mixture was stirred until the solvent had evaporated. The residue was removed from the glovebox and dissolved in hexane, and the solution was filtered to remove the salts. Removal of the hexane left a solid that was analyzed further by mass and NMR spectroscopy. The addition of the ^{2}H atom to a methylene carbon was confirmed by mass spectroscopy (m/z = 658 ($N_3P_3(CH_2SiMe_3)_5CHDSiMe_3$)) and ^{2}H NMR (THF, C_6D_6 lock; 2.6 ppm, d, J_{PCD} = 57.3 Hz).

Synthesis of *gem*-$N_3P_3(CH_2SiMe_3)_4F_2$ (3). Hexafluorocyclotriphosphazene (1; 2.0 g, 8.0 mmol) was dissolved in dry THF, and the solution was warmed to 40 °C. ((Trimethylsilyl)methyl)lithium (1.0 M solution in pentane, 35.0 mmol, 4.1 equiv) was added slowly to the stirred solution of 1. The reaction was monitored by ^{31}P NMR spectroscopy until no further change was detected. The pentane was removed under reduced pressure, and the remaining solution was poured into water. The solution was extracted twice with CH_2Cl_2, and the organic layers were combined and dried over $MgSO_4$. Filtration, followed by solvent removal, produced a light yellow oil. The crude mixture was purified by column chromatography on silica gel and eluted with hexane–CH_2Cl_2 (3:1); isolated yield 2.1 g (51%). ^{1}H NMR ($CDCl_3$): δ = 1.2 ppm (d, PCH_2, $^2J_{PH}$ = 15.4 Hz); δ = 0.03 ppm (s, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ = 27.0 ppm (d, PCH_2, J_{PC} = 84.8 Hz); δ = 0.3 ppm (s, $SiCH_3$). Additional characterization data are listed in Table I.

Synthesis of $N_3P_3(CH_2SiMe_3)_5F$. This reaction was carried out in a manner similar to the preparation of 3. Thus, hexafluorocyclotriphosphazene (1; 2.0 g, 8.0 mmol) was dissolved in dry THF and the solution was warmed to 40 °C. ((Trimethylsilyl)methyl)lithium (1.0 M solution in pentane, 44.0 mmol, 5.1 equiv) was added to the stirred solution of 1. The reaction was terminated when no further change was detected by ^{31}P NMR spectroscopy. After solvent removal and extraction with CH_2Cl_2, the crude product was found to contain a mixture of tetra-, penta-, and hexasubstituted trimers, as determined by GC retention times. The mixture was purified by column chromatography on silica gel and was eluted with hexane–CH_2Cl_2 (3:1); isolated yield 1.2 g (21%) of $N_3P_3(CH_2SiMe_3)_5F$. ^{1}H NMR ($CDCl_3$): δ = 1.1 ppm (d, PCH_2, $^2J_{PH}$ = 13.5 Hz); δ = 0.1 ppm (s, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ = 27.5 ppm (d, PCH_2, J_{PC} = 81.5 Hz); δ = 0.6 ppm (s, $SiCH_3$). See Table I for additional characterization data.

Synthesis of $(NPMe_2)_3$ by C–Si Bond Cleavage.[34] Crude 5 (2.0 g, 0.30 mmol) was placed in a sublimator and was mixed with $^nBu_4N^+F^-\cdot 3H_2O$. The solid mixture was heated under vacuum (0.2 mmHg). $(NPMe_2)_3$ had sublimed onto the cold finger after 4–6 h. The sublimation was continued for an additional 6 h, and the contents of the sublimator were stirred occasionally. $(NPMe_2)_3$ was collected from the cold finger and was recrystallized from hot heptane to remove traces of $^nBu_4N^+F^-$ that had cosublimed with the product: isolated yield 0.41 g (60% yield); mp 188–190 °C. ^{1}H NMR ($CDCl_3$): δ = 1.4 ppm (d, PCH_3, $^2J_{PH}$ = 12.3 Hz). ^{13}C NMR ($CDCl_3$): δ = 23.4 ppm (d, PCH_3, J_{PC} = 94.1 Hz). ^{31}P NMR ($CDCl_3$): δ = 24.4 ppm (s, $^2J_{PH}$ = 12.3 Hz).

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Supplementary Material Available: Positional parameters (Table VII), general displacement parameter expressions (Table VIII), an ORTEP diagram, including methyl groups (Figure 4), and a table of least-squares planes for 5 (6 pages); a listing of structure factor amplitudes (41 pages). Ordering information is given on any current masthead page.

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[34] C–Si bond cleavage by $^nBu_4N^+F^-$ was also found to be effective when carried out in solution. However, it was found that yields improved significantly if the reaction was carried out in the solid state.

Displacement of Hard Bases from a Soft Center by a Soft Ligand: Reaction of $Ir(CO)(OH)(SO_4)L_2$ (L = PPh_3, $P(p\text{-tolyl})_3$) with CO and the Crystal Structure of $[Ir(CO)_3(PPh_3)_2{}^+][HSO_4{}^-]\cdot{}^1/_3H_2O$

Sherri L. Randall, Jeffrey S. Thompson, Lisa A. Buttrey, Joseph W. Ziller,
Melvyn Rowen Churchill,* and Jim D. Atwood*

Departments of Chemistry, University at Buffalo, State University of New York,
Buffalo, New York 14214, and University of California, Irvine, California 92717

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The iridium(III) complexes $Ir(CO)(OH)(SO_4)L_2$, L = PPh_3, $P(p\text{-tolyl})_3$, have been prepared and shown to react with CO, yielding the iridium(I) species $[Ir(CO)_3L_2{}^+][HSO_4{}^-]$ (L = PPh_3, $P(p\text{-tolyl})_3$) and CO_2. The species $[Ir(CO)_3(PPh_3)_2{}^+][HSO_4{}^-]\cdot{}^1/_3H_2O$ crystallizes in the centrosymmetric rhombohedral space group $R\bar{3}$ [C_{3i}^2; No. 148]. Cell parameters (for the hexagonal setting) are a = 40.938 (7) Å, c = 11.850 (2) Å, V = 17 199 Å^3, and Z =18. Diffraction data (Mo K$\bar{\alpha}$, 2θ = 4.0–45.0°) were collected on a Syntex $P2_1$ diffractometer, and the structure was refined to R_F = 6.1% for all 4772 unique data (R_F = 4.2% for those 3673 data with $|F_o| > 6.0\sigma(|F_o|)$).

In many respects classical coordination chemistry ("Werner chemistry") and organometallic chemistry have followed divergent paths. Coordination complexes typically contain ligands with oxygen and nitrogen donor atoms surrounding the metal in an octahedral configuration, and the reactivity is dominated by the d-electron configuration of the metal. Organometallic complexes typically contain carbon and phosphorus donor atoms (with π-acceptor capabilities), and the 18-electron rule controls both the number of coordinated ligands and the reactivity. In recent years there has been a growth of interest in organometallic complexes containing oxygen (especially alkoxy) and nitrogen ligands, but these complexes are organometallic in most of their characteristics.[1]

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* To whom correspondence should be addressed at the State University of New York.

Hard ligands that are weakly bound to organometallic centers have been used to provide accessible sites for catalytic activity.[2-8] Chin and co-workers have described the use of *trans*-$Ir(CO)(PPh_3)_2ClO_4$ in several catalytic cycles.[3-5] Since the bidentate ClO_4^- ligand can easily be displaced, the iridium has two accessible coordination sites. Sen and co-workers used weakly solvated metal cations for catalytic reactions.[6,7] Crabtree has also used complexes $IrH_2S_2L_2^+$ (where S is a weakly bound solvent ligand such as THF, CH_3OH, $CH_3C(O)CH_3$, etc.) in olefin hydrogenation and in alkane dehydrogenation reactions.[8]

In addition to the complexes used in catalytic reactions, there have been a few other reports of complexes containing both typical organometallic and typical coordination chemistry ligands.[9-14] Two very interesting examples were recently reported. The species $(\eta^6\text{-}C_6H_6)M(H_2O)_3^{2+}$ (M = Ru, Os), have octahedral coordination of the metal with (formally) three olefinic bonds to the $\eta^6\text{-}C_6H_6$ ligand and three bonds to water.[9] Both the structure and water-exchange rate were reported for these complexes.[9] Complexes of the type $ML_2\ (\text{solvent})_2^{2+}$ (M = Pd, Pt; L_2 = dppe, $2PMe_2Ph$, $2PPh_3$; solvent = py, DMSO, acetone) have also been reported.[10] The solvent molecules could readily be displaced even by such weak ligands as ClO_4^-. Reactions of HX (X = BF_4^-, $C_4F_9SO_3^-$) with *trans*-$Ir(N_2)(PPh_3)_2Cl$ gave six-coordinate complexes, $Ir(H)(X)(N_2)(PPh_3)_2Cl$.[11] Both the X^- and the N_2 ligand were weakly coordinated and easily displaced by ligands such as H_2O or $CH_3C(O)CH_3$.[11] Sulfonato ligands have also been used as ligands weakly coordinating to iridium.[12,13] The very interesting Re(VII) complexes, $RReO_3$ (R = Me, Cp*), have also been prepared.[14]

Our oxidation chemistry from the dioxygen complex $MeIr(O)_2(CO)L_2$[15,16] provides a route to Ir(III) complexes that contain both hard and soft ligands.

$$MeIr(O_2)(CO)L_2 + CO \rightarrow MeIr(CO_3)(CO)L_2 \quad (1)$$

$$MeIr(O_2)(CO)L_2 + SO_2 \rightarrow MeIr(SO_4)(CO)L_2 \quad (2)$$

The iridium(III) centers are six-coordinate, with approximately octahedral coordination geometry, and contain bidentate CO_3^{2-} and SO_4^{2-} ligands. Octahedral coordination complexes of d^6 iridium(III) are usually quite inert to substitution, but these complexes (which contain both hard and soft ligands) appear to be relatively labile. The alkoxy analogues provide a further set of complexes which contain a hard ligand that may readily be displaced.[17]

$$MeOIr(Me)(I)(CO)L_2 + {}^*CO \rightarrow MeO^*C(O)Ir(Me)(I)(CO)L_2 \quad (3)$$

$$MeOIr(Me)(I)(CO)L_2 + I^- \rightarrow Ir(Me)(I)_2(CO)L_2 + OMe^- \quad (4)$$

The reactivity of complexes containing mixtures of hard and soft ligands is largely unexplored. We here report the preparation and reactivity of $Ir(CO)(OH)(SO_4)(PPh_3)_2$.

Experimental Section

$IrCl_3{\cdot}xH_2O$ was borrowed from Johnson Matthey. Triphenylphosphine and tri-*p*-tolylphosphine were purchased from Strem Chemical Co. SO_2 (anhydrous) and CO (cp grade) were purchased from Matheson. Benzene, toluene, and tetrahydrofuran were all dried by refluxing over CaH_2, distilling onto Na/benzophenone, refluxing over Na/benzophenone, and distilling into an air-free container. The purified solvents were stored in an inert-atmosphere glovebox.

Elemental analysis was performed by Oneida Research Services, Inc. Infrared spectra of KBr pellets and solutions were measured on a Beckman 4240 infrared spectrophotometer or a Mattson Polaris FTIR instrument in the region 2200–750 cm^{-1}. *trans*-$Ir(CO)(OMe)(PPh_3)_2$ and $Ir(CO)(OMe)(SO_4)(PPh_3)_2$ were prepared as described previously.[17]

The hydroxy complex $Ir(CO)(OH)(SO_4)(PPh_3)_2$ can be prepared by two procedures. (A) A solution of *trans*-$Ir(CO)(OMe)(PPh_3)_2$ in THF was prepared in a Schlenk flask inside an inert-atmosphere glovebox, removed from the box, and attached to a Schlenk line. Deareated water (6 mL) was added and the solution stirred under N_2 for 1 h. The volatile components were removed under vacuum. Acetone was added and also removed by vacuum, resulting in a bright yellow solid. The IR spectrum (KBr) showed ν_{O-H} at 3590 (w, br) and ν_{CO} at 1918 (s) cm^{-1}.[18] This complex, *trans*-$Ir(CO)(OH)(PPh_3)_2$, was then treated with SO_2 in toluene solution for 1 h before adding O_2. The mixture was stirred under O_2 for 14 h, resulting in $Ir(CO)(OH)(SO_4)(PPh_3)_2$. The product was isolated by removal of the volatile components and could be purified by precipitation from a THF solution with hexane. (B) A solution of $Ir(CO)(OMe)(SO_4)(PPh_3)_2$[17] in THF was stirred with 1.5 mL of deareated H_2O under a N_2 atmosphere for 1 h. The volatile materials were removed by vacuum; acetone was added and also removed by vacuum. This resulted in a yellow powder in 85% yield based on $MeOIr(CO)(PPh_3)_2$. The infrared spectrum (KBr) (ν_{O-H} = 3400 (m, br), ν_{CO} = 2040 (vs) cm^{-1} and SO_4^{2-} bands typical for bidendate coordination) and microanalysis support the formulation (Anal. Calc: C, 51.8; H, 3.6; S, 3.7. Found: C, 50.5; H, 4.3; S, 3.8).

The P(*p*-tolyl)$_3$ analogue was prepared by a procedure similar to A through *trans*-$HOIr(CO)(P(p\text{-tolyl})_3)_2$ (ν_{CO} = 1925 cm^{-1} in C_6H_6; ^1H NMR (C_6D_6) 1.9 (s), 1.12 (t), ~7 (m) ppm; ^{31}P NMR 24.9 (s) ppm). This complex was reacted with SO_2 for 1 h and then with O_2 overnight. The toluene was removed by vacuum and the product taken into an inert-atmosphere glovebox. It was recrystallized from benzene/hexane. The complex, $Ir(CO)(OH)(SO_4)(P(p\text{-tolyl})_3)_2$, was characterized by infrared (2040 cm^{-1}) and NMR ($CDCl_3$: ^1H 6.6–8(m), 2.3 (s) ppm; ^{31}P 29.8 (s) ppm) analysis.

Reaction of $Ir(CO)(OH)(SO_4)(PPh_3)_2$ with CO. The hydroxy sulfate complex was dissolved in THF in an inert-atmosphere glovebox. An infrared spectrum in the carbonyl stretching region showed only the ν_{CO} at 2041 cm^{-1}. The solution was removed from the glovebox and placed under CO at room temperature. Infrared spectra taken over 2 weeks showed only the loss of the absorption at 2041 and growth of a CO_2 absorption band at 2330 cm^{-1}.[19] An air-stable white precipitate also formed during the reaction. After 2 weeks this precipitate was collected.

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Table I. Structure Determination Summary

	Crystal Data
mol formula	$[Ir(CO)_3(PPh_3)_2^+][HSO_4^-]\cdot{}^1/_3H_2O$
emp formula	$C_{39}H_{31.67}O_{7.33}P_2SIr$
cryst size, mm	0.04 × 0.11 × 0.17
cryst syst	rhombohedral (hexagonal setting)
space group	$R\bar{3}$
unit cell dimens	
a, Å	40.938 (7)
b, Å	40.938 (7)
c, Å	11.850 (2)
V, Å^3	17 199 (5)
Z	18
fw	903.8
D(calc), Mg/m^3	1.569
abs coeff, mm^{-1}	3.660
F(000)	8034
	Data Collection
diffractometer syst	Syntex $P2_1$
λ(Mo Kα radiation), Å	0.710 73
T, K	296
monochromator	highly oriented graphite cryst
2θ range, deg	4.0–45.0
scan type	θ–2θ
scan speed, deg/min	constant; 4.00 (in 2θ)
scan range (2θ), deg	2.00 (plus Kα separation)
standard reflns	3 measd every 97 reflns
index ranges	$-41 \le h \le 41$, $0 \le k \le 41$, $0 \le l \le 12$
no. of rflns collcd	8152
no. of ind rflns	4772 (R_{int} = 2.25%); ($\lvert F_o\rvert$) > 0)
no. of obsd reflns	4772 ($\lvert F_o\rvert > 0.0\sigma(\lvert F_o\rvert)$)
abs corr	semiempirical (ψ-scan method)
min/max transm	0.8314/0.9668

The white powder was recrystallized by allowing pentane to slowly diffuse into a saturated CH_2Cl_2 solution, resulting in colorless crystals. The IR spectrum (KBr) of the crystals in the carbonyl stretching region showed bands (in cm^{-1}) at 2074 (w), 2020 (vs), and 1995 (vs), identical with that previously observed for $[Ir(CO)_3(PPh_3)_2^+][ClO_4^-]$.[20] A single-crystal X-ray diffraction study of this product, described below, shows it to be $[Ir(CO)_3(PPh_3)_2^+][HSO_4^-]\cdot{}^1/_3H_2O$. A similar procedure for reaction of $Ir(CO)(OH)(SO_4)(P(p\text{-}tolyl)_3)_2$ resulted in $Ir(CO)_3(P(p\text{-}tolyl)_3)_2^+$, as shown by a KBr infrared spectrum, 2079, 2019, and 1998 cm^{-1}.

Collection of X-ray Diffraction Data. A colorless crystal of approximate dimensions 0.04 × 0.11 × 0.17 mm was inserted into a thin-walled glass capillary under an inert (Ar) atmosphere. It was then mounted and accurately aligned (with its extended direction close to coincident with the ϕ axis) on the Syntex $P2_1$ automated four-circle diffractometer at the University at Buffalo-SUNY. Laue symmetry determination of the crystal class, the unit cell parameters and the crystal's orientation matrix were carried out by previously described techniques.[21] Intensity data were collected at room temperature (23 °C) by using the θ–2θ scan technique with Mo K$\bar{\alpha}$ radiation under the conditions given in Table I. The following points should be noted: (1) The crystal belongs to the rhombohedral subset of the trigonal/hexagonal crystal system. It possesses only $\bar{3}$ (S_6 or C_{3i}) diffraction symmetry and not $\bar{3}m$ (D_{3d}) symmetry. (2) The 8152 data were corrected for absorption and for Lorentz and polarization effects and were merged ($R(I)$ = 2.3%) to yield 4772 unique reflections with $\lvert F_o\rvert > 0$. (3) We elected to use hexagonal axes of the triple cell rather than the primitive rhombohedral setting. (4) The systematic absences $hk(i)l$ for $-h{+}k{+}l \neq 3n$ are compatible only with the centrosymmetric rhombohedral space group $R\bar{3}$ [C_{3i}^2; No. 148][22a] or its noncentrosymmetric subgroup $R3$ [C_3^4; No. 146].[22b] Intensity statistics strongly favored the centrosymmetric space group $R\bar{3}$; this choice was confirmed by the successful solution of the structure in this higher symmetry space group.

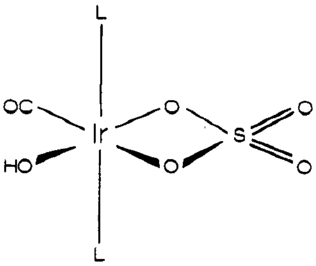

Figure 1. Suggested structure of $Ir(CO)(OH)(SO_4)(PPh_3)_2$.

Solution and Refinement of the Crystal Structure. All crystallographic calculations were carried out by using either the UCI-modified version of the UCLA Crystallographic Computing Package[23] or the SHELXTL PLUS program set.[24] The analytical scattering factors for neutral atoms were used throughout the analysis;[25] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[25] were included. The quantity minimized during least-squares analysis was $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, where $w = [\sigma^2(\lvert F_o\rvert) + 0.0008\lvert F_o\rvert^2]^{-1}$.

The positions of the iridium and phosphorus atoms were located from an automatic Patterson synthesis (SHELXTL PLUS). The remaining non-hydrogen atoms were located from a series of difference-Fourier syntheses. Hydrogen atoms of the PPh_3 ligands were included by using a riding model with d(C–H) = 0.96 Å[26] and U(iso) = 0.08 Å^2. At this point we ascertained that the crystal contained $[Ir(CO)_3(PPh_3)_2^+]$ cations and a tetrahedral anion (SO_4^{2-} or some derivative thereof), each in general positions, and a species containing an oxygen atom, lying on the crystallographic 3-fold axis. The only stoichiometry consistent with overall charge neutrality of the crystal is $[Ir(CO)_3(PPh_3)_2^+][HSO_4^-]\cdot{}^1/_3H_2O$ (see Discussion). Full-matrix least-squares refinement of positional and thermal parameters led to convergence ($\Delta/\sigma \le 0.001$ for all parameters) with R_F = 6.1%, R_{wF} = 6.6%, and GOF = 1.51 for 454 variables refined against all 4772 data (R_F = 5.1% and R_{wF} = 6.5% for those 4203 data with $\lvert F_o\rvert > 3.0\ \sigma(\lvert F_o\rvert)$; R_F = 4.2% and R_{wF} = 6.1% for those 3673 data with $\lvert F_o\rvert > 6.0\ \sigma(\lvert F_o\rvert)$).[27]

A final difference-Fourier synthesis showed features only in the range −1.1 to +1.6 e/Å^3. The strongest peaks were either close to the positions of heavy atoms or were on the 3-fold axis (where statistical errors in electron density are enhanced). The locations of hydrogen atoms of the HSO_4^- and H_2O moieties were not determined. Final atomic positions are collected in Table II.

Results and Discussion

The complex $Ir(CO)(OH)(SO_4)(PPh_3)_2$ can be prepared by two different routes from *trans*-$MeOIr(CO)(PPh_3)_2$.

$$\begin{tikzcd}
trans\text{-}MeOIr(CO)(PPh_3)_2 \arrow[r, "H_2O"] \arrow[d, "SO_2/O_2"] & trans\text{-}HOIr(CO)(PPh_3)_2 \arrow[d, "SO_2/O_2"] \\
Ir(CO)(OMe)(SO_4)(PPh_3)_2 \arrow[r, "H_2O"] & Ir(CO)(OH)(SO_4)(PPh_3)_2
\end{tikzcd} \tag{5}$$

The routes differ only in whether the sulfate group (SO_2/O_2) or the hydroxide ligand is placed on the iridium first. $Ir(CO)(OH)(SO_4)(P(p\text{-}tolyl)_3)_2$ was prepared from the reaction of SO_2/O_2 with *trans*-$HOIr(CO)(P(p\text{-}tolyl)_3)_2$. The complexes produced are completely analogous to the methoxy analogue,[17] with an octahedral arrangement of ligands including a bidentate sulfate. The structure suggested, on the basis of the similarity to the methoxy analogue, is shown in Figure 1.

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[27] $R_F = 100\Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$; $R_{wF} = 100[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$; GOF = $[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO - NV)]^{1/2}$, where NO = number of observations and NV = number of variables.

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	y	z	U(eq)[a]
Ir(I)	1083.9 (0.1)	5343.0 (0.1)	3384.5 (0.3)	36.8 (0.2)
P(1)	1081 (1)	5359 (1)	5379 (2)	37 (1)
P(2)	1108 (1)	5366 (1)	1392 (2)	39 (1)
S(1)	196 (1)	3685 (1)	3344 (3)	77 (2)
O(1)	220 (3)	4925 (3)	3331 (8)	95 (6)
O(2)	1428 (3)	4834 (3)	3408 (8)	91 (6)
O(3)	1577 (3)	6199 (3)	3401 (8)	102 (6)
O(4)	535 (3)	3892 (5)	3909 (14)	232 (12)
O(5)	84 (5)	3920 (4)	2821 (13)	212 (14)
O(6)	272 (3)	3455 (3)	2506 (9)	123 (8)
O(7)	−127 (3)	3462 (3)	4125 (9)	120 (7)
C(1)	539 (3)	5085 (3)	3331 (9)	61 (7)
C(2)	1306 (3)	5021 (3)	3398 (9)	54 (6)
C(3)	1389 (4)	5878 (3)	3398 (9)	62 (7)
C(4)	719 (3)	4930 (3)	6033 (8)	44 (5)
C(5)	626 (3)	4578 (3)	5601 (10)	59 (6)
C(6)	357 (3)	4254 (3)	6162 (11)	69 (7)
C(7)	170 (3)	4267 (3)	7106 (10)	65 (7)
C(8)	268 (4)	4618 (3)	7542 (10)	78 (7)
C(9)	539 (3)	4956 (3)	7006 (10)	64 (6)
C(10)	1529 (3)	5454 (3)	6001 (8)	45 (5)
C(11)	1539 (3)	5298 (3)	6998 (10)	70 (7)
C(12)	1879 (4)	5399 (5)	7509 (12)	93 (9)
C(13)	2208 (4)	5649 (4)	7028 (12)	74 (8)
C(14)	2197 (3)	5796 (4)	6012 (12)	75 (7)
C(15)	1864 (3)	5702 (3)	5470 (10)	65 (6)
C(16)	1001 (3)	5726 (3)	5947 (8)	43 (5)
C(17)	1220 (3)	5966 (3)	6768 (10)	63 (6)
C(18)	1126 (5)	6224 (4)	7234 (11)	84 (9)
C(19)	810 (5)	6230 (4)	6881 (13)	87 (9)
C(20)	587 (4)	5989 (4)	6046 (13)	85 (9)
C(21)	683 (3)	5736 (3)	5562 (10)	65 (7)
C(22)	1000 (3)	4920 (3)	709 (8)	42 (5)
C(23)	1201 (4)	4915 (3)	−196 (10)	74 (7)
C(24)	1094 (4)	4578 (3)	−721 (12)	88 (9)
C(25)	806 (4)	4251 (3)	−354 (11)	72 (7)
C(26)	620 (4)	4257 (3)	550 (11)	75 (7)
C(27)	705 (3)	4577 (3)	1104 (10)	74 (7)
C(28)	1575 (3)	5706 (3)	834 (9)	48 (5)
C(29)	1881 (3)	5712 (4)	1266 (12)	92 (8)
C(30)	2232 (4)	5957 (6)	807 (15)	125 (12)
C(31)	2256 (5)	6204 (4)	−44 (16)	115 (10)
C(32)	1951 (4)	6180 (4)	−473 (15)	107 (10)
C(33)	1620 (3)	5939 (3)	−14 (11)	77 (7)
C(34)	791 (3)	5514 (3)	775 (8)	43 (5)
C(35)	791 (3)	5822 (3)	1158 (10)	65 (7)
C(36)	589 (4)	5964 (4)	637 (12)	72 (7)
C(37)	378 (4)	5782 (4)	−276 (11)	79 (8)
C(39)	572 (3)	5335 (3)	−148 (10)	62 (6)
O(8)	3333	6667	4920 (13)	64 (5)

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

Our previous research on complexes of Ir(I) and Ir(III) that contain hard ligands indicated rather facile elimination of the hard ligand from the coordination sphere.[20,28]

$$trans\text{-}\mathrm{Ir(CO)(OMe)(PPh_3)_2} + 2\mathrm{CO} \rightarrow [[\mathrm{Ir(CO)_3(PPh_3)_2^+}][\mathrm{OMe^-}]] \quad (6)$$

$$\mathrm{Ir(CO)(I)(OMe)(Me)(PPh_3)_2} + \mathrm{CO} \rightarrow [[\mathrm{Ir(CO)_2(I)(Me)(PPh_3)_2^+}][\mathrm{OMe^-}]] \quad (7)$$

We were interested in determining whether the hard ligands, OH^- and SO_4^{2-}, could easily be replaced in $Ir(CO)(OH)(SO_4)(PPh_3)_2$. Reaction of $Ir(CO)(OH)(SO_4)L_2$, L = PPh_3 or P(*p*-tolyl)$_3$, with CO at room temperature in THF or toluene resulted in a white precipitate and elimination of CO_2. The IR spectrum (KBr) of the white precipitate, as shown in Figure 2, can be interpreted as a combination of those of $[Ir(CO)_3L_2^+]$, L = PPh_3 or P(*p*-tolyl)$_3$, and $[HSO_4^-]$. However, to confirm this analysis and ascertain any possible coordination mode of HSO_4^-, we have determined the crystal structure of $[Ir(CO)_3(PPh_3)_2^+][HSO_4^-]$. X-ray-quality crystals were grown from slow diffusion of pentane into a saturated solution in CH_2Cl_2. The completed crystal structure also reveals the presence of adventitious water of crystallization (see below).

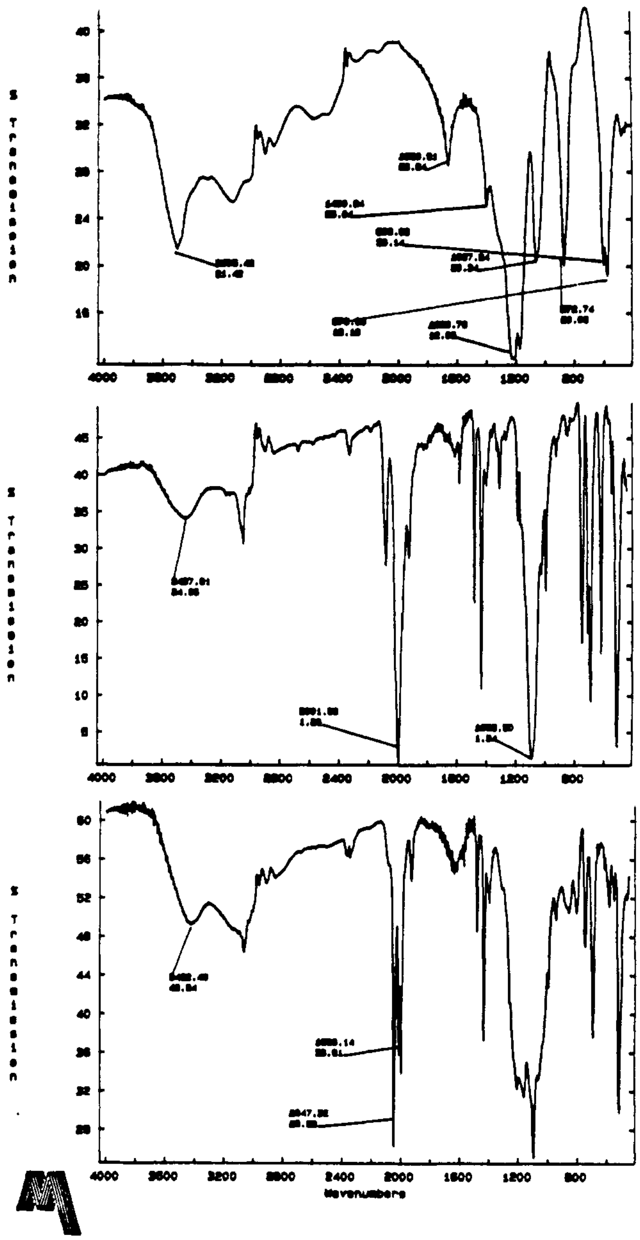

Figure 2. Infrared spectra of $NaHSO_4$ (A), $[Ir(CO)_3(PPh_3)_2^+][ClO_4^-]$ (B), and $[Ir(CO)_3(PPh_3)_2^+][HSO_4^-]$.

Crystal Structure. The X-ray diffraction experiment revealed the presence of three different species in the crystal; the charges (if any) on the species must be inferred from chemical reasoning. These species were as follows: (A) an $[Ir(CO)_3(PPh_3)_2]$ fragment in the 18-fold general position (Wyckoff position *f*);[22a] (B) a slightly distorted tetrahedral species derived from the sulfate ion, in the 18-fold general position *f*; (C) a species based upon a central oxygen atom in a 6-fold special position of C_3 (3) symmetry (at $^1/_3$, $^2/_3$, z; Wyckoff position *c*). The only stoichiometry that yields overall charge neutrality for the crystal is $[Ir(CO)_3(PPh_3)_2^+][HSO_4^-]\cdot{}^1/_3H_2O$. [The charge on the pentacoordinate iridium species must be +1. The sulfate-based species could be SO_4^{2-} (which would require

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(28) Bernard, K. A.; Atwood, J. D. *Organometallics* **1989**, *8*, 795.

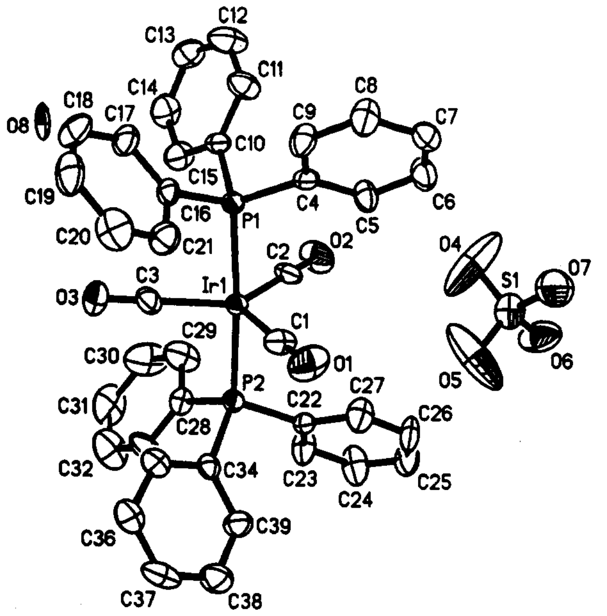

Figure 3. ORTEP-II depiction of the structure of [$Ir(CO)_3(PPh_3)_2^+$][HSO_4^-]·$^1/_3H_2O$ (30% probability ellipsoids; all hydrogen atoms omitted for clarity).

Table III. Interatomic Distances (Å) with Esd's

Ir(1)–P(1)	2.364 (3)	Ir(1)–P(2)	2.363 (3)
Ir(1)–C(1)	1.934 (13)	Ir(1)–C(2)	1.942 (16)
Ir(1)–C(3)	1.902 (12)	O(1)–C(1)	1.130 (15)
O(2)–C(2)	1.104 (21)	O(3)–C(3)	1.144 (14)
P(1)–C(4)	1.811 (9)	P(1)–C(10)	1.829 (12)
P(1)–C(16)	1.819 (13)	P(2)–C(22)	1.839 (11)
P(2)–C(28)	1.834 (9)	P(2)–C(34)	1.834 (13)
S(1)–O(4)	1.384 (13)	S(1)–O(5)	1.399 (21)
S(1)–O(6)	1.502 (14)	S(1)–O(7)	1.493 (10)
C(4)–C(5)	1.391 (16)	C(4)–C(9)	1.401 (16)
C(5)–C(6)	1.396 (14)	C(6)–C(7)	1.370 (19)
C(7)–C(8)	1.382 (18)	C(8)–C(9)	1.419 (14)
C(10)–C(11)	1.353 (17)	C(10)–C(15)	1.384 (13)
C(11)–C(12)	1.378 (20)	C(12)–C(13)	1.344 (17)
C(13)–C(14)	1.358 (21)	C(14)–C(15)	1.378 (19)
C(16)–C(17)	1.354 (14)	C(16)–C(21)	1.396 (20)
C(17)–C(18)	1.406 (24)	C(18)–C(19)	1.370 (28)
C(19)–C(20)	1.373 (19)	C(20)–C(21)	1.400 (24)
C(22)–C(23)	1.358 (17)	C(22)–C(27)	1.397 (13)
C(23)–C(24)	1.370 (19)	C(24)–C(25)	1.339 (15)
C(25)–C(26)	1.322 (20)	C(26)–C(27)	1.346 (18)
C(28)–C(29)	1.344 (20)	C(28)–C(33)	1.331 (18)
C(29)–C(30)	1.390 (18)	C(30)–C(31)	1.394 (28)
C(31)–C(32)	1.308 (28)	C(32)–C(33)	1.330 (18)
C(34)–C(35)	1.341 (19)	C(34)–C(39)	1.372 (14)
C(35)–C(36)	1.373 (23)	C(36)–C(37)	1.352 (18)
C(37)–C(38)	1.355 (25)	C(38)–C(39)	1.358 (24)

the remaining fragment to be H_xO^{3+}!), HSO_4^- (consistent with H_2O as the third species), or most improbably, H_2SO_4 (requiring the third fragment to be H_xO^{3-}!).] Notice also that hydrogen atoms of the H_2O molecule must be disordered, since this molecule lies on a site of C_3 symmetry.

The labeling of atoms is shown in Figure 3. Interatomic distances and angles are collected in Tables III and IV.

The $Ir(CO)_3(PPh_3)_2^+$ cation is associated with the mutually trans Ir–P distances Ir(1)–P(1) = 2.364 (3) Å and Ir(1)–P(2) = 2.363 (3) Å, with an interligand angle of P(1)–Ir(1)–P(2) = 176.6 (1)°. The equatorial carbonyl ligands have Ir–CO linkages defined by Ir(1)–C(1) = 1.934 (13) Å, Ir(1)–C(2) = 1.942 (16) Å, and Ir(1)–C(3) = 1.902 (12) Å (average = 1.926 Å). The Ir–C–O systems are close to linear (177.4 (12)–179.2 (13)°) with C–O distances of 1.104 (21)–1.144 (14)Å. Angles between the equatorial ligands show some deviation from D_{3h} symmetry, with C(1)–Ir(1)–C(2) = 115.6 (6)° as compared to C(2)–Ir(1)–C(3) = 121.3 (6)° and C(1)–Ir(1)–C(3) = 123.0 (7)°. The axial–equatorial angles are all close to 90°, ranging from P(1)–Ir(1)–C(3) = 88.2 (3)° to P(1)–Ir(1)–C(1) = 91.6 (3)°. The Ir–P–C angles are all expanded from the ideal tetrahedral value (range 112.9 (4)–114.5 (3)°) and the C(ipso)–P–C(ipso′) angles are all compressed (range 103.7 (5)–107.1 (5)°); P–C distances range from P(1)–C(4) = 1.811 (9) Å to P(2)–C(22) = 1.839 (11) Å. The overall connectivity is similar to, but more accurate than, that observed for the Ir(I) center in [$Ir(CO)_3(PMe_2Ph)_2^+$][ClO_4^-], in which Ir–P = 2.29 (2)–2.34 (2) Å and Ir–CO = 1.81 (5)–1.94 (6) Å.[29] It is also similar to that observed in the isoelectronic Os(0) species $Os(CO)_3(PPh_3)_2$, in which average distances are Os–P = 2.36 (3) Å and Os–CO = 1.92 (5) Å.[30]

Table IV. Interatomic Angles (deg) with Esd's

P(1)–Ir(1)–P(2)	176.6 (1)	P(1)–Ir(1)–C(1)	91.6 (3)
P(2)–Ir(1)–C(1)	90.2 (3)	P(1)–Ir(1)–C(2)	91.2 (3)
P(2)–Ir(1)–C(2)	90.6 (3)	C(1)–Ir(1)–C(2)	115.6 (6)
P(1)–Ir(1)–C(3)	88.2 (3)	P(2)–Ir(1)–C(3)	88.4 (3)
C(1)–Ir(1)–C(3)	123.0 (7)	C(2)–Ir(1)–C(3)	121.3 (6)
Ir(1)–P(1)–C(4)	114.4 (3)	Ir(1)–P(1)–C(10)	113.0 (3)
C(4)–P(1)–C(10)	106.2 (5)	Ir(1)–P(1)–C(16)	113.5 (4)
C(4)–P(1)–C(16)	104.2 (5)	C(10)–P(1)–C(16)	104.6 (5)
Ir(1)–P(2)–C(22)	114.5 (3)	Ir(1)–P(2)–C(28)	113.4 (3)
C(22)–P(2)–C(28)	103.7 (5)	Ir(1)–P(2)–C(34)	112.9 (4)
C(22)–P(2)–C(34)	107.1 (5)	C(28)–P(2)–C(34)	104.2 (5)
O(4)–S(1)–O(5)	111.4 (10)	O(4)–S(1)–O(6)	104.2 (10)
O(5)–S(1)–O(6)	112.2 (9)	O(4)–S(1)–O(7)	112.6 (8)
O(5)–S(1)–O(7)	101.7 (9)	O(6)–S(1)–O(7)	115.1 (6)
Ir(1)–C(1)–O(1)	177.4 (12)	Ir(1)–C(2)–O(2)	179.2 (10)
Ir(1)–C(3)–O(3)	179.2 (13)	P(1)–C(4)–C(5)	121.1 (8)
P(1)–C(4)–C(9)	119.1 (8)	C(5)–C(4)–C(9)	119.8 (9)
C(4)–C(5)–C(6)	119.1 (11)	C(5)–C(6)–C(7)	122.8 (12)
C(6)–C(7)–C(8)	117.9 (10)	C(7)–C(8)–C(9)	121.5 (12)
C(4)–C(9)–C(8)	118.8 (11)	P(1)–C(10)–C(11)	121.1 (8)
P(1)–C(10)–C(15)	119.4 (9)	C(11)–C(10)–C(15)	119.4 (11)
C(10)–C(11)–C(12)	120.4 (10)	C(11)–C(12)–C(13)	121.3 (14)
C(12)–C(13)–C(14)	118.2 (13)	C(13)–C(14)–C(15)	122.5 (11)
C(10)–C(15)–C(14)	118.2 (11)	P(1)–C(16)–C(17)	122.5 (11)
P(1)–C(16)–C(21)	117.2 (8)	C(17)–C(16)–C(21)	120.1 (13)
C(16)–C(17)–C(18)	119.8 (14)	C(17)–C(18)–C(19)	120.5 (12)
C(18)–C(19)–C(20)	120.0 (17)	C(19)–C(20)–C(21)	119.8 (16)
C(16)–C(21)–C(20)	119.8 (11)	P(2)-C(22)-C(23)	121.0 (7)
P(2)–C(22)–C(27)	120.6 (9)	C(23)–C(22)–C(27)	118.4 (11)
C(22)–C(23)–C(24)	118.7 (10)	C(23)–C(24)–C(25)	122.6 (14)
C(24)–C(25)–C(26)	118.1 (13)	C(25)–C(26)–C(27)	122.8 (10)
C(22)–C(27)–C(26)	119.2 (12)	P(2)–C(28)–C(29)	119.0 (9)
P(2)–C(28)–C(33)	122.4 (10)	C(29)–C(28)–C(33)	118.6 (11)
C(28)–C(29)–C(30)	118.9 (15)	C(29)–C(30)–C(31)	118.6 (17)
C(30)–C(31)–C(32)	120.7 (14)	C(31)–C(32)–C(33)	118.3 (17)
C(28)–C(33)–C(32)	124.6 (15)	P(2)–C(34)–C(35)	120.6 (8)
P(2)–C(34)–C(39)	121.5 (10)	C(35)–C(34)–C(39)	117.7 (13)
C(34)–C(35)–C(36)	122.0 (11)	C(35)–C(36)–C(37)	118.8 (15)
C(36)–C(37)–C(38)	120.9 (17)	C(37)–C(38)–C(39)	118.9 (12)
C(34)–C(39)–C(38)	121.7 (13)		

The HSO_4^- Anion. Although the hydrogen atom was not located, the observed S–O distances define a system of C_{2v} rather than T_d symmetry. Two such bonds are short (S(1)–O(4) = 1.384 (13) Å and S(1)–O(5) = 1.399 (21) Å), while two are substantially longer (S(1)–O(6) = 1.502 (14) Å and S(1)–O(7) = 1.493 (10) Å). One is tempted, therefore, to suggest either an ordered structure (A) or a disordered structure (B) to accommodate these observations. Further crystallographic information relating to the deviations of this species from quasi-spherical T_d symmetry is as follows: (1) The two smallest O–S–O angles are O(5)–S(1)–O(7) = 101.7 (9)° and O(4)–S(1)–O(6) = 104.2 (10)°; the largest is O(6)–S(1)–O(7) = 115.1 (6)°. (2) Atoms O(4) and O(5) (i.e. those associated with the *shorter* S–O

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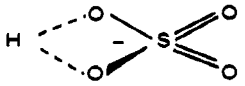
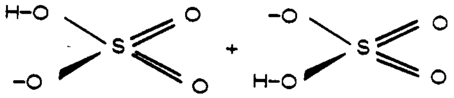


A



B

distances) have substantially larger thermal vibration ellipsoids than do O(6) and O(7). Unfortunately, we have no simple explanation for these two perturbations; a purely librational shortening of S(1)–O(4) and S(1)–O(5) is unlikely.

Summary

The observed reaction shows the ready displacement by carbon monoxide of ligands bound through oxygen to the Ir(III) center.

$$\mathrm{Ir(CO)(OH)(SO_4)L_2 + 3CO \rightarrow [Ir(CO)_3L_2{}^+][HSO_4{}^-] + CO_2} \tag{8}$$

$$\mathrm{L = PPh_3 \ or \ P(\mathit{p}\text{-}tolyl)_3}$$

The formation of CO_2 almost certainly occurs by displacement of the hydroxide by CO, followed by attack of the OH^- on the carbon of a carbonyl of the cationic complex to form an iridium carboxylic acid.[20,31] Such complexes are known to eliminate CO_2.[31] The sequence to $Ir(CO)(OH)(SO_4)L_2$, L = PPh_3 or P(*p*-tolyl)$_3$, and its subsequent reaction with CO leads from Ir(I) and back to Ir(I) and can be presented as

$$\mathrm{OH^- + O_2 + SO_2 + CO \xrightarrow{Ir(I)} HSO_4{}^- + CO_2} \tag{9}$$

This reaction, which has considerable environmental importance, is not completely accurate because the Ir(I) is not a catalyst in the currently described reaction. However, it provides a useful example of the potential for unusual transformations on transition-metal centers containing mixtures of hard and soft ligands.

Reaction 8 provides the third example[20,28] of displacement by CO of ligands coordinated through one or more oxygen atoms to iridium(I) or iridium(III) at ambient conditions. Thus, "hard" ligands that are bound to relatively soft metal centers exhibit considerable lability.

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Supplementary Material Available: Tables of anisotropic displacement coefficients and H atom coordinates (3 pages); a listing of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Ferromagnetic Behavior of Linear-Chain Electron-Transfer Complexes. Synthesis and Characterization of Decaethylferrocene, $Fe(C_5Et_5)_2$, and Its Electron-Transfer Salts: Structure and Magnetic Properties of $[Fe(C_5Et_5)_2]^{\bullet+}[A]^{\bullet-}$ [A = TCNE and TCNQ]

Kai-Ming Chi,[1a,b] Joseph C. Calabrese,[1a] William M. Reiff,*[,1c] and Joel S. Miller*[,1a]

Central Research and Development Department, E. I. du Pont de Nemours and Company,
Experimental Station E328, Wilmington, Delaware 19880-0328, Department of Physics,
The Ohio State University, Columbus, Ohio 43210-1106, and Department of Chemistry,
Northeastern University, Boston, Massachusetts 02115

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1,2,3,4,5-Pentaethylcyclopentadiene as well as $Fe(C_5Et_5)_2$ (D) and several electron-transfer salts have been prepared. The structure of the $[TCNQ]^{\bullet-}$ (A) salt has been determined [A = 9.416 (2) Å, b = 9.966 (1) Å, c = 11.710 Å, α = 93.83 (1)°, β = 109.29 (1)°, γ = 109.05 (1)°, V = 961.4 Å^3, Z = 1, T = −70 °C] to have a $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ structural motif. The ^{57}Fe Mössbauer spectra of $[TCNE]^{\bullet-}$ and $[TCNQ]^{\bullet-}$ salts of $[Fe(C_5Et_5)_2]^{\bullet+}$ are typical of ferrocenium ions and magnetic hyperfine splitting characteristic of either slow paramagnetic relaxation or extended magnetic order is not observed above 1.5 K. The 5-K EPR spectrum of $[Fe(C_5Et_5)_2]^{\bullet+}$ has a strong absorption at $g_{\parallel}$ = 4.59. The Faraday magnetic susceptibility (2–320 K) can be fit to the Curie–Weiss expression, μ_{eff} = 3.37, 3.15, and 3.62 μ_B and θ = 6.9, 7.5, and 6.1 K, for the $[PF_6]^-$, $[TCNE]^{\bullet-}$, and $[TCNQ]^{\bullet-}$ salts of $[Fe(C_5Et_5)_2]^{\bullet+}$, consistent with ferromagnetic coupling, respectively.

Introduction

Pentamethylcyclopentadienyl, C_5Me_5, Cp*, has been widely used as an electron-donating ligand in organometallic chemistry, and convenient synthetic routes to C_5Me_5H have been reported.[2] The synthesis of the ethyl analogue, 1,2,3,4,5-pentaethylcyclopentadiene (1), however, has not been reported. With the observation of bulk ferromagnetic behavior for the electron-transfer salt of decamethylferrocene, FeCp*$_2$, and tetracyanoethylene,

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[1] (a) Du Pont. (b) Ohio State University. (c) Northeastern University.

[2] Baker, R. T. *Inorg. React. Methods*, in press. Maitlis, P. *Chem. Soc. Rev.* 1981, *10*, 1. King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* 1967, *8*, 287.

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