Inorg. Chem. **1996,** *35,* 3683−3686 **3683**

Reactions of $Ir(CO)(H)(P(p\text{-tolyl})_3)_3$ with SO_2 and O_2 Mixtures and with H_2SO_4, Formation of a Sulfate-Bridged Dimer, and Crystal and Molecular Structure of $Ir(CO)(H)(SO_2)(P(p\text{-tolyl})_3)_2$

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Received September 26, 1995⊗

Reactions of $HIr(CO)(P(p\text{-tolyl})_3)_3$ with SO_2, O_2, mixtures of SO_2 and O_2, and H_2SO_4 are described. Reactions with mixtures of SO_2/O_2 and with H_2SO_4 lead to a common product, $Ir_2H_4(\mu\text{-}SO_4)(P(p\text{-tolyl})_3)_6$, where a bidentate SO_4^{2-} bridges the iridium centers. The complex $HIr(CO)(P(p\text{-tolyl})_3)_3$ is stable toward O_2 but reacts readily with SO_2 to give $HIr(CO)(SO_2)(P(p\text{-tolyl})_3)_2$, which was characterized by a crystal structure determination. The species $Ir(CO)(H)(SO_2)(P(p\text{-tolyl})_3)_2$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 10.675(1)$ Å, $b = 10.882(1)$ Å, $c = 17.740(2)$ Å, $\alpha = 84.626(10)°$, $\beta = 83.432(10)°$, $\gamma = 87.043(10)°$, $V = 2036.6(3)$ Å^3, and $Z = 2$. Diffraction data (Mo Kα, $2\theta = 4.5{-}45.0°$) were collected on a Siemens R3m/V diffractometer, and the structure was refined to $R = 3.00\%$ for 4218 independent reflections with $F_o > 6\sigma(F_o)$. The five-coordinate iridium(I) center has a distorted environment (closer to trigonal bipyramidal than to square pyramidal) with H(1)−Ir(1)−S(1) = 171.4(23)°. Bond lengths are Ir−P = 2.303(2) and 2.320(2) Å, $Ir{-}SO_2 = 2.372(2)$ Å, Ir−CO = 1.906(8) Å, and Ir−H = 1.65(7) Å. The SO_2 ligand has bond distances of S(1)−O(1) = 1.442(7) and S(1)−O(2) = 1.441(7) Å, with O(1)−S(1)−O(2) = 113.1(4)°.

Reactions of hydride complexes are fundamental for organometallic chemistry and for homogeneous catalysis.[1,2] Relatively few studies have focused on reactions of metal hydrides with species such as O_2, SO_2, or H_2SO_4 because strong oxidants and a metal hydride are inherently reactive. A dispute[3] regarding the reaction of SO_2 with $Ir(CO)(H)(PPh_3)_3$ was recently resolved.[4c]

$$Ir(CO)(H)(PPh_3)_3 + SO_2 \rightarrow Ir(CO)(H)(SO_2)(PPh_3)_2 + PPh_3 \rightleftarrows Ir(CO)(SO_2H)(PPh_3)_2 + PPh_3$$

The insertion product, $Ir(CO)(SO_2H)(PPh_3)_2$, is similar to the insertion products we have observed for various hydroxide and alkoxide complexes.[4] Changing from PPh_3 to $P(p\text{-tolyl})_3$ frequently improves solubility to allow better characterization of reaction products. As a part of our continuing studies[4] of reactions of sulfur dioxide with iridium complexes, we examined the reactions of $Ir(CO)(H)(P(p\text{-tolyl})_3)_3$ with SO_2, O_2, mixtures of SO_2 and O_2, and H_2SO_4.

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 O_2 (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 argon-filled inert-atmosphere glovebox. Infrared spectra of KBr pellets and solutions were measured on a Mattson Polaris FTIR instrument in the 2200−400 cm^{-1} region. NMR spectra were recorded on a Varian VXR 400 spectrometer and were referenced to the deuterated solvent for ^1H spectra or to H_3PO_4 for ^{31}P spectra.

Preparation of $Ir(CO)(H)(P(p\text{-tolyl})_3)_3$. In an argon atmosphere, *trans*-$Ir(CO)(Cl)(P(p\text{-tolyl})_3)_2$[5] (101 mg, 0.117 mmol) and $P(p\text{-tolyl})_3$ (177 mg) were placed in a Schlenk flask equipped with a gas adapter. The reaction vessel was sealed and transferred to a hood, where 30 mL of dearated ethanol was added with a positive N_2 pressure. The solution was brought to reflux, and a dearated solution of $NaBH_4$ (100 mg) in absolute ethanol (25 mL) was added to the flask. The solution was allowed to reflux for a further 15 min under a nitrogen atmosphere. The reaction mixture was cooled under N_2 and allowed to stir overnight with a reduced volume of ethanol (40 mL total remaining). After 15 h, a light yellow powder had precipitated. The solid was filtered off (109 mg, 0.0906 mmol, 82.1% yield) and transferred to an argon atmosphere glovebox. The product was characterized by IR spectroscopy [ν_{CO} (KBr) 1925 (vs) cm^{-1}, ν_{Ir-H} 2050 (s) cm^{-1}] and NMR spectroscopy [^{31}P NMR ($CDCl_3$) 12.2 ppm; ^1H NMR resonances −10.7 (q) [$J = 20$ Hz], 2.4 (s), 7.0−7.2 (m) ppm]. The characterization data are similar to those previously reported.[6]

Preparation of $Ir(CO)(H)(SO_2)(P(p\text{-tolyl})_3)_2$. In an argon atmosphere, $Ir(CO)(H)(P(p\text{-tolyl})_3)_3$ was suspended in hexanes in a Schlenk flask equipped with a gas adapter. The reaction vessel was sealed and transferred to a hood where 1 atm of SO_2 was passed over the solution for 20 min, turning the yellow solution orange. The orange precipitate was filtered off in the hood and transferred into the drybox. An infrared spectrum in KBr showed ν_{CO} 2064 (vs) cm^{-1}, ν_{Ir-H} 1965 (s) cm^{-1}, and ν_{SO} 1037, 1177 cm^{-1}. NMR: ^1H, −2.8 (t) ppm; ^{31}P, 16.8 ppm (−7.4 ppm for free $P(p\text{-tolyl})_3$). On the basis of the data, the product is assigned as $Ir(CO)H(P(p\text{-tolyl})_3)_2(SO_2)$. This is consistent with the previously reported $Ir(CO)H(PPh_3)_2(SO_2)$ complex [ν_{CO} 2050 (vs), ν_{Ir-H} 1965 (s), ν_{SO} 1037, 1175 cm^{-1}).[3] NMR: ^{31}P, 16.7 ppm; ^1H, −2.8 (t)

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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ppm, $J_{P-H} = 18.0$ Hz]. A saturated solution of the SO$_2$ complex in benzene was placed in one side of a H-tube, and hexanes were placed in the other. After 5 days, crystals suitable for X-ray crystallography formed.

Preparation of Ir$_2$(μ-SO$_4$)(H)$_4$(P(p-tolyl)$_3$)$_6$. Ir(CO)H(P(p-tolyl)$_3$)$_3$ (0.152 g) was dissolved in 30 mL of THF in an argon atmosphere. The Schlenk flask was sealed and transferred to a hood, where 5 drops of dearated H$_2$SO$_4$ were added under a positive N$_2$ pressure. The resulting solution was stirred for 1 h (less time may result in the presence of starting material in the reaction products), after which the volume of THF was reduced (15 mL), followed by the addition of dearated distilled water to precipitate a yellow-white solid (0.121 g). Attempts to recrystallize this product were unsuccessful (benzene/hexane; THF/hexane; slow evaporation of benzene; CD$_2$Cl$_2$ in a freezer).

Reaction of SO$_2$ and O$_2$ with Ir(CO)(H)(P(p-tolyl)$_3$)$_3$ or O$_2$ with Ir(CO)(H)(SO$_2$)(P(p-tolyl)$_3$)$_2$. These two reactions are similar in producing a major product in a mixture. For reaction of Ir(CO)(H)(P(p-tolyl)$_3$)$_3$ with SO$_2$ and O$_2$, a saturated solution of Ir(CO)H(P(p-tolyl)$_3$)$_3$ in CD$_2$Cl$_2$ was prepared under an argon atmosphere. An NMR tube equipped with a vacuum adapter was transferred to the high-vacuum line, where 50 Torr of SO$_2$ was added to the frozen solution and the solution was thawed. Next the solution was refrozen, and 50 Torr of O$_2$ was added. The NMR tube was sealed, the contents were thawed, and an NMR spectrum was recorded. ^{1}H NMR: −11 (dtd), −9.6 (qd), −7.3 (m), −2.8 (t), 2.3−2.4 (m), 6.8−7.9 (m) ppm. The −2.8 (t) ppm signal is assigned to the previously prepared Ir(CO)H(SO$_2$)(P(p-tolyl)$_3$)$_2$ complex. The ^{31}P NMR spectrum resulted in several resonances as well: −7.4 (br), −5, −0.4, 16.8, 28 ppm. The −7.4 ppm resonance is assigned to free phosphine, the 16.8 ppm resonance to Ir(CO)H(SO$_2$)(P(p-tolyl)$_3$)$_2$, and the 28 ppm resonance to phosphine oxide. The solution was allowed to remain in the NMR tube for 3 days, and another NMR spectrum was recorded. The −11 (dtd) ppm resonance [J = 100, 18, 3.6 Hz] and the −9.6 (qd) ppm resonance [16.4, 3.6] remained in the ^{1}H NMR spectrum. The hydride peaks at −11 (dtd) and −9.6 (qd) ppm were in a ratio of 1:1. Two triplets at −19.5 and −5.3 ppm were present in smaller, variable amounts. The solvent was removed, and an IR (KBr) spectrum was recorded giving rise to two absorbances in the Ir−H stretching region of 2002 and 2050 (sh) and multiple absorbances in the SO region of 448, 568, 657, 729, 910, 1115, and 1176 cm^{-1} but no indication of a C≡O stretch.

Reaction of Ir(CO)(H)(SO$_2$)(P(p-tolyl)$_3$)$_2$ with O$_2$ proceeded similarly.

(a) In an argon atmosphere, a dilute solution of Ir(CO)H(SO$_2$)(P(p-tolyl)$_3$)$_2$ in toluene was prepared. The sealed Schlenk flask was transferred to a hood and O$_2$ was passed over the solution with stirring for 2 h. An IR spectrum was recorded giving rise to two absorbances at 2036 (s) and 2070 (sh) cm^{-1}.

(b) An NMR spectroscopic study of the same reaction as in part a was performed. In an argon atmosphere, a saturated solution of Ir(CO)H(SO$_2$)(P(p-tolyl)$_3$)$_2$ in CD$_2$Cl$_2$ was prepared. The NMR tube was removed from the box, and O$_2$ was bubbled into the solution for 5 min. The solution remained under an O$_2$ atmosphere for 24 h before an NMR spectrum was recorded. The resonances in the ^{31}P NMR spectrum are as follows: −19.4, −3.5, −3.4, −1.6, −0.4, 6.4, 6.9, and 28 ppm, with the major resonances being at 28 and −3.4 ppm. The 28 ppm resonance is attributed to phosphine oxide.

Collection of X-ray Diffraction Data for Ir(CO)(H)(SO$_2$)(P(p-tolyl)$_3$)$_2$. A single crystal, with approximate dimensions of 0.2 × 0.2 × 0.3 mm, was selected for the diffraction study. It was sealed in a thin-walled glass capillary and aligned on a Siemens R3m/V diffractometer with its extended direction close to collinear with the ϕ axis. Crystal alignment, determination of cell dimensions, and data collection (coupled θ(crystal)−2θ(counter) mode) were carried out as described previously;[7] details are provided in Table 1.

The crystal belongs to the triclinic system ($\bar{1}$ or C_i symmetry of diffraction only), possible space groups being the noncentrosymmetric $P1$ (C_1^1; No. 1) and the centrosymmetric $P\bar{1}$ (C_i^1; No. 2). The latter, centrosymmetric, possibility was selected on the basis of (i) intensity statistics and (ii) its far greater frequency of occurrence, particularly with $Z = 2$.[8] This choice was confirmed by the successful solution and refinement of the structure in this higher-symmetry space group. All reflections were corrected for Lorentz and polarization effects and for absorption.

Table 1. Crystallographic Data for Ir(CO)(H)(SO$_2$)(P(p-tolyl)$_3$)$_2$

empirical formula C$_{43}$H$_{43}$IrO$_3$P$_2$S	fw = 894.0
$a = 10.675(1)$ Å	space group = $P\bar{1}$ (No. 2)
$b = 10.882(1)$ Å	$T = 297$ K
$c = 17.740(2)$ Å	$\lambda = 0.710\ 73$ Å
$\alpha = 84.626(10)°$	$\rho_{calc} = 1.458$ Mg/m^3
$\beta = 83.432(10)°$	$\mu = 3.426$ mm^{-1}
$\gamma = 87.043(10)°$	$R(F_o)^a = 3.00\%$
$V = 2036.6(3)$ Å^3	$R_w(F_o) = 3.94\%$
$Z = 2$	

^{a} The R values are for observed data.

Solution and Refinement of the Structure. All calculations were performed with the Siemens SHELXTL PLUS program package.[9] The analytical scattering factors for the neutral atoms were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.[10] The structure was solved by a combination of Patterson, difference-Fourier, and least-squares refinement methods. Convergence was reached with $R(F) = 3.00\%$ and $R_w(F) = 3.94\%$ for those 4218 reflections with $F_o > 6\sigma(F_o)$. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydride ligand (H(1)) was located and refined, while the remaining organic hydrogen atoms were placed in optimized locations with d(C−H) = 0.96 Å.[11] Final coordinates are collected in the Supporting Information.

Results and Discussion

Reaction with SO$_2$. The hydride, Ir(CO)(H)(P(p-tolyl)$_3$)$_3$, readily reacted with SO$_2$ to form Ir(CO)(H)(SO$_2$)(P(p-tolyl)$_3$)$_2$. This complex is characterized by IR and ^{31}P and ^{1}H NMR data as the hydride. The data are completely consistent with those previously reported for Ir(CO)(H)(SO$_2$)(PPh$_3$)$_2$.[3,4] For the synthesis as a suspension in hexane, no evidence is seen for the inserted complex, Ir(CO)(SO$_2$H)(P(p-tolyl)$_3$)$_2$; the expected ^{1}H resonance at ∼4.5 ppm and the ^{31}P signal at ∼20 ppm were absent. To confirm the structural assignment of this complex and the previous assignments of the PPh$_3$ analogue, we determined the structure of Ir(CO)(H)(SO$_2$)(P(p-tolyl)$_3$)$_2$.

Description of the Molecular Structure of Ir(CO)(H)(SO$_2$)(P(p-tolyl)$_3$)$_2$. The crystal consists of ordered molecular units of Ir(CO)(H)(SO$_2$)(P(p-tolyl)$_3$)$_2$, separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. The overall molecular geometry and labeling of atoms are depicted in Figure 1; selected interatomic distances and angles are collected in Table 2.

The central iridium(I) atom has an irregular coordination environment (local symmetry m or C_s) almost midway between trigonal bipyramidal (with the H and SO$_2$ ligands in axial sites) and square pyramidal (with the CO ligand in the unique axial site). There are two particularly large interligand angles, H(1)−Ir(1)−S(1) = 171.4(23)° and P(1)−Ir(1)−P(2) = 153.9(4)°, which might be taken as indicative of *trans*-basal angles in a square pyramidal geometry. However, one would then expect the P−Ir−P angle (which is associated with the most bulky ligands) to be more obtuse than the H−Ir−S angle; this is not the case. Furthermore, the apical−basal angle C(11)−Ir(1)−H(1) is acute (79.1(24)°), rather than obtuse. We therefore

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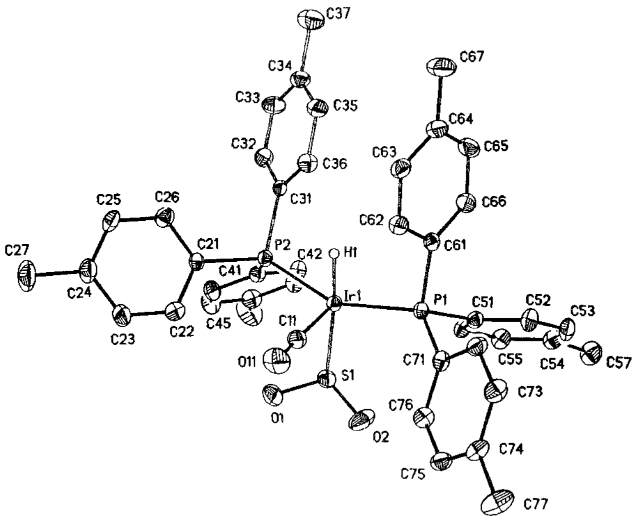

Figure 1. Molecular geometry and labeling of atoms for $Ir(CO)(H)(SO_2)(P(p\text{-tolyl})_3)_2$ shown by an ORTEP2 diagram with 20% probability contours for the atomic vibration ellipsoids. Hydrogen atoms (other than the hydride ligand, H(1)) have been omitted for the sake of clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $Ir(CO)(H)(SO_2)(P(p\text{-tolyl})_3)_2$

(A) Iridium−Ligand Distances			
Ir(1)−H(1)	1.648(69)	Ir(1)−P(1)	2.303(2)
Ir(1)−P(2)	2.320(2)	Ir(1)−S(1)	2.372(2)
Ir(1)−C(11)	1.906(8)		
(B) Phosphorus−Carbon Distances			
P(1)−C(51)	1.822(7)	P(2)−C(21)	1.831(7)
P(1)−C(61)	1.821(7)	P(2)−C(31)	1.818(7)
P(1)−C(71)	1.816(7)	P(2)−C(41)	1.820(7)
(C) Sulfur-Oxygen and Carbon-Oxygen Distances			
S(1)−O(1)	1.442(7)	C(11)−O(11)	1.129(10)
S(1)−O(2)	1.441(7)		
(D) Angles around Iridium Atom			
H(1)−Ir(1)−P(1)	78.2(27)	H(1)−Ir(1)−P(2)	85.8(27)
P(1)−Ir(1)−P(2)	153.9(1)	H(1)−Ir(1)−S(1)	171.4(23)
P(1)−Ir(1)−S(1)	103.7(1)	P(2)−Ir(1)−S(1)	95.2(1)
H(1)−Ir(1)−C(11)	79.1(24)	P(1)−Ir(1)−C(11)	95.9(3)
P(2)−Ir(1)−C(11)	101.2(3)	S(1)−Ir(1)−C(11)	92.3(2)
(E) Angles around Phosphorus Atoms			
Ir(1)−P(1)−C(51)	118.1(2)	C(51)−P(1)−C(61)	106.6(3)
Ir(1)−P(1)−C(61)	101.6(2)	C(51)−P(1)−C(71)	102.3(3)
Ir(1)−P(1)−C(71)	121.9(2)	C(61)−P(1)−C(71)	104.8(3)
Ir(1)−P(2)−C(21)	118.3(2)	C(21)−P(2)−C(31)	103.9(3)
Ir(1)−P(2)−C(31)	108.9(2)	C(21)−P(2)−C(41)	105.4(3)
Ir(1)−P(2)−C(41)	115.0(2)	C(31)−P(2)−C(41)	104.0(3)
(F) Angles within $Ir-SO_2$ and Ir−C−O Systems			
Ir(1)−S(1)−O(1)	107.2(2)	Ir(1)−S(1)−O(2)	107.2(2)
O(1)−S(1)−O(2)	113.1(4)	Ir(1)−C(11)−O(11)	175.3(7)
(G) P−C(ipso)−C(ortho) Angles			
P(2)−C(21)−C(22)	119.7(6)	P(2)−C(21)−C(26)	123.1(5)
P(2)−C(31)−C(32)	122.4(5)	P(2)−C(31)−C(36)	120.4(5)
P(2)−C(41)−C(42)	119.4(5)	P(2)−C(41)−C(46)	123.0(5)
P(1)−C(51)−C(52)	120.6(5)	P(1)−C(51)−C(56)	121.0(5)
P(1)−C(61)−C(62)	118.3(5)	P(1)−C(61)−C(66)	123.1(5)
P(1)−C(71)−C(72)	122.3(5)	P(1)−C(71)−C(76)	120.0(5)
(H) C−C(ipso)−C Angles			
C(22)−C(21)−C(26)	117.2(7)	C(52)−C(51)−C(56)	118.3(7)
C(32)−C(31)−C(36)	117.2(6)	C(62)−C(61)−C(66)	118.3(6)
C(42)−C(41)−C(46)	117.6(6)	C(72)−C(71)−C(76)	117.7(6)

choose to discuss the molecule within the framework of the trigonal bipyramidal description.

The axial sites are then occupied by a hydride ligand (with Ir(1)−H(1) = 1.65(7) Å) and an S-bonded sulfur dioxide ligand (Ir(1)−S(1) = 2.372(2) Å). The equatorial sites are occupied by two tri-*p*-tolylphosphine ligands (Ir(1)−P(1) = 2.303(2) Å and Ir(1)−P(2) = 2.320(2) Å) and a carbonyl ligand (Ir(1)−C(11) = 1.906(8) Å, with C(11)−O(11) = 1.129(10) Å and Ir(1)−C(11)−O(11) = 175.3(7)°). The angle between the apical ligands (H(1)−Ir(1)−S(1) = 171.4(23)°) is close to 180°, but is of limited precision. The diequatorial angles are irregular (P(1)−Ir(1)−P(2) = 153.9(1)°, P(2)−Ir(1)−C(11) = 101.2(3)°, and P(1)−Ir(1)−C(11) = 95.9(3)°). The iridium atom lies +0.328 Å from the P(1)···P(2)···C(11) plane, with other relevant displacements of atoms being +2.671 Å for S(1) and −1.32 Å for H(1). Clearly, the equatorial ligands are displaced so as to encroach on the cone angle normally occupied by an axial ligand more substantial than a hydride ligand; thus we have H(1)−Ir(1)−P(1) = 78.2(27)°, H(1)−Ir(1)−C(11) = 79.1(24)°, and H(1)−Ir(1)−P(2) = 85.8(27)°. This observation is in keeping with studies on $Rh(H)(PPh_3)_4$[12] and $Rh(H)(AsPh_3)(PPh_3)_3$,[13] in which the arrangement of triphenylpnictogen ligands is such as to produce an essentially tetrahedral RhP_4 or $RhAsP_3$ moiety, with the hydride ligand appearing to have no obvious stereochemical effect on the geometry.

The sulfur dioxide ligand is S-bonded to the iridium(I) center and has equivalent sulfur−oxygen bond lengths (S(1)−O(1) = 1.442(7) Å and S(1)−O(2) = 1.441(7) Å). The sulfur atom has a pyramidal geometry with bond angles of O(1)−S(1)−O(1) = 113.1(4)°, Ir(1)−S(1)−O(1) = 107.2(2)°, and Ir(1)−S(1)−O(2) = 107.2(2)°.

The tri-*p*-tolylphosphine ligands have the expected P−C(ipso) distances, ranging from 1.816(7) to 1.831(7) Å and averaging 1.821 Å. The internal angles at the ipso carbon atoms are all less than 120° (ranging from C(32)−C(31)−C(36) = 117.2(6)° to C(62)−C(61)−C(66) = 118.3(6)° and averaging 117.7°; this distortion of the carbocyclic ring from D_{6h} to C_{2v} symmetry is well established[14] and is the result of the electronegative phosphorus atom at the ipso position.[15] One unexpected result is the large range of Ir−P−C(ipso) angles (from Ir(1)−P(1)−C(61) = 101.6(2) to 121.9(2)°). In most triphenylphosphine complexes these angles are greater than the regular sp^3 angle of 109.5°, with the C−P−C angles typically being less than 109.5°. In the present structural study, the anomalous angles are Ir(1)−P(1)−C(61) = 101.6(2)° and Ir(1)−P(2)−C(31) = 108.9(2)°; in each case, these small angles result from the phenyl group being displaced from its regular position into the cavity around the axial hydride ligand.

All other distances and angles are self-consistent and are within accepted norms. This structural study provides the first example of an iridium complex containing both hydride and SO_2 ligands. It also provides the first example of a five-coordinate SO_2 adduct that is trigonal bipyramidal rather than square planar.[4] In this complex, the SO_2 is pyramidal as in the previous examples.[4,16]

Reaction of $Ir(CO)(H)(P(p\text{-tolyl})_3)_3$ with SO_2 and O_2. Reaction of $Ir(CO)(H)(P(p\text{-tolyl})_3)_3$ with O_2 in solution ($CDCl_3$ or CH_2Cl_2) results in a small amount of a product consistent with the equilibrium.

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$$\mathrm{Ir(CO)(H)(P(}p\text{-}\mathrm{tolyl})_3)_3 + \mathrm{O_2} \rightleftarrows \mathrm{Ir(CO)(H)(O_2)(P(}p\text{-}\mathrm{tolyl})_3)_2 + \mathrm{P(}p\text{-}\mathrm{tolyl})_3$$

The ^{1}H NMR characterization (−11.0 (t) ppm, $J_{\mathrm{P-H}} = 7.6$) is consistent with a small amount of Ir(CO)(H)(O$_2$)(P(p-tolyl)$_3$)$_2$ being formed, although the amount was less than 5% after 3 days. Basically, Ir(CO)(H)(P(p-tolyl)$_3$)$_3$ can be considered stable to oxygen.

Reaction of Ir(CO)(H)(P(p-tolyl)$_3$)$_3$ with SO$_2$ and O$_2$ produces a number of products; the same mixture is obtained from Ir(CO)(H)(SO$_2$)(P(p-tolyl)$_3$)$_2$ reacting with O$_2$ and from Ir(CO)(H)(P(p-tolyl)$_3$)$_3$ reacting with mixtures of SO$_2$ and O$_2$. Since Ir(CO)(H)(SO$_2$)(P(p-tolyl)$_3$)$_2$ is observed when Ir(CO)(H)(P(p-tolyl)$_3$)$_3$ reacts with SO$_2$ and O$_2$, it is likely the common intermediate. Both free P(p-tolyl)$_3$ and OP(p-tolyl)$_3$ indicate phosphine lability in the system. A major iridium-containing product (described fully below) and two minor products are apparent. The minor products contain two equivalent P(p-tolyl)$_3$ ligands and a hydride (triplets at −19.5 and −5.3 ppm). Conversion of SO$_2$ and O$_2$ to sulfate is commonly observed on iridium(I) centers,[4,18] and it is likely that all of the products are iridium(III) sulfates. The minor products could have the sulfate group as bidentate on one iridium or μ-η^4 bridging two iridium centers, but the amounts are too low for definitive characterization.

Reaction of Ir(CO)(H)(P(p-tolyl)$_3$)$_3$ with H$_2$SO$_4$. To provide further information on the possible products from reactions of Ir(CO)(H)(P(p-tolyl)$_3$)$_3$ with SO$_2$ and O$_2$, the iridium hydride complex was reacted with sulfuric acid. A saturated solution of Ir(CO)H(P(p-tolyl)$_3$)$_3$ in CD$_2$Cl$_2$ was prepared in an NMR tube in the inert-atmosphere glovebox. The NMR tube was transferred to a hood, and a drop of dearated H$_2$SO$_4$ was added, causing the formation of a gray suspension. A ^{1}H NMR spectrum of the resulting solution was recorded giving rise to two hydride resonances at −15.2 (dtd) [J = 113.6, 18.4, 3.6 Hz] and −13.3 (qd) ppm [J = 16.8, 3.6 Hz] in a ratio of 1:1. The ^{31}P NMR spectrum only combined two resonances as well; −3.3 (t) [J = 14.6 Hz] and −0.3 (d) ppm [J = 14.6 Hz] in a ratio of 2:1. This reaction was also performed as a synthetic reaction (see Experimental Section); unfortunately, all efforts to crystallize the product failed.

Nature of the Primary Product. Even in the absence of crystallographic or analytical data, the spectroscopic data unambiguously allow assignment of the structure of the common product as Ir$_2$H$_4$(μ-SO$_4$)(P(p-tolyl)$_3$)$_6$. The required structure is shown in Figure 2. The hydride portion of the NMR spectrum consists of two resonances in a 1:1 ratio. The resonance for H$_a$ is a doublet ($J_{\mathrm{P_a-H_a}}$ = 100 Hz) of triplets ($J_{\mathrm{P_b-H_a}}$ = 18 Hz) of doublets ($J_{\mathrm{H_b-H_a}}$ = 3.6 Hz) at −11.6 ppm as required for the structure shown in Figure 2. The resonance for H$_b$ is a quartet ($J_{\mathrm{P-H_b}}$ = 16.4 Hz) of doublets ($J_{\mathrm{H_a-H_b}}$ = 3.6 Hz) at −9.7 ppm. The three *cis* phosphorus atoms must appear equivalent to give the quartet. The ^{31}P spectrum, proton decoupled, shows a doublet ($J_{\mathrm{P-P}}$ = 14.6 Hz) at −0.5 ppm and a triplet ($J_{\mathrm{P-P}}$ = 14.6 Hz) at −3.3 ppm in a 2:1 ratio. These NMR data require the geometry shown in Figure 2. The infrared data are also consistent with this structure. Two Ir−H stretches are observed at 2050 (sh) and 2002 (s) cm^{-1}. The bridging sulfate is also confirmed by the infrared spectral data in Table 3, where a comparison is made to a known complex with sulfate bridging two metals.[17] Reaction of H$_2$SO$_4$ with a cobalt complex produced a very similar μ-SO$_4$ complex.[18]

The spectroscopic data, ^{1}H and ^{31}P NMR and IR, are in excellent agreement with the suggested structure (Figure 2). The formation of Ir$_2$H$_4$(μ-SO$_4$)(P(p-tolyl)$_3$)$_6$ from two very different routes also supports this formulation. The reaction of Ir(CO)(H)(P(p-tolyl)$_3$)$_3$ with H$_2$SO$_4$ provides the cleanest route.

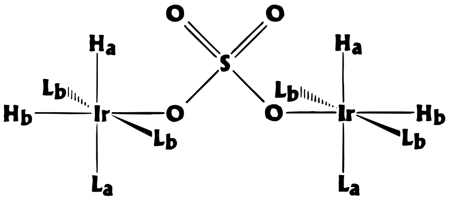

Figure 2. Geometry of the sulfate-bridged dimer, Ir$_2$(H)$_4$(μ-SO$_4$)L$_6$ (L = P(p-tolyl)$_3$), showing the inequivalent phosphorus and hydrogen atoms.

Table 3. Infrared Data in the Sulfate Region for Ir$_2$H$_4$(μ-SO$_4$)(P(p-tolyl)$_3$)$_6$ Compared to Those for Co$_2$(NH$_3$)$_8$(μ-NH$_2$)(μ-SO$_4$)$^{3+}$ [17]

ν_1	ν_2	ν_3	ν_4
	Ir$_2$H$_4$(μ-SO$_4$)(P(p-tolyl)$_3$)$_6$		
910 (br)	448 (br)	1034 (m)	729 (s)
		1178 (sh)	657 (s)
		1115 (s)	568 (m)
	Co$_2$(NH$_3$)$_8$(μ-NH$_2$)(μ-SO$_4$)$^{3+}$		
995 (m)	462 (m)	1050−1060 (m)	641 (s)
		1170 (s)	610 (s)
		1105 (s)	571 (m)

$$2\mathrm{Ir(CO)(H)(P(}p\text{-}\mathrm{tolyl})_3)_3 + \mathrm{H_2SO_4} \rightarrow \mathrm{Ir_2H_4(}\mu\text{-}\mathrm{SO_4)(P(}p\text{-}\mathrm{tolyl})_3)_6 + 2\mathrm{CO}$$

Reaction of Ir(CO)(H)(P(p-tolyl)$_3$)$_3$ with SO$_2$/O$_2$ also provides a route, though other species are also formed and hydrogen must be scavenged. Conversion of SO$_2$ and O$_2$ to sulfate by Ir(I) complexes is commonly observed.[4,19] The minor products from reaction of SO$_2$/O$_2$ with Ir(CO)(H)(P(p-tolyl)$_3$)$_3$ show triplets for the hydrides and likely involve P(p-tolyl)$_3$ dissociation (OP(p-tolyl)$_3$ is observed), perhaps to give sulfate as bidentate on one iridium or μ-η^4, but the amounts observed are too low for definitive characterization.

Conclusion

In this paper we have reported the first crystal structure of an iridium complex containing both hydride and pyramidally coordinated SO$_2$. Reaction of this complex with O$_2$ produces a new complex containing a sulfate bridging two iridium centers. The same complex is prepared in better yield from reaction of H$_2$SO$_4$ with Ir(CO)(H)(P(p-tolyl)$_3$)$_3$.

Acknowledgment. Purchase of the Siemens R3m/V diffractometer was made possible by Grant 89-13733 from the Chemical Instrumentation Program of the National Science Foundation. The Varian VXR-400 NMR instrument was purchased through a grant from the Department of Education (2-2-01011). T.S.J. acknowledges support from the Research Corp. (Grant C2971RR).

Supporting Information Available: Listings of crystal data, atomic coordinates, complete interatomic distances and angles, anisotropic thermal parameters, and calculated positions of hydrogen atoms for the structural study of Ir(CO)(H)(SO$_2$)(P(p-tolyl)$_3$)$_2$ (6 pages). Ordering information is given on any current masthead page.

IC951249Y

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