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Carbonylation of Iridium(I) and Iridium(III) Complexes, *trans*-$Ir(CO)(R)(P(p\text{-tolyl})_3)_2$ (R = Me, OMe, OCH_2Ph, OC_6H_4Me, OH) and $Ir(CO)(Me)(SO_4)(P(p\text{-tolyl})_3)_2$, and Facile Elimination of Hard Ligands: Crystal and Molecular Structures of $Ir(CO)(Me)(SO_4)(P(p\text{-tolyl})_3)_2$ and $[Ir(CO)_3(P(p\text{-tolyl})_3)_2][HSO_4]$

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Carbonylation of several iridium(I) complexes, *trans*-$Ir(CO)(R)(P(p\text{-tolyl})_3)_2$ lead to products $Ir(CO)_2(C(O)R)(P(p\text{-tolyl})_3)_2$, R = Me, OCH_2Ph; and $Ir_2(CO)_6(P(p\text{-tolyl})_3)_2$, R = OH, OMe, and OC_6H_4Me) that depend on the nature of the R group. Carbonylation of the iridium(III) complex, $Ir(CO)(Me)(SO_4)(P(p\text{-tolyl})_3)_2$ leads to two iridium products, $[Ir(CO)_3(P(p\text{-tolyl})_3)_2{}^+]$ and $Ir(CO)_3(C(O)Me)(P(p\text{-tolyl})_3)_2$ by two different pathways. Structures of $Ir(CO)(Me)(SO_4)(P(p\text{-tolyl})_3)_2$ and $[Ir(CO)_3(P(p\text{-tolyl})_3)_2][HSO_4]$ were determined to assist in the interpretation. The complex $Ir(CO)(Me)(SO_4)(P(p\text{-tolyl})_3)_2$ crystallizes in the orthorhombic space group *Pbcn* with $a = 18.237(3)$, $b = 12.572(2)$, $c = 18.584(2)$ Å, $V = 4260.9(11)$ Å^3 and $Z = 4$. The structure was refined to $R = 1.98\%$ for 1640 reflections with $F > 6\sigma(F)$. The molecule lies on a site of C_2 symmetry, necessitating a disorder of carbonyl and methyl ligands. Bond distances around the octahedral iridium(III) center include Ir−CO = 1.823(13), $Ir-CH_3$ = 2.127(14), Ir−P = 2.398(1) and $Ir-O(SO_4)$ = 2.119(4) Å. The species $[Ir(CO)_3(P(p\text{-tolyl})_3)_2][HSO_4]$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.490(2)$, $b = 12.255(3)$, $c = 30.873(7)$ Å, $\beta = 92.826(17)°$, $V = 4342.0(15)$ Å^3 and $Z = 4$. The structure was refined to $R = 6.09\%$ for 2591 reflections with $F > 6\sigma(F)$. The $Ir(CO)_3P_2$ core of the cation has a geometry slightly distorted from D_{3h} symmetry, with Ir−P = 2.363(5) and 2.374(5) Å and Ir−CO = 1.921(21)−2.012(28) Å. The $HSO_4{}^-$ anion undergoes substantial librational motion (or is disordered) and is associated with S−O distances ranging from 1.31(4) through 1.49(3) Å.

Organometallic complexes containing hard ligands form a very interesting class of compounds.[1] A number of researchers have exploited weakly bound ligands in catalytic reactions.[2] Hard ligands bound to organometallic centers frequently show enhanced reactivity. For example $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3{}^{2+}]$ undergoes H_2O exchange three orders of magnitude more rapidly than does $[Ru(H_2O)_6{}^{2+}]$.[3] Similarly $[IrCl_2(H_2O)(PMe_2Ph)_3{}^+]$ loses H_2O several orders of magnitude more rapidly than $[Ir(H_2O)_6{}^{3+}]$.[4] Several recent reports of organometallic complexes containing hard ligands have appeared.[5]

Our studies of iridium(III) complexes have shown that hard ligands are readily replaced.[6]

$$Ir(CO)(I)(OMe)(Me)(PPh_3)_2 + {}^*CO \rightarrow Ir(CO)(I)({}^*C(O)OMe)(Me)(PPh_3)_2 \quad (1)$$

$$Ir(CO)(I)(OMe)(Me)(PPh_3)_2 + I^- \rightarrow Ir(CO)(I)_2(Me)(PPh_3)_2 + OMe^- \quad (2)$$

$$Ir(CO)(OH)(SO_4)(PPh_3)_2 + 3CO \rightarrow [Ir(CO)_3(PPh_3)_2{}^+][HSO_4{}^-] + CO_2 \quad (3)$$

These reactions occur at room temperature indicating unusual reactivity for iridium(III) complexes. In this

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Table 1. Experimental Data for the X-ray Diffraction Studies on Ir(CO)(Me)(SO_4)(P(*p*-tolyl)$_3$)$_2$ and [Ir(CO)$_3$(P(*p*-tolyl)$_3$)$_2$](HSO_4)

	Ir(CO)(Me)(SO_4)(P(*p*-tol)$_3$)$_2$	[Ir(CO)$_3$(P(*p*-tol)$_3$)$_2$](HSO_4)
molec formula	$C_{44}H_{45}IrO_5P_2S$	$C_{45}H_{43}IrO_7P_2S$
cryst size (mm)	0.4 × 0.3 × 0.2	0.17 × 0.13 × 0.07
cryst system	orthorhombic	monoclinic
space group	*Pbcn* (No. 60)	$P2_1/n$ (No. 14)
a, Å	18.237(3)	11.490(2)
b, Å	12.572(2)	12.255(3)
c, Å	18.584(2)	30.873(7)
β, deg	(90)	92.826(17)
V, Å^3	4260.9(11)	4342.0(15)
Z	4	4
fw	940.0	982.1
D(calc), Mg/m^3	1.465	1.502
abs coeff, mm^{-1}	3.282	3.226
temp (K)	295	298
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73
2θ range, deg	5.0–45.0	5.0–45.0
scan type	$2\theta-\theta$	ω
index ranges	$0 \le h \le 19, -13 \le k \le 0, -20 \le l \le 20$	$0 \le h \le 12, -13 \le k \le 13, -33 \le l \le 33$
reflcns collcd	6150	13 477
indpdt reflcns[a]	2801 ($R_{int} = 1.54\%$)	5718 ($R_{int} = 4.21\%$)
reflcns > 6σ	1640	2591
min/max transm	0.1612/0.1820	0.2292/0.4195
extinction corr	$\chi = 0.000042(12)$	$\chi = 0.00003(3)$
*F**	where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$	
R indices (6σ data)	$R = 1.98\%$, w$R = 2.14\%$	$R = 6.09\%$, w$R = 6.12\%$
R indices (all data)	$R = 5.24\%$, w$R = 2.80\%$	$R = 8.13\%$, w$R = 9.00\%$
goodness-of-fit	1.06	1.07
largest and mean Δ/σ	0.008, 0.000	0.048, 0.003
largest diff peak, e Å^{-3}	0.58	1.93 (~1.2 Å from Ir(1))

[a] $I > 0.3\sigma(I)$.

paper we show that hard ligands bound to iridium(I) and iridium(III) are readily displaced by carbon monoxide.

Experimental Section

$IrCl_3 \cdot xH_2O$ was purchased from Johnson Matthey. Tri-*p*-tolylphosphine was 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. Infrared spectra of KBr pellets and solutions were measured on a Mattson Polaris FTIR instrument in the region 2200–750 cm^{-1}. NMR spectra were recorded on a Varian VXR 400 spectrometer.

The compounds *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$[7] (IR: ν_{CO} = 1944 cm^{-1} in THF; NMR (CD_2Cl_2): ^{1}H = 7.1–7.5 (m), 2.3 (s), −0.3 (t) (J_{P-H} = 9.2 Hz); ^{31}P = 29.9 (s) ppm), *trans*-Ir(CO)(OMe)(P(*p*-tolyl)$_3$)$_2$[8] (IR: ν_{CO} = 1945 cm^{-1} in THF; NMR(CD_2Cl_2): ^{1}H = 7.2–7.6 (m), 3.0 (s), 2.3 (s) ppm; ^{31}P = 22.1 ppm) and *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$[9] (IR: ν_{CO} = 1928 cm^{-1} in THF; NMR(CD_2Cl_2): ^{1}H = 7.2–7.6 (m), 2.4 (s), 0.4 (t) (J_{P-H} = 7.2 Hz) ppm and ^{31}P = 26.2 ppm) were prepared by previously published procedures. Through an omission, the microanalysis of *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ (obs (calc): C, 62.29 (62.63); H, 5.38 (5.34)) had not been previously published.

The sulfate complexes, Ir(CO)(Cl)(SO_4)(P(*p*-tolyl)$_3$)$_2$[10] and Ir(CO)(Me)(SO_4)(P(*p*-tolyl)$_3$)$_2$[7] were prepared by procedures similar to the literature procedures in yields of 83% and 62%, respectively. The characterization data (Ir(CO)(Cl)(SO_4)(P(*p*-tolyl)$_3$)$_2$: IR, ν_{CO} = 2043 cm^{-1}; NMR, ^{1}H = 7.2–7.5 (m), 2.4 (s) ppm and ^{31}P(CD_2Cl_2) = −2.5 (s) ppm and Ir(CO)(Me)(SO_4)(P(*p*-tolyl)$_3$)$_2$: IR, ν_{CO} = 2018 cm^{-1}; NMR, ^{1}H = 7.2–7.4 (m), 2.4 (s), 1.1 (t), J_{P-H} = 5.6 Hz and ^{31}P = 2.7(s)) were in excellent agreement with previously reported values. Crystallographic quality crystals of Ir(CO)(Me)(SO_4)(P(*p*-tolyl)$_3$)$_2$ were grown by slow diffusion of hexane into a saturated THF solution.

Reactions with CO. In an inert atmosphere glovebox a solution of iridium complex (~100 mL of 2 × 10^{-4} M) in THF was prepared in a Schlenk flask. The flask was sealed, removed from the glovebox, attached to a Schlenk line and an initial infrared spectrum recorded. The flask was then placed under a CO atmosphere and infrared spectra recorded periodically. After times ranging from a few minutes to several weeks, the THF was removed and the products analyzed by infrared and NMR spectroscopies.

Collection of X-ray Diffraction Data for Ir(CO)(Me)(SO_4)(P(*p*-tolyl)$_3$)$_2$. A single crystal was mounted in a thin-walled glass capillary and aligned on a Siemens R3m/V diffractometer. Crystal alignment, determination of cell parameters and data collection were performed as described previously;[11] details are presented in Table 1. The D_{2h} (*mmm*) diffraction symmetry and the systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$ and $hk0$ for $h + k = 2n + 1$ uniquely define the centrosymmetric orthorhombic space group *Pbcn* (No. 60). Two forms of the data ($h\bar{k}l$ and $h\bar{k}\bar{l}$) were collected and merged (R_{int} = 1.54%).

Collection of X-ray Diffraction Data for [Ir(CO)$_3$(P(*p*-tolyl)$_3$)$_2$][HSO_4]. Only poor-quality crystals of this species were obtained. A rather small crystal (~0.17 × 0.13 × 0.07 mm in dimension) was sealed into a thin-walled glass capillary and data were collected as indicated above; details are presented in Table 1. The C_{2h} (2/*m*) diffraction symmetry and the systematic absences h0*l* for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ unambiguously define the centrosymmetric monoclinic space group $P2_1/n$ (No. 14). Four octants of data rep-

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Table 2. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $Ir(CO)(Me)(SO_4)(P(p\text{-tolyl})_3)_2$

	x	*y*	*z*	*U*(eq)[a]
Ir(1)	0	2100(1)	2500	42(1)
S(1)	0	4295(2)	2500	72(1)
O(1)	377(2)	3504(3)	3011(2)	62(1)
O(2)	530(3)	4910(3)	2118(3)	111(2)
C(1)	−563(8)	1078(10)	1774(8)	47(4)
C(3)	−372(7)	1020(11)	1956(7)	50(4)
O(3)	−654(6)	406(7)	1605(5)	85(4)
P(1)	−1083(1)	2046(1)	3232(1)	47(1)
C(11)	−1145(3)	801(4)	3725(3)	54(2)
C(12)	−1182(3)	−148(5)	3354(4)	76(3)
C(13)	−1206(3)	−1109(5)	3712(4)	80(3)
C(14)	−1208(4)	−1156(6)	4440(4)	86(3)
C(15)	−1172(4)	−226(6)	4805(4)	100(4)
C(16)	−1139(3)	746(5)	4461(3)	76(3)
C(17)	−1311(7)	−2224(6)	4830(6)	136(5)
C(21)	−1940(3)	2143(5)	2740(3)	53(2)
C(22)	−2038(3)	2956(5)	2242(3)	79(3)
C(23)	−2704(3)	3089(6)	1909(3)	83(3)
C(24)	−3278(3)	2429(5)	2030(3)	70(2)
C(25)	−3182(3)	1618(5)	2512(4)	79(2)
C(26)	−2526(3)	1476(5)	2861(3)	66(2)
C(27)	−4029(4)	2590(7)	1676(5)	106(4)
C(31)	−1143(3)	3042(4)	3927(3)	51(2)
C(32)	−1778(3)	3603(5)	4060(3)	68(2)
C(33)	−1820(4)	4277(5)	4635(4)	81(3)
C(34)	−1245(3)	4428(5)	5106(3)	63(2)
C(35)	−604(3)	3901(4)	4956(3)	62(2)
C(36)	−551(3)	3223(4)	4376(3)	61(2)
C(37)	−1327(5)	5144(6)	5750(4)	93(3)

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

Table 3. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[Ir(CO)_3(P(p\text{-tolyl})_3)_2](HSO_4)$

	x	*y*	*z*	*U*(eq)[a]
Ir(1)	898(1)	186(1)	1454(1)	45(1)
P(1)	794(5)	−1705(4)	1615(2)	46(2)
P(2)	753(5)	2049(4)	1262(2)	46(2)
C(11)	936(20)	−205(20)	822(9)	69(7)
O(11)	948(21)	−390(14)	474(6)	116(10)
C(21)	−410(17)	352(16)	1813(7)	44(5)
O(21)	−1172(16)	518(14)	2014(7)	103(9)
C(31)	2345(18)	363(17)	1786(7)	51(5)
O(31)	3247(14)	517(13)	1958(7)	93(8)
C(1)	2174(16)	−2449(15)	1663(6)	35(7)
C(2)	3081(17)	−2075(16)	1390(7)	46(8)
C(3)	4169(21)	−2605(19)	1427(8)	69(10)
C(4)	4359(28)	−3529(20)	1706(9)	81(12)
C(5)	3401(23)	−3855(19)	1955(9)	75(11)
C(6)	2369(22)	−3355(17)	1921(9)	73(11)
C(7)	5599(22)	−4029(19)	1766(10)	90(12)
C(8)	206(16)	−1954(15)	2143(7)	42(8)
C(9)	816(19)	−1752(18)	2516(8)	57(9)
C(10)	388(20)	−1931(19)	2910(8)	60(10)
C(11)	−725(22)	−2385(18)	2960(8)	65(10)
C(12)	−1351(20)	−2527(20)	2563(9)	70(11)
C(13)	−895(21)	−2337(17)	2161(7)	57(9)
C(14)	−1223(23)	−2627(24)	3392(9)	89(12)
C(15)	−161(21)	−2466(19)	1223(8)	61(10)
C(16)	30(21)	−3532(16)	1113(7)	59(9)
C(17)	−696(24)	−4097(22)	850(8)	83(11)
C(18)	−1648(28)	−3633(20)	649(9)	80(12)
C(19)	−1855(22)	−2572(27)	739(10)	94(14)
C(20)	−1104(23)	−1962(19)	1041(9)	78(11)
C(21)	−2458(25)	−4208(27)	314(9)	112(14)
C(22)	−272(18)	2267(15)	790(6)	41(7)
C(23)	−1338(22)	1811(17)	763(9)	74(11)
C(24)	−2144(20)	2004(18)	421(10)	73(11)
C(25)	−1866(22)	2656(20)	81(8)	64(10)
C(26)	−775(23)	3125(24)	118(8)	85(12)
C(27)	61(22)	2904(22)	459(8)	83(11)
C(28)	−2691(24)	2831(25)	−284(9)	98(13)
C(29)	243(15)	2861(16)	1703(7)	40(8)
C(30)	−745(21)	3502(17)	1661(7)	59(9)
C(31)	−1166(20)	4063(21)	2011(9)	73(11)
C(32)	−658(20)	4033(19)	2397(9)	66(10)
C(33)	402(19)	3429(18)	2435(7)	58(9)
C(34)	820(22)	2830(17)	2103(8)	64(10)
C(35)	−1046(26)	4675(23)	2800(8)	94(12)
C(36)	2096(19)	2736(16)	1123(7)	53(9)
C(37)	2206(21)	3827(17)	1178(8)	61(10)
C(38)	3114(31)	4374(24)	1039(11)	95(15)
C(39)	3957(29)	3853(23)	802(9)	82(13)
C(40)	3875(17)	2757(27)	738(7)	76(12)
C(41)	2922(18)	2164(16)	897(7)	50(8)
C(42)	5052(26)	4440(27)	610(10)	114(15)
S(1C)	5261(12)	−268(11)	670(5)	149(6)
O(1C)	5469(25)	666(20)	418(9)	167(14)
O(2C)	5392(21)	−1279(25)	408(11)	184(17)
O(3C)	4166(33)	−237(22)	773(20)	362(38)
O(4C)	6248(39)	−370(30)	978(13)	246(24)

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

resenting two symmetry-equivalent forms were collected ($hkl = h\bar{k}l$ and $hkl = h\bar{k}\bar{l}$) and were merged ($R_{int} = 4.21\%$). Data from the crystal were of relatively poor quality as indicated by the 13 477 data merging to 5718 independent reflections with $I > 0.3\sigma(I)$ and only 2591 reflections above 6σ.

Solution and Refinement of the Structure of $Ir(CO)(Me)(SO_4)(P(p\text{-tolyl})_3)_2$. All crystallographic calculations were performed under the Siemens SHELXTL PLUS system[12] on a VAXstation 3100 computer. The analytical scattering factors for neutral atoms were corrected for both the real and the imaginary components of anomalous dispersion.[13] The structure was solved by a combination of direct methods and difference-Fourier syntheses. Least-squares refinement converged with $R = 5.24\%$ for all 2801 independent reflections and $R = 1.98\%$ for those 1640 reflections above 6σ. All hydrogen atoms were included in idealized locations with $d(C-H) = 0.96$ Å.[14]

Final atomic coordinates are collected in Table 2. Note that the molecule lies about a 2-fold axis at $x = 0$ and $z = {}^1/_4$ (Wyckoff position c)[15] necessitating that the carbonyl and methyl ligands be disordered. Much to our surprise, we were able to refine the appropriate carbon and oxygen atoms independently.

Solution and Refinement of the Structure of $[Ir(CO)_3(P(p\text{-tolyl})_3)_2][HSO_4]$. This proceeded as for the previous structure, convergence being reached with $R = 8.13\%$ for all data and $R = 6.09\%$ for those 2591 reflections above 6σ. Final atomic coordinates are collected in Table 3. It should be noted that our investigations led to the anion being identified as the HSO_4^- moiety, rather than as the possible $MeOSO_3^-$ anion. Nevertheless we must emphasize that the HSO_4^- moiety (defined by atoms S(1c), O(1c), O(2c), O(3c) and O(4c)) is either subject to large librational motions or is disordered. The hydrogen atom associated with the anion was not located directly and its presence is surmised on the basis of "chemical sense" and analogy with the related species $[Ir(CO)_3(PPh_3)_2{}^+][HSO_4{}^-]\cdot{}^1/_3H_2O$.[16]

Results

Reaction of *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ with CO. The initially yellow solution of *trans*-Ir(CO)(Me)-

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(12) *Siemens SHELXTL PLUS Manual*, 2nd ed.; Siemens Analytical Instruments: Madison, WI, 1990.

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(14) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(15) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1965; Vol. 1, p 149.

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$(\mathrm{P(}p\text{-tolyl})_3)_2$ rapidly decolorized. After 30 min, an IR of the solution showed $\mathrm{Ir(C(O)Me)(CO)_3(P(}p\text{-tolyl})_3)$ to be present[17] (ν_{CO} = 2046, 1981, 1967, and 1656 cm^{-1}). Removal of solvent gave $\mathrm{Ir(CO)_2(Me)(P(}p\text{-tolyl})_2$[6c] and $\mathrm{Ir(C(O)Me)(CO)_2(P(}p\text{-tolyl})_3)_2$[6c] as shown by infrared and ^{31}P NMR data ($\mathrm{Ir(CO)_2(Me)(P(}p\text{-tolyl})_3)_2$, ν_{CO} (KBr) = 1955, 1903 cm^{-1}, ^{31}P NMR ($\mathrm{CD_2Cl_2}$) 3.9 ppm; $\mathrm{Ir(C(O)Me)(CO)_2(P(}p\text{-tolyl}_3)_2$, ν_{CO} = 1973, 1920, 1619 cm^{-1}, ^{31}P NMR −2.4 ppm).

trans-$\mathrm{Ir(CO)(Me)(P(}p\text{-tolyl})_3)_2$ was regenerated by heating a THF solution of the above products, or upon standing of the solution under an inert atmosphere for 24 h. To ensure formation of $\mathrm{Ir(C(O)Me)(CO)_3(P(}p\text{-tolyl})_3)$, the reaction was also monitored by ^{31}P NMR ($\mathrm{CD_2Cl_2}$). Upon addition of CO to the NMR tube, the orange solution was rapidly decolorized and the resulting spectra showed the major products to be $\mathrm{Ir(C(O)Me)(CO)_2(P(}p\text{-tolyl})_3)_2$ (−2.4 ppm), free $\mathrm{P(}p\text{-tolyl})_3$ (−6.7 ppm) and $\mathrm{Ir(C(O)Me)(CO)_3(P(}p\text{-tolyl})_3)$ (7.7 ppm).

Reaction of $\mathrm{Ir(CO)(Me)(SO_4)(P(}p\text{-tolyl})_3)_2$ with CO. The pale yellow solution (ν_{CO} = 2020 cm^{-1}) of $\mathrm{Ir(CO)(Me)(SO_4)(P(}p\text{-tolyl})_3)_2$ in THF was stirred under an atmosphere of CO for 7 weeks during which time the pale yellow solution became nearly colorless, and a white precipitate formed. The changes in the infrared spectrum were monitored during this time. *trans*-$\mathrm{Ir(CO)(Me)(P(}p\text{-tolyl})_3)_2$, ($\nu_{\mathrm{CO}}$ (THF) = 1942 cm^{-1}), $\mathrm{CO_2}$ (ν_{CO} = 2336 cm^{-1}), $\mathrm{Ir(C(O)Me)(CO)_3(P(}p\text{-tolyl})_3)$ (ν_{CO} = 2046, 1983, 1968, and 1655 cm^{-1}), and $\mathrm{Ir(CO)_3(P(}p\text{-tolyl})_3)_2^+$ (ν_{CO} = 2017, 2005 cm^{-1}) formed as the absorbance at 2020 cm^{-1}, due to starting material, diminished.

The volatile components were removed and the flask brought into the inert atmosphere glovebox. The solid was extracted with THF, resulting in 0.146 g of gray, insoluble material and an orange filtrate that gave 30 mg of solid upon removal of THF. The insoluble material was identified as containing the $\mathrm{Ir(CO)_3(P(}p\text{-tolyl})_3)_2^+$ cation, based on its infrared (ν_{CO} = 2076, 2021, 1993 cm^{-1}) and ^{31}P NMR (−3.7 ppm) spectra.[6c] The THF soluble species were identified as *trans*-$\mathrm{Ir(CO)(Me)(P(}p\text{-tolyl})_3)_2$ (ν_{CO} = 1945 cm^{-1}) and $\mathrm{Ir(CO)_3(P(}p\text{-tolyl})_3)_2^+$ based on IR data. *trans*-$\mathrm{Ir(CO)(Me)(P(}p\text{-tolyl})_3)_2$ was isolated by benzene extraction followed by selective precipitation of the cation with hexanes. Filtration and solvent removal gave *trans*-$\mathrm{Ir(CO)(Me)(P(}p\text{-tolyl})_3)_2$, based on a single ^{31}P resonance at 29.8 ppm ($\mathrm{CD_2Cl_2}$), identical to that of an independently prepared sample.[7]

Reaction of *trans*-$\mathrm{Ir(CO)(OH)(P(}p\text{-tolyl})_3)_2$ with CO. After 10 min of reaction of *trans*-$\mathrm{Ir(CO)(OH)(P(}p\text{-tolyl})_3)_2$ with CO in THF a yellow precipitate formed. The solution was left to stir for 6 days, during which time $\mathrm{CO_2}$ was detected by its IR absorbance at 2336 cm^{-1}. Absorbances at 1943 and 1902 cm^{-1} were also present. The solvent was removed in vacuo and the flask brought into the box. The solid was extracted with THF to isolate the yellow precipitate (0.135 g). The solid was identified as $\mathrm{Ir_2(CO)_6(P(}p\text{-tolyl})_3)_2$ and characterized by its infrared spectrum in KBr (ν_{CO} = 1975 (sh, s), 1946 (vs), 1902 (sh, m) cm^{-1}).[19] The filtrate was found to be primarily composed of free $\mathrm{P(}p\text{-tolyl})_3$ based on its ^{31}P NMR in $\mathrm{CD_2Cl_2}$: −6.3 ppm, along with a small amount of $\mathrm{O{=}P(}p\text{-tolyl})_3$ (^{31}P 28.8 ppm). An attempt was made to obtain NMR data on the resultant dimer, but it proved to be too insoluble to obtain a spectrum. The ^{1}H spectrum (d_8-toluene) showed $\mathrm{H_2O}$ at 4.26 (s) ppm to be present.

Reaction of *trans*-$\mathrm{Ir(CO)(OMe)(P(}p\text{-tolyl})_3)_2$ with CO. After 1 h of reaction with CO in THF, a pale yellow precipitate formed and an IR spectrum of the solution showed ν_{CO} = 1985 (w) in addition to *trans*-$\mathrm{Ir(CO)(OMe)(P(}p\text{-tolyl})_3)_2$ at 1943 (s) cm^{-1}. The solution stirred 6 days after which there was no change in the IR spectrum. Solvent was removed and the flask brought into the box. The yellow precipitate was isolated (1.027 g) by washing the solid with THF. The solid was identified as $\mathrm{Ir_2(CO)_6(P(}p\text{-tolyl})_3)_2$ (see above) based on its infrared spectrum in KBr. The washings were shown to contain mostly free $\mathrm{P(}p\text{-tolyl})_3$ (^{31}P −6.3 ppm), along with small amounts of $\mathrm{O{=}P(}p\text{-tolyl})_3$ (28.8 ppm), *trans*-$\mathrm{Ir(CO)(OMe)(P(}p\text{-tolyl})_3)_2$ (22.0 ppm), and $\mathrm{Ir(C(O)Me)(CO)_2(P(}p\text{-tolyl})_3)_2$ (−2.8 ppm) based on ^{31}P data in $\mathrm{CD_2Cl_2}$.

The reaction was also examined by NMR. A saturated solution of $\mathrm{Ir(CO)(OMe)(P(}p\text{-tolyl})_3)_2$ in $\mathrm{CD_2Cl_2}$ was placed in an NMR tube and the tube sealed under a CO atmosphere. $\mathrm{Ir(C(O)Me)(CO)_2(P(}p\text{-tolyl})_3)_2$ was identified by its ^{31}P resonance at −2.7 ppm and ^{1}H (7.0–7.4 (m), 2.85 (s), 2.3 (s) ppm) along with free $\mathrm{P(}p\text{-tolyl})_3$ observed as a broad resonance centered at −6.7 ppm. In addition, a pale yellow precipitate, which has previously been shown to be $\mathrm{Ir_2(CO)_6(P(}p\text{-tolyl})_3)_2$, formed in the tube.

Reaction of *trans*-$\mathrm{Ir(CO)(OC_6H_4Me)(P(}p\text{-tolyl})_3)_2$ with CO. A pale yellow precipitate formed immediately upon exposure of *trans*-$\mathrm{Ir(CO)(OC_6H_4Me)(P(}p\text{-tolyl})_3)_2$[20] ($\nu_{\mathrm{CO}}$ = 1954 cm^{-1}) to a CO atmosphere in toluene. After 7 h of stirring, the solution was filtered and the precipitate identified as $\mathrm{Ir_2(CO)_6(P(}p\text{-tolyl})_3)_2$ based on its infrared spectrum in KBr.

The reaction was also examined by NMR to determine the soluble products. In an inert atmosphere glovebox, a saturated solution of *trans*-$\mathrm{Ir(CO)(OC_6H_4Me)(P(}p\text{-tolyl})_3)_2$ in $\mathrm{CD_2Cl_2}$ was prepared in a Schlenk flask. The flask was sealed, removed from the box, placed in a hood under an atmosphere of CO and stirred for 5 m at room temperature. The flask was placed in a dry ice/acetone bath (−78 °C) and stirred for 10 m. The solution was filtered with a fine frit and a NMR spectrum of the pale yellow liquid recorded. $\mathrm{HOC_6H_4Me}$ was identified based on ^{1}H NMR ($\mathrm{CD_2Cl_2}$) resonances:[22] 6.9(m), 6.7(m), 5.6(br), 2.2(s). $\mathrm{Ir(CO)_2(H)(P(}p\text{-tolyl})_3)_2$ was identified by ^{1}H NMR:[23] −11.1 (t) ppm, J = 9.2 Hz.

Reaction of *trans*-$\mathrm{Ir(CO)(OCH_2Ph)(P(}p\text{-tolyl})_3)_2$ with CO. Reaction of *trans*-$\mathrm{Ir(CO)(OCH_2Ph)(P(}p\text{-}$

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[17] The $\mathrm{Ir(CO)_3(C(O)Me)(P(}p\text{-tolyl})_3)$ complex has not been previously reported, but the IR spectrum is very similar to that reported for $\mathrm{Ir(CO)_3(C(O)Et)(P(}i\text{-Pr})_3)$ (ν_{CO} = 2041 (w), 1978 (s), 1959 (s) and 1671 (m) cm^{-1}).[18]

[18] Whyman, R. *J. Organomet. Chem.* **1975**, *94*, 303.

[19] Drakesmith, A. J.; Whyman, R. *J. Chem. Soc. Dalton* **1973**, 363.

[20] The syntheses of *trans*-$\mathrm{Ir(CO)(OC_6H_4Me)(P(}p\text{-tolyl})_3)_2$ and *trans*-$\mathrm{Ir(CO)(OCH_2Ph)(P(}p\text{-tolyl})_3)_2$ are by a similar procedure to the OMe and OPh analogues. The syntheses are reported separately.[21]

[21] Miller, C. A.; Janik, T. S.; Lake, C. H.; Toomey, L. M.; Churchill, M. R.; Atwood, J. D. *Organometallics* **1994**, *13*, 5080.

[22] A ^{1}H NMR spectrum of *p*-creosol (*p*-$\mathrm{HOC_6H_4Me}$) was independently recorded and compared to the spectrum of the mixture.

[23] This compound was prepared analogously to its $\mathrm{PPh_3}$ analogue.[24] Yield, 25%; IR (KBr): $\nu_{\mathrm{Ir-H}}$ = 2037 (w), ν_{CO} = 1972 (m), 1918 (s) cm^{-1}; ^{1}H NMR ($\mathrm{CD_2Cl_2}$): −11.1 (t, $J_{\mathrm{P-H}}$ = 11.2 Hz), 2.3 (s), 7.0–7.2 (m) ppm; ^{31}P NMR ($\mathrm{CD_2Cl_2}$): 4.4 (s) ppm. These data are consistent with those previously reported for the $\mathrm{PPh_3}$ analogue.[24]

[24] Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 725.

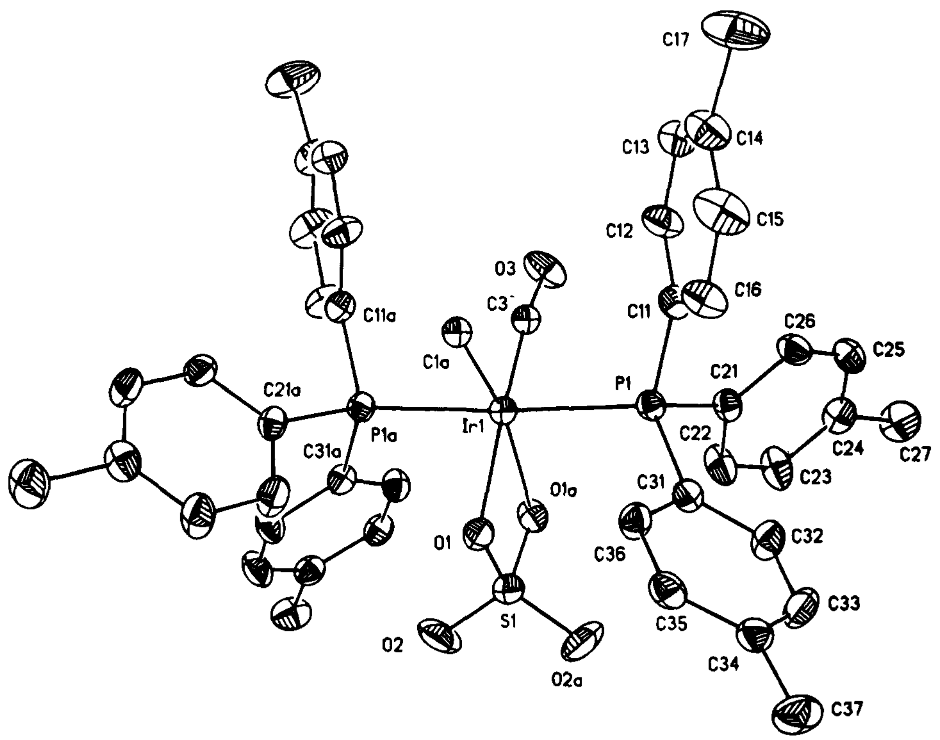

Figure 1. Molecular geometry of Ir(CO)(Me)(SO_4)(P(*p*-tolyl)$_3$)$_2$. Note that a crystallographic C_2-axis passes through Ir(1) and S(1) and only one location is shown for the disordered methyl C(1a) and carbonyl (C(3)–O(3)) ligands.

tolyl)$_3$)$_2$[10] with CO in toluene did not produce a yellow precipitate. The toluene was removed in a stream of CO and the light yellow product was identified as Ir(CO)$_2$[C(O)OCH_2Ph](P(*p*-tolyl)$_3$)$_2$ based on IR data ν_{CO}(KBr): 1986 (s), 1934 (s), and 1650 (m) cm^{-1}. This is very similar to the previously published Ir(CO)$_2$(C(O)OPh)(PPh$_3$)$_2$ analog[6b] with IR (KBr) ν_{CO}: 1985 (s), 1938 (vs) and 1675 (m) cm^{-1}. Some *trans*-Ir(CO)(OCH$_2$Ph)(P(*p*-tolyl)$_3$)$_2$ remains which is identified by ν_{CO} = 1944 (vs) cm^{-1}.

Description of the Molecular Geometry of Ir(CO)(Me)(SO_4)(P(*p*-tolyl)$_3$)$_2$. The crystal consists of an array of neutral monomeric molecules disordered in such a way that a site of crystallographic C_2 symmetry is preserved by the "scrambling" of methyl (C(1) and C(1a)) and carbonyl (C(3)–O(3) and C(3a)–O(3a)) ligands. The deconvoluted molecule is shown in Figure 1, while the scrambling of methyl and carbonyl ligands is depicted in Figure 2. Interatomic distances and angles are collected in Table 4.

The central iridium(III) atom is octahedrally coordinated to two tri(*p*-tolyl)phosphine ligands, a carbonyl ligand, a methyl ligand and a bidentate sulfate ligand.

The SO_4 ligand is bound to the iridium atom through two oxygen atoms (O(1) and O(1a)) which are symmetry-related by the 2-fold axis, the iridium–oxygen distances each being 2.119(4) Å. The nonbonding distances between the iridium and sulfur atoms is 2.759(2) Å. The singly-bonded S–O distances are 1.537(4) Å to the coordinated oxygen atoms, while the doubly bonded S=O distances to the terminal oxygen atoms are 1.427(5) Å. The Ir–O–S angles are 96.7(2)° and the O(coordinated)–S–O(terminal) angles are 110.8(2)°. Other angles at the sulfur atom are O(1)–S(1)–O(1a) = 99.4(3)° for the "bite-angle" between the coordinated oxygen atoms and O(2)–S(1)–O(2a) = 114.4(4) between the terminal oxygen atoms.

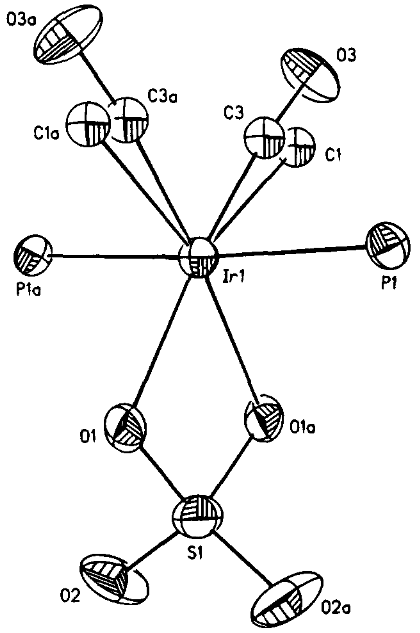

Figure 2. The Ir(CO)(Me)(SO_4)P_2 core of Ir(CO)(Me)(SO_4)(P(*p*-tolyl)$_3$)$_2$ showing the disorder of methyl (C(1) and C(1a)) and carbonyl (C(3)–O(3) and C(3a)–O(3a)) ligands. The crystallographic C_2 axis is vertical.

The carbonyl and methyl ligands on the iridium center are disordered about the 2-fold axis. It proved possible to refine atoms of both ligands. The Ir–C(Me) distance is 2.127(14) Å, and the Ir–C(carbonyl) distance is 1.823(13) Å, with the C–Ir–C angle between these two ligands being 94.7(6)°. The C–O distance within the carbonyl ligand is 1.135(17) Å.

The distances between the iridium atom and the two symmetry-related phosphorus atoms are each 2.398(1) Å, with the P(1)–Ir(1)–P(1a) angle being 176.8(1)°. Other angles about the iridium center involving phos-

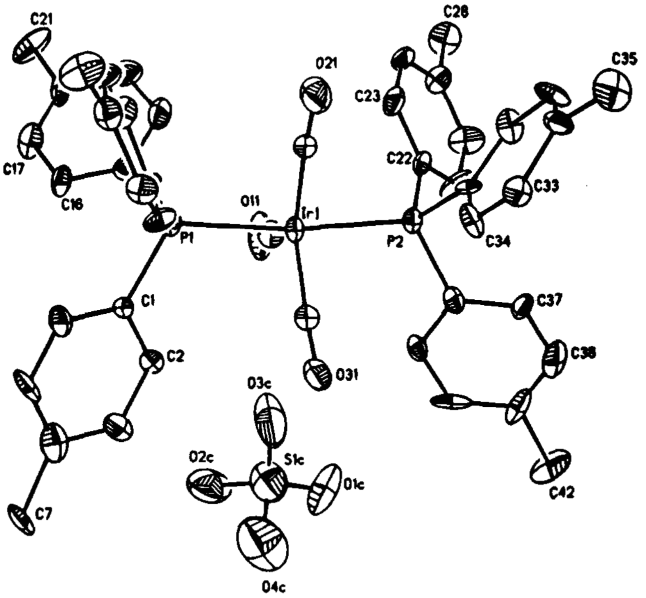

Figure 3. Geometry of $[Ir(CO)_3(P(p\text{-tolyl})_3)_2^+][HSO_4^-]$.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $Ir(CO)(Me)(SO_4)(P(p\text{-tolyl})_3)_2$ (1)

Ir(1)–S(1)	2.759(2)	Ir(1)–O(1)	2.119(4)
Ir(1)–C(3)	1.823(13)	Ir(1)–P(1)	2.398(1)
Ir(1)–O(1A)	2.119(4)	Ir(1)–C(1A)	2.127(14)
Ir(1)–P(1A)	2.398(1)	S(1)–O(1)	1.537(4)
S(1)–O(2)	1.427(5)	S(1)–O(1A)	1.537(4)
S(1)–O(2A)	1.427(5)	C(3)–O(3)	1.135(17)
P(1)–C(11)	1.818(6)	P(1)–C(21)	1.816(5)
P(1)–C(31)	1.801(5)		
O(1)–Ir(1)–C(3)	171.6(4)	O(1)–Ir(1)–P(1)	92.1(1)
C(3)–Ir(1)–P(1)	89.3(4)	O(1)–Ir(1)–O(1A)	67.2(2)
C(3)–Ir(1)–O(1A)	104.5(4)	P(1)–Ir(1)–O(1A)	90.6(1)
O(1)–Ir(1)–C(1A)	93.6(4)	C(3)–Ir(1)–C(1A)	94.7(6)
P(1)–Ir(1)–C(1A)	91.2(4)	O(1A)–Ir(1)–C(1A)	160.7(4)
O(1)–Ir(1)–P(1A)	90.6(1)	C(3)–Ir(1)–P(1A)	88.3(4)
P(1)–Ir(1)–P(1A)	176.8(1)	O(1A)–Ir(1)–P(1A)	92.1(1)
C(1A)–Ir(1)–P(1A)	86.9(4)	O(1)–S(1)–O(2)	110.8(2)
O(1)–S(1)–O(1A)	99.4(3)	O(2)–S(1)–O(1A)	110.2(2)
O(1)–S(1)–O(2A)	110.2(2)	O(2)–S(1)–O(2A)	114.4(4)
O(1A)–S(1)–O(2A)	110.8(2)	Ir(1)–O(1)–S(1)	96.7(2)
Ir(1)–C(3)–O(3)	174.0(12)	Ir(1)–P(1)–C(11)	111.2(2)
Ir(1)–P(1)–C(21)	114.9(2)	C(11)–P(1)–C(21)	104.9(3)
Ir(1)–P(1)–C(31)	116.0(2)	C(11)–P(1)–C(31)	103.5(2)
C(21)–P(1)–C(31)	105.1(2)	P(1)–C(11)–C(12)	119.7(4)
P(1)–C(11)–C(16)	123.1(4)	P(1)–C(21)–C(22)	119.7(4)
P(1)–C(21)–C(26)	123.0(4)	P(1)–C(31)–C(32)	122.4(4)
P(1)–C(31)–C(36)	119.9(4)		

Table 5. Selected Distances (Å) and Angles (deg) for $[Ir(CO)_3(P(p\text{-tolyl})_3)_2](HSO_4)$

(A) Cation			
Distances			
Ir(1)–P(1)	2.374(5)	Ir(1)–P(2)	2.363(5)
Ir(1)–C(11)	2.012(28)	Ir(1)–C(21)	1.921(20)
Ir(1)–C(31)	1.921(21)	P(1)–C(1)	1.828(19)
P(1)–C(8)	1.821(22)	P(1)–C(15)	1.846(24)
P(2)–C(22)	1.849(20)	P(2)–C(29)	1.807(21)
P(2)–C(36)	1.827(22)	O(11)–C(11)	1.098(34)
O(21)–C(21)	1.118(28)	O(31)–C(31)	1.157(27)
Angles			
P(1)–Ir(1)–P(2)	172.8(2)	P(1)–Ir(1)–C(11)	88.5(7)
P(2)–Ir(1)–C(11)	89.5(7)	P(1)–Ir(1)–C(21)	86.2(6)
P(2)–Ir(1)–C(21)	89.7(6)	C(11)–Ir(1)–C(21)	129.7(9)
P(1)–Ir(1)–C(31)	92.9(6)	P(2)–Ir(1)–C(31)	94.2(6)
C(11)–Ir(1)–C(31)	118.9(9)	C(21)–Ir(1)–C(31)	111.2(9)
Ir(1)–P(1)–C(1)	116.8(6)	Ir(1)–P(1)–C(8)	112.1(6)
C(1)–P(1)–C(8)	101.7(9)	Ir(1)–P(1)–C(15)	112.9(8)
C(1)–P(1)–C(15)	106.6(10)	C(8)–P(1)–C(15)	105.6(10)
Ir(1)–P(2)–C(22)	111.8(6)	Ir(1)–P(2)–C(29)	111.4(7)
C(22)–P(2)–C(29)	107.3(9)	Ir(1)–P(2)–C(36)	117.0(7)
C(22)–P(2)–C(36)	105.1(10)	C(29)–P(2)–C(36)	103.5(9)
Ir(1)–C(11)–O(11)	178.1(23)	Ir(1)–C(21)–O(21)	175.5(18)
Ir(1)–C(31)–O(31)	174.5(20)		
(B) HSO_4^- Anion			
Distances			
S(1C)–O(1C)	1.411(29)	S(1C)–O(2C)	1.492(34)
S(1C)–O(3C)	1.312(43)	S(1C)–O(4C)	1.449(43)
Angles			
O(1C)–S(1C)–O(2C)	110.4(19)	O(1C)–S(1C)–O(3C)	107.5(23)
O(2C)–S(1C)–O(3C)	106.2(21)	O(1C)–S(1C)–O(4C)	106.5(21)
O(2C)–S(1C)–O(4C)	100.8(20)	O(3C)–S(1C)–O(4C)	124.9(33)

phorus are P(1)–Ir(1)–C(1a) = 91.2(4)°, C(3)–Ir(1)–P(1) = 89.3(4)° and O(1)–Ir(1)–P(1) = 92.1(1)°. The P–C bond distances are P(1)–C(11) = 1.818(6) Å, P(1)–C(21) = 1.816(5) Å and P(1)–C(31) = 1.801(5) Å. The C–P–C angles average 104.5 ± 0.9°, while the Ir–P–C angles average 114.0 ± 2.5°.

Description of the Structure of $[Ir(CO)_3(P(p\text{-tolyl})_3)_2][HSO_4]$. The structure consists of an ordered 1:1 arrangement of $[Ir(CO)_3(P(p\text{-tolyl})_3)_2^+]$ cations and HSO_4^- anions. Each species lies in a general position with no symmetry requirements. Distances and angles are collected in Table 5. The structure is illustrated in Figure 3. The $[Ir(CO)_3(P(p\text{-tolyl})_3)_2^+]$ cation contains an iridium(I) atom in a distorted trigonal bipyramidal geometry. The two axial (mutually *trans*) Ir–P distances are Ir(1)–P(1) = 2.374(5) and Ir(1)–P(2) = 2.363(5) Å (Ir–P(av) = 2.368 Å as compared to 2.364 Å in the PPh_3 analog[16]). The interligand angle is P(1)–Ir(1)–P(2) = 172.8(2) Å. The three equatorial carbonyl ligands are associated with Ir–CO distances of Ir(1)–C(11) = 2.012(28), Ir(1)–C(21) = 1.921(20) and Ir(1)–C(31) = 1.921(21) Å (Ir–CO(av) = 1.951 Å as compared to 1.926 Å in the PPh_3 analog[16]). The Ir–C–O systems are all close to linear (178.1(23), 175.5(18), 174.5(20)°, sequentially), with associated C–O distances of 1.098(34), 1.118(28) and 1.157(27) Å (C–O(av) = 1.124 Å). Angles between the equatorial ligands are C(11)–Ir(1)–C(21) = 129.7(9)°, C(11)–Ir(1)–C(31) = 118.9(9)° and C(21)–Ir(1)–C(31) = 111.2(9)°. This deviation from 3-fold symmetry (ideally D_{3h}) is surprising but follows that found in the $[Ir(CO)_3(PPh_3)_2^+]$ cation (115.6(6)°, 121.3(6)° and 123.0(7)°).

The $[HSO_4^-]$ ion is undergoing substantial librational motion (or could even be disordered). The four independent sulfur–oxygen distances (in order of increasing bond length) are S(1c)–O(3c) = 1.312(43) Å, S(1c)–O(1c) = 1.411(29) Å, S(1c)–O(4c) = 1.449(43) Å and S(1c)–O(2c) = 1.492(34) Å. As is common for tetrahedral or pseudotetrahedral XO_4^{n-} type anions, the libration (or disorder) leads to a wide range in the observed O–S–O angles (from O(2c)–S(1c)–O(4c) = 100.8(20)° through to O(3c)–S(1c)–O(4c) = 124.9(33)°). We are reluctant to assign any chemical significance to these variations and conclude that we are unable to determine the location of the hydrogen atom in the HSO_4^- anion.

Discussion

Reactions with carbon monoxide are important in many catalytic reactions. Hydroformylation involves carbonylation of an alkyl to an acyl group. This reaction is modeled by the reaction of *trans*-Ir(CO)(Me)(P(*p*-

tolyl)$_3$)$_2$ with CO.

$$\mathit{trans}\text{-Ir(CO)(Me)L}_2 \xrightarrow{\text{CO}} \text{Ir(CO)}_2\text{(Me)L}_2 \xrightarrow{\text{CO}}$$
$$\text{Ir(CO)}_2\text{(C(O)Me)L}_2 \xrightarrow{\text{CO}} \text{Ir(CO)}_3\text{(C(O)Me)L} + \text{L} \quad (4)$$

$$\text{L} = \text{P}(p\text{-tolyl})_3$$

Reaction 4 is completely analogous to that previously reported for the PPh_3 analogue,[6b,25] but with further dissociation of one P(*p*-tolyl)$_3$ ligand. Carboalkoxylation of an alkene involves a step where CO inserts into a metal alkoxo bond to form a carboalkoxo group. Carbonylation of the benzyl alkoxo complex, Ir(CO)(OCH_2Ph)(P(*p*-tolyl)$_3$)$_2$, leads to a carboalkoxo complex similar to complexes previously reported for a number of alkoxo iridium complexes with PPh_3 ligands.[6b,25]

$$\text{Ir(CO)(OCH}_2\text{Ph)(P(}p\text{-tolyl)}_3)_2 + 2\text{CO} \rightarrow$$
$$\text{Ir(C(O)OCH}_2\text{Ph)(CO)}_2\text{(P(}p\text{-tolyl)}_3)_2 \quad (5)$$

In other catalytic reactions such as the water-gas shift reaction, oxidation of CO to CO_2 is important. Reaction of the hydroxy complex, *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$, with CO provides an example of such a carbonylation.

$$2[\mathit{trans}\text{-Ir(CO)(OH)L}_2] + 5\text{CO} \rightarrow$$
$$\text{Ir}_2\text{(CO)}_6\text{L}_2 + \text{CO}_2 + \text{H}_2\text{O} + 2\text{L} \quad (6)$$

$$\text{L} = \text{P}(p\text{-tolyl})_3$$

The iridium dimer, CO_2, H_2O and free P(*p*-tolyl)$_3$ were all identified in the product mixture. Although no intermediates could be identified, the products could be formed through the following sequence:

$$\mathit{trans}\text{-Ir(CO)(OH)L}_2 + 2\text{CO} \rightleftharpoons \text{Ir(CO)}_2\text{(C(O)OH)L}_2 \quad (7)$$

$$\text{Ir(CO)}_2\text{(C(O)OH)L}_2 \rightarrow \text{HIr(CO)}_2\text{L}_2 + \text{CO}_2 \quad (8)$$

$$\text{HIr(CO)}_2\text{L}_2 + \mathit{trans}\text{-Ir(CO)(OH)L}_2 \xrightarrow{\text{CO}}$$
$$\text{H}_2\text{O} + \text{Ir}_2\text{(CO)}_6\text{L}_2 + 2\text{L} \quad (9)$$

$$\text{L} = \text{P}(p\text{-tolyl})_3$$

Reactions 7–9 account for the four observed products in a sequence that is similar to that suggested for the water-gas shift reaction. Carbonylation of platinum hydroxide complexes to yield hydroxycarbonyl species has been previously reported.[26] Decarboxylation of an iridium hydroxycarbonyl has also been reported.[27] The iridium dimer, $Ir_2(CO)_6(PPh_3)_2$, was also formed in carbonylation of *trans*-Ir(CO)(OMe)(P(*p*-tolyl)$_3$)$_2$ and *trans*-Ir(CO)(OC_6H_4Me)(P(*p*-tolyl)$_3$)$_2$.[28] No CO_2 or CH_3OH is formed in the carbonylation of the methoxy complex, indicating a different reaction sequence. However, the observation of creosol and $Ir(CO)_2(H)$(P(*p*-tolyl)$_3$)$_2$ for carbonylation of *trans*-Ir(CO)(OC_6H_4Me)(P(*p*-tolyl)$_3$)$_2$ supports a sequence similar to reactions 7–9. The fate of the OMe upon carbonylation of *trans*-Ir(CO)(OMe)(P(*p*-tolyl)$_3$)$_2$ was not determined; free P(*p*-tolyl)$_3$, P(O)(*p*-tolyl)$_3$ and $Ir(C(O)Me)(CO)_2$(P(*p*-tolyl)$_3$)$_2$ were also products in this reaction.

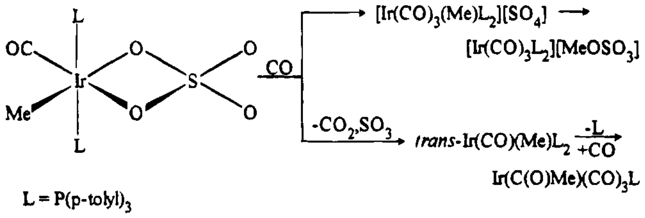

Figure 4. Reaction of CO with Ir(CO)(Me)(SO_4)(P(*p*-tolyl)$_3$)$_2$.

Carbonylation of iridium(I) complexes produces insertion products (reactions 4 and 5) and CO oxidation products. The reaction course appears to be affected by subtle changes in the iridium coordination sphere. For example, carbonylation of *trans*-Ir(CO)(OMe)(PPh_3)$_2$ gave exclusively the carbomethoxy complex, Ir(C(O)OMe)(CO)$_2$(PPh_3)$_2$,[6b] while under identical conditions carbonylation of *trans*-Ir(CO)(OMe)(P(*p*-tolyl)$_3$)$_2$ gives none of the carbomethoxy complex. The products of these reactions are readily distinguished by spectroscopic properties and solubility. $Ir_2(CO)_6$(P(*p*-tolyl)$_3$)$_2$ is only sparingly soluble in THF or toluene. To form the iridium(0) dimer an electron transfer must occur. For the PPh_3 complex, carbonylation was shown to occur through $Ir(CO)_3(PPh_3)_2^+$ which was attacked by the OMe^- nucleophile.[6b] It is possible that the better donor P(*p*-tolyl)$_3$ ligands stabilize the cation such that nucleophilic attack by OMe is not favored and electron transfer is observed instead. Similarly *trans*-Ir(CO)(OH)(PPh_3)$_2$ produces $Ir(CO)_2(OH)(PPh_3)_2$ reversibly, while *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ reacts readily with CO irreversibly according to reaction 6. Possibly the small increase in electron density at iridium for the P(*p*-tolyl)$_3$ complex is sufficient for formation of the hydroxycarbonyl.

Carbonylation of the Ir(III) complex, Ir(CO)(Me)(SO_4)(P(*p*-tolyl)$_3$)$_2$, produces Ir(I) complexes (Figure 4): $Ir(CO)_3$(P(*p*-tolyl)$_3$)$_2^+$ and those based on carbonylation of *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ (reaction 4). For each product the SO_4^{2-} is removed from the iridium coordination sphere. The cation formation is similar to that previously reported for the hydroxy analogue.[6d] An ^1H NMR spectrum recorded during the carbonylation shows that the triplet from the methyl collapses to a singlet (1.2 ppm, nearly coincident with the starting triplet) and then shifts to a broad resonance at 4.5 ppm. This resonance would be consistent with formation of $CH_3OSO_3^-$,[29] but during recrystallization the CH_3 is hydrolyzed to $HOSO_3^-$. The second pathway for carbonylation of Ir(CO)(Me)(SO_4)(P(*p*-tolyl)$_3$)$_2$ results in the same products as those for carbonylation of *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ apparently by reduction and loss of the sulfate. Carbon dioxide is formed (IR absorption at 2336 cm^{-1}). The products would be balanced by loss of SO_3, but we have not observed SO_3.

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(28) For the OC_6H_4Me complex $Ir(CO)_2(H)$(P(*p*-tolyl)$_3$)$_2$ was also identified as a product.

(29) The resonance is close to that observed for dimethyl sulfate (3.87 ppm),[30] but we have no other characterization data.

(30) Serial No. 307, Selected NMR Spectral Data, Vol. 1, 1978.

Conclusions

Carbonylation of iridium complexes model steps important in several catalytic reactions. While a number of different reactions have been observed, in each case reaction with CO changes a harder oxygen-donor ligand for a softer carbon-donor ligand. These reactions suggest an inherent reactivity arising from hard ligands coordinated to organoiridium centers.

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Supplementary Material Available: Complete listings of interatomic distances, bond angles, anisotropic thermal parameters, and calculated positions for hydrogen atoms for the two structural studies (7 pages). Ordering information is given on any current masthead page.

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