)	
C_2CoC_3	35.9(1)	36.1(1,4,7)	$C_2C_3C_3'$	120.2(2)	
C_3CoC_3'	35.4(2)		$C_1C_1C_{m1}$	118.9(4)	
			$C_2C_1C_{m1}$	121.5(4)	120.0(4,7,15)
C_1CoC_3'	76.8(1)	76.6(1,2,2)	$C_1C_2C_{m2}$	118.9(5)	
C_2CoC_2	76.4(1)		$C_3C_2C_{m2}$	120.9(5)	
			$C_2C_3C_{m3}$	119.4(5)	
C_1CoC_3''	103.2(1)		$C_3C_3C_{m3}$	120.3(4)	
C_2CoC_2''	103.6(1)				
			$C_1C_{m1}H_{11}$	90(3)	
C_1CoC_2''	114.7(1)		$C_1C_{m1}H_{12}$	121(5)	
C_1CoC_3'''	114.8(1)	115.1(1,4,6)	$C_1C_{m1}H_{13}$	110(4)	
C_2CoC_3''	115.7(1)		$H_{11}C_{m1}H_{12}$	88(5)	
			$H_{11}C_{m1}H_{13}$	120(5)	
C_1CoC_1''	143.5(1)		$H_{12}C_{m1}H_{13}$	121(6)	
C_1CoC_2'''	143.5(1)	143.9(1,4,7)	$C_2C_{m2}H_{21}$	96(3)	
C_2CoC_3'''	144.1(1)		$C_2C_{m2}H_{22}$	117(4)	
C_3CoC_3''	144.6(2)		$C_2C_{m2}H_{23}$	112(4)	109(5,7,21)
			$H_{21}C_{m2}H_{22}$	110(5)	
F_1PF_2	90.3(1)		$H_{21}C_{m2}H_{23}$	108(5)	
F_1PF_2''	89.7(1)	89.7(1,6,12)	$H_{22}C_{m2}H_{23}$	113(6)	
F_2PF_2'	90.3(1)		$C_3C_{m3}H_{31}$	111(3)	
F_2PF_2''	88.5(1)		$C_3C_{m3}H_{32}$	111(3)	
			$C_3C_{m3}H_{33}$	98(4)	
F_1PF_1''	180.0[d]		$H_{31}C_{m3}H_{32}$	113(5)	
F_2PF_1'''	180.0[d]		$H_{31}C_{m3}H_{33}$	111(5)	
			$H_{32}C_{m3}H_{33}$	111(5)	

[a] Figures in parentheses following an individual entry are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Table I, Figure 1, and the scheme described in the text. [c] See ref 19. [d] These are symmetry-required values and are listed without an estimated standard deviation.

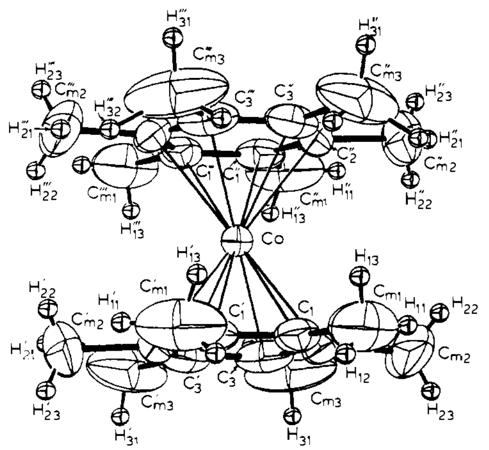


Figure 1. ORTEP drawing of the $[\eta^6\text{-}C_6(CH_3)_6]_2Co^+$ cation as observed in single crystals of its PF_6^- salt. All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density; hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity. The cobalt ion occupies a twofold position of C_{2h}-$2/m$ symmetry in the lattice. The notation scheme is described in the text.

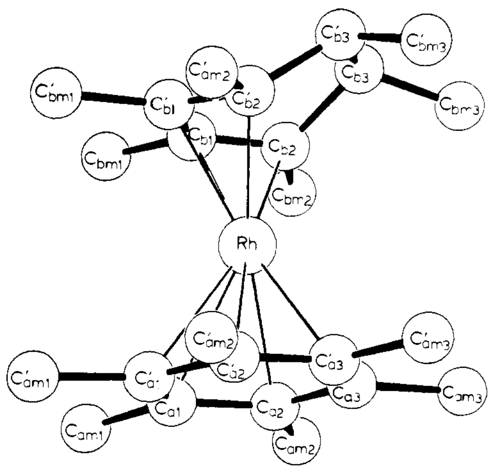


Figure 2. Perspective drawing (adapted from an ORTEP plot) of the nonhydrogen atoms for the $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+$ cation as observed in single crystals of its PF_6^- salt. All atoms are represented by arbitrarily sized open circles which are in no way representative of their true thermal motion. The rhodium ion occupies a fourfold position of C_s-m symmetry in the lattice. The notation scheme is described in the text.

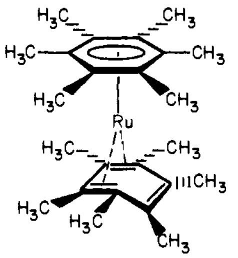
Table VI. Bond Lengths and Angles in Crystalline {(η^6-$C_6(CH_3)_6$)Rh(η^4-$C_6H_2(CH_3)_6$}$^+${PF_6}$^-$ (**2**)

type[b]	value	av[c]	type[b]	value	av[c]
		Bond Lengths (Å)			
Rh-C_{a1}	2.316(7)		C_{b2}-C_{b3}	1.49(2)	
Rh-C_{a2}	2.308(8)	2.301(7,15,23)			
Rh-C_{a3}	2.278(7)		C_{b3}-C_{b3}'	1.45(3)	
Rh-C_{b1}	2.095(10)	2.117(10,22,22)	C_{a1}-C_{am1}	1.54(1)	
Rh-C_{b2}	2.138(10)		C_{a2}-C_{am2}	1.52(1)	
			C_{a3}-C_{am3}	1.55(1)	1.53(2,2,3)
Rh···C_{b3}	2.99(1)		C_{b1}-C_{bm1}	1.50(2)	
			C_{b2}-C_{bm2}	1.52(2)	
C_{a1}-C_{a1}'	1.39(2)				
C_{a1}-C_{a2}	1.42(1)	1.38(1,3,4)	C_{b3}-C_{bm3}	1.47(2)	
C_{a2}-C_{a3}	1.36(1)				
C_{a3}-C_{a3}'	1.34(1)		P-F_1	1.49(1)	
			P-F_2	1.51(1)	1.52(1,2,3)
C_{b1}-C_{b1}'	1.45(3)		P-F_3	1.55(1)	
			P-F_4	1.53(1)	
C_{b1}-C_{b2}	1.28(2)				
		Bond Angles (deg)			
$C_{a1}RhC_{a1}'$	35.0(5)		$C_{a1}'C_{a1}C_{a2}$	118.6(6)	
$C_{a1}RhC_{a2}$	35.7(3)		$C_{a1}C_{a2}C_{a3}$	120.2(8)	
$C_{a2}RhC_{a3}$	34.6(3)	35.0(4,4,8)	$C_{a2}C_{a3}C_{a3}'$	121.2(6)	
$C_{a3}RhC_{a3}'$	34.2(5)		$C_{a1}'C_{a1}C_{am1}$	120.4(9)	
$C_{b1}RhC_{b2}$	35.3(5)		$C_{a2}C_{a1}C_{am1}$	121.0(12)	120.0(10,9,14)
			$C_{a1}C_{a2}C_{am2}$	118.8(14)	
$C_{b1}RhC_{b1}'$	40.4(9)		$C_{a3}C_{a2}C_{am2}$	120.9(14)	
			$C_{a2}C_{a3}C_{am3}$	118.6(12)	
$C_{a1}RhC_{a3}$	63.4(3)		$C_{a3}'C_{a3}C_{am3}$	120.2(9)	
$C_{a1}RhC_{a2}'$	63.1(4)	62.8(4,6,10)			
$C_{a2}RhC_{a3}'$	61.8(4)		$C_{b1}'C_{b1}C_{b2}$	114.7(9)	
$C_{b1}RhC_{b2}'$	65.8(5)		$C_{b1}C_{b2}C_{b3}$	119.9(11)	
$C_{a1}RhC_{a3}'$	74.2(3)		$C_{b2}C_{b3}C_{b3}'$	111.1(7)	
$C_{a2}RhC_{a2}'$	73.2(4)	72.7(5,5,5)			
$C_{b2}RhC_{b2}'$	72.2(5)		$C_{b1}'C_{b1}C_{bm1}$	118.6(16)	
			$C_{b2}C_{b1}C_{bm1}$	126.6(21)	
$C_{a1}RhC_{b1}$	111.3(3)		$C_{b1}C_{b2}C_{bm2}$	107.7(25)	
			$C_{b3}C_{b2}C_{bm2}$	121.5(20)	
$C_{a2}RhC_{b2}$	106.5(5)		$C_{b2}C_{b3}C_{bm3}$	107.4(21)	
			$C_{b3}'C_{b3}C_{bm3}$	119.0(16)	
$C_{a3}RhC_{b2}$	112.3(5)				
			F_1PF_2	178.1(9)	178.8(8,7,7)
$C_{a1}RhC_{b2}$	122.4(4)	120.6(5,18,18)	F_3PF_4'	179.5(7)	
$C_{a2}RhC_{b1}$	118.8(5)				
			F_1PF_3	90.6(6)	
$C_{a3}RhC_{b1}$	141.9(6)		F_1PF_4	88.9(5)	
			F_2PF_3	90.8(6)	
$C_{a3}RhC_{b2}'$	136.5(6)		F_2PF_4	89.7(7)	89.5(6,20,42)
			F_3PF_3'	86.5(6)	
$C_{a1}RhC_{b2}'$	152.8(5)	153.0(6,3,3)	F_3PF_4	93.7(4)	
$C_{a2}RhC_{b1}'$	153.3(6)		F_4PF_4'	86.1(7)	
$C_{a2}RhC_{b2}'$	170.4(6)	171.0(5,6,6)			
$C_{a3}RhC_{b1}$	171.6(4)				

[a] Figures in parentheses following an individual entry are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Table II, Figure 2, and the scheme described in the text. [c] See ref 19.

Waals value.[26] The 1.398 (5, 7, 13, 4) Å[19] average value for the ring bond lengths clearly indicates the near equivalence of all six ring C-C bonds and is nearly identical with the generally accepted value for these bonds in uncomplexed benzene; the 1.519 (5, 5, 8, 3) Å[19] average length for the ring-to-methyl C-C bond is essentially the value obtained by summing the single-bond radii of 0.743[27] and 0.772 Å[28] for sp^2- and sp^3-hybridized carbon, respectively. An average C-H bond length of 0.93 (7, 13, 26, 9) Å[19] for the substituent methyl groups in **1** is the expected X-ray value for this bond and is in excellent agreement with those determined by high-precision X-ray studies[29] of other compounds; the average value of 109 (5, 7, 21, 18)° for the C-C_m-H and H-C_m-H angles is essentially the idealized tetrahedral value. While there are several intraligand H···H contacts which are significantly shorter than the 2.40 Å van der Waals value,[26] there is no seriously short nonbonded contact in **1**.

Structural features of the [η^6-$C_6(CH_3)_6$]Rh[η^4-$C_6H_2(CH_3)_6$]$^+$ cation of **2** are very similar to those established in the isoelectronic and neutral arene-Ru-diene complexes [η^6-$C_6(CH_3)_6$]Ru(η^4-C_8H_8)[30] and [η^6-C_6H_6]Ru(η^4-1,5-C_8H_{12}).[31] The only significant structural differences between **2** and neutral [η^6-$C_6(CH_3)_6$]Ru[η^4-$C_6(CH_3)_6$][9] (**5**) are the necessary ones at the C_{b3} and C_{b3}' centers. The C_{b3}-C_{b3}' bond in **2** is 0.12 Å longer than its unsaturated analogue in **5**, and the C_{b3} carbon atoms in **2** are clearly sp^3 hybridized with the hydrogen atoms on the side of the hexamethylcyclohexadiene ring away from rhodium. In the rhodium complex, the average diene Rh-C bond length is slightly shorter (av = 0.02 Å) and the average hexamethylbenzene C-Rh bond length is ~0.05



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Å longer than those established for similar bonds in the three isoelectronic neutral ruthenium complexes. Although small, these differences in Rh-C and Ru-C bond distances are significant and probably have an electronic origin (see below).

The hexamethylbenzene methyl carbon atoms are displaced by 0.02-0.15 Å from the ring mean plane away from the rhodium atom in a manner similar to that for the η^6-bonded hexamethylbenzene ligand in **5**. In both structures, the same methyl carbon atom has the largest displacement (carbon atom labeled C_{am2} in **2**). The separation of the Rh atom from the hexamethylbenzene ring mean plane[32] is 1.84 Å, and from the mean plane of the bonded hexamethylcyclohexadiene ring atoms,[33a] 1.72 Å. This latter four-ring atom (C_{b1}, C_{b2}, C_{b1}' and C_{b2}') grouping is within 4.7° of being parallel to the hexamethylbenzene ring mean plane.[33a,34] Methyl carbon atoms C_{bm1} and C_{bm2} in **2** are displaced from this four-atom mean plane toward Rh by 0.04 and 0.22 Å, respectively, in a manner similar to that observed in the η^4-hexamethylbenzene ligand in **5**. The short[35] 3.48 (2) Å inter-ring $C_{am2}\cdots C_{bm2}$ contact could be responsible for the ~0.05-Å elongation (relative to analogous ruthenium complexes) of the hexamethylbenzene C-Rh bonds, but this slight displacement of the rhodium atom from the arene ligand toward the diene more probably has an electronic origin. There is a folding of the hexamethylcyclohexadiene ring by 40.0° along the $C_{b2}\cdots C_{b2}'$ vector, and a dihedral angle of 54.4° between the mean plane[33b] through C_{b2}, C_{b3}, C_{b2}', and C_{b3}' and the plane[33c] containing C_{b3}, C_{bm3}, C_{b3}', and C_{bm3}'. No nonbonded contact significantly less than the corresponding van der Waals[26] value is evident in this structure.

As the thermal parameters in Table IV indicate, the ligand atoms in **2** are all highly anisotropic. Presumably this high degree of anisotropy is a reflection of the η^4-bonded hexamethylcyclohexadiene ligand having slightly different conformations from molecule to molecule. This would produce a slight disordering of the cation (and particularly the hexamethylcyclohexadiene ligand) across the crystallographic mirror plane. Fortunately, however, the reduced precision introduced by such perturbations did not prevent an accurate characterization of the most significant stereochemical feature of this rhodium complex: the exo stereochemistry of the two hydrogen atoms at the reduced carbon sites of the cyclohexadiene ring. Clearly the reduction of $[C_6(CH_3)_6]_2Rh^{2+}$ with zinc and acid to give $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+$ occurs with hydrogenation of the one aromatic C-C bond. This accompanying hydrogenation process cannot comprise hydrogen addition to the rhodium center followed by transfer to the ligand carbon centers because this would yield the endo isomer. Apparently, the hydrogenation process occurs at the zinc metal surface—a process that should yield the exo isomer. The crystallographic analysis was, of course, performed with a single crystal and the question may be raised as to whether the crystal used was unique, was representative of a minority or majority product, or was representative of the only product. Microscopically, the crystals appeared similar and the crystal used appeared to be representative. Other crystals of **2** were also examined in partial or total diffraction experiments and proved to be identical. Lattice constants and a partial set of diffracted intensities were measured for several of these crystals and a complete structural analysis was performed for one. Hence the established stereochemistry of the initial single crystal of **2** appears to be that of the majority (or all) of the crystalline product. More significantly, the ^{13}C and $^{13}C\{^1H\}$ NMR spectra were fully consistent (see assignments and details in the Experimental Section) with the crystallographically determined structure; there were only trace, unexplained resonances that might be ascribed to other stereoisomers. However, the ^1H NMR spectra of the rhodium complex varied slightly from one preparation to another. There clearly were minor intensity resonances that might have been representative of other stereoisomers or even other structural or compositional isomers. Because of accidental degeneracies and because the resonances for the two unique aliphatic C-H protons in the cyclohexadiene ligand could not be unambiguously assigned, no spectral assignments were made for the ^1H spectrum.

Catalytic Chemistry. Unlike $[\eta^6\text{-}C_6(CH_3)_6]Ru[\eta^4\text{-}C_6(CH_3)_6]$, the cobalt and rhodium complexes, **1** and **2**, respectively, were not detectably active catalysts for the hydrogenation of aromatic hydrocarbons.[2] Both underwent reduction and decomposition on exposure to hydrogen; rates were low at 35-60 °C but the rhodium complex rapidly formed rhodium metal at temperatures in the 75-100 °C range.

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Supplementary Material Available: A listing of anisotropic thermal parameters for nonhydrogen atoms of $[\eta^6\text{-}C_6(CH_3)_6]_2Co^+PF_6^-$ (**1**) (Table III) and nonhydrogen atoms of $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+PF_6^-$ (**2**) (Table IV) and observed and calculated structure factors from the respective final cycles of least-squares refinement (18 pages). Ordering information is given on any current masthead page.

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(33) Least-squares mean plane defined by (a) $-0.528X + 0.000Y + 0.849Z = 1.699$. (b) $0.140X + 0.000Y + 0.990Z = 3.218$. (c) $-0.724X + 0.000Y + 0.690Z = 2.032$.

(34) The angle subtended at rhodium by the centers of gravity for the hexamethylbenzene ring and the four η^4-bonded hexamethylcyclohexadiene atoms is 171°.

(35) The van der Waals diameter[26] for a methyl group is 4.00 Å.

Crystal Structure and Properties of Tetrathiafulvalenium Triiodide

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Abstract: Slow cooling of a hot acetonitrile solution of tetrathiafulvalene (TTF) and iodine yields a mixture of crystalline products including monoclinic crystals of high iodine content: TTF·I_3. A single-crystal X-ray structure analysis has been carried out on these crystals of symmetry $P2_1/n$ with four molecules per unit cell. The cell parameters are $a = 9.411$ (2) Å, $b = 18.787$ (3) Å, $c = 7.771$ (1) Å, $\beta = 103.2$ (1)°, and $V = 1374$ (1) Å^3. The structure consists of integrated stacks along the ⟨102⟩ axis with TTF^+ dimers interspersed between pairs of triiodide ions. Consistent with the structural results, single-crystal measurements indicate that this material exhibits high electrical resistivity with $\sigma_{RT} < 9 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$.

Introduction

Considerable attention in recent years has been focused on the chemistry and physics of materials which exhibit highly anisotropic electrical, optical, and magnetic properties.[3] Of particular interest have been organic and metal-organic solids which exhibit metal-like charge transport along one crystalline axis. The discovery of the "organic metal" tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) prompted a number of studies of TTF as an electron donor and precursor for other highly conductive solids. Halogen oxidation, for example, yields a variety of charge-transfer salts.[4]

One direction of activity in our laboratories and others has involved the iodine-containing TTF salts, TTF·I_x. The stoichiometries prepared to date range from $x = 0.71$ to 3.0, but detailed single-crystal characterization has been restricted to a limited number of low iodine phases. The most conductive of these is TTF·$I_{0.71}$[4a,b] with a room temperature conductivity of ca. 300 Ω^{-1} cm^{-1} along the needle axis. This material possesses an ordered, modulated crystal structure containing stacks of eclipsed, partially oxidized TTF molecules[4h] and parallel chains of I^- ions.[4h,5] Two additional phases of intermediate stoichiometry with $x \sim 2.0$ have been isolated which vary only in the degree of order-disorder. The first TTF·I_2 structure (space group *Immm*) contains disordered chains of triiodide ions and disordered TTF stacks ($(TTF^{0.7+})(I_3^-)_{0.7}$).[4c,6,7] Preliminary X-ray crystallographic investigations suggest that the second TTF·I_2 phase (space group *Fddd*) is a superstructure of the first TTF·I_2 phase with ordered TTF stacks, but again with disordered triiodide ions.[6,7] Full expositions of the TTF·I_2 structures, spectroscopy, and transport properties are in preparation. In view of the accumulating knowledge on the above TTF-iodine complexes, it would clearly be of interest to investigate, for comparative purposes, the phase of greatest iodine content. This would provide information on how the crystal structure,[8] degree of partial oxidation, and transport properties adjust to the increased dopant level. Such information might also shed light on how large amounts of iodine are sometimes accommodated in metal glyoximate[9] and phthalocyanine[10] lattices. Here, again, phases with very high iodine content have been isolated.[9,10] We report here the synthesis, X-ray diffraction structure determination, and single-crystal conductivity of the high-iodine TTF phase, TTF·I_3.

Experimental Section

Synthesis of TTF·I_3. Tetrathiafulvalenium triiodide was prepared under a nitrogen atmosphere by adding dropwise a solution of 80 mg (0.39 mmol) of TTF (Aldrich Chemical Co.) in 10 mL of acetonitrile (freshly distilled from P_2O_5 under nitrogen) to a stirring solution of 120 mg (0.47 mmol) of triply sublimed I_2 in 10 mL of freshly distilled acetonitrile. Sufficient acetonitrile was added until the total volume was 50 mL. The solution was heated to 50 °C with constant stirring until all of the solid present dissolved. Upon slow cooling to room temperature, a mixture of crystals of TTF·$I_{0.71}$, TTF·I_2, and, in trace amounts, TTF·I_3 resulted. The product was then washed with freshly distilled benzene and dried with a stream of nitrogen. The morphology of the TTF·I_3 crystals is sufficiently different from the other phases

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