

**Synthesis and Characterization of New Square Planar Iridium Complexes [*trans*-Ir(CO)L<sub>2</sub>X] (L = PCy<sub>3</sub>, X = OH or OCH<sub>3</sub>; L = P(*p*-tolyl)<sub>3</sub>, X = OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> or O(*p*-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>)): Crystal and Molecular Structures of *trans*-Ir(CO)-(OH)(PCy<sub>3</sub>)<sub>2</sub>, *trans*-Ir(CO)(OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>, and *trans*-Ir(CO)(O-*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>**

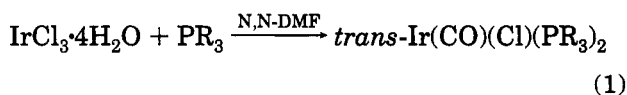
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Three new Ir(I) complexes have been prepared, characterized and studied by X-ray crystallography. No evidence is found for pi-donation from an alkoxy (Ir(CO)(OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>) or an aryloxy (Ir(CO)(O-*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>) to iridium. The phenylmethoxy complex Ir(CO)(OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub> crystallizes in the triclinic space group *P* $\bar{1}$  with *a* = 10.5187(16), *b* = 12.8320(15), *c* = 17.4940(19)Å,  $\alpha$  = 71.447(8),  $\beta$  = 84.907(11),  $\gamma$  = 72.407(11)°, *V* = 2133.8(5)Å<sup>3</sup> and *Z* = 2. The structure was solved and refined to *R* = 2.48% for 4567 reflections with *F*<sub>o</sub> > 6σ(*F*<sub>o</sub>). Interatomic distances of note are Ir-P = 2.306(2) and 2.334(2), Ir-CO = 1.806(6) and Ir-O = 2.022(4)Å. The *p*-cresolate derivative crystallizes as the *p*-cresol adduct Ir(CO)(OC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>·CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH in the monoclinic space group *P*2<sub>1</sub>/*c* with *a* = 21.1172(28), *b* = 12.0167(15), *c* = 22.5658(31)Å,  $\beta$  = 117.180(10)°, *V* = 5094.0(12)Å<sup>3</sup> and *Z* = 4. The structure was refined to *R* = 4.26% for 3296 reflections with *F*<sub>o</sub> > 6σ(*F*<sub>o</sub>). Interatomic distances include Ir-P = 2.322(4) and 2.330(4), Ir-CO = 1.781(13) and Ir-O = 2.067(7)Å. The hydroxy derivative Ir(CO)(OH)(PCy<sub>3</sub>)<sub>2</sub> crystallizes in the triclinic space group *P* $\bar{1}$  with *a* = 9.916(3), *b* = 10.305(4), *c* = 10.825(4)Å,  $\alpha$  = 114.16(3),  $\beta$  = 109.55(3),  $\gamma$  = 90.14(3)°, *V* = 938.6(5)Å<sup>3</sup> and *Z* = 1. This structure is disordered with a scrambled image of the carbonyl and hydroxide ligands. Distances of note are Ir-P = 2.331(1), Ir-CO = 1.887(13) and Ir-OH = 1.978(12)Å; the Ir-CO and Ir-OH distances may suffer from systematic errors due to disorder.

Four-coordinate, 16-electron, square-planar Ir(I) complexes are very important in the study of organometallic chemistry. Vaska's complex<sup>1</sup> and analogues have open coordination sites and have been known to undergo reactions such as oxidative addition,<sup>2</sup> ligand substitution,<sup>3</sup> simple adduct formation<sup>4</sup> and insertion.<sup>5</sup> Synthesis of these complexes has traditionally been accomplished by reduction of an Ir(III) salt at elevated temperature in the presence of a phosphine ligand and a reducing agent:<sup>1</sup>

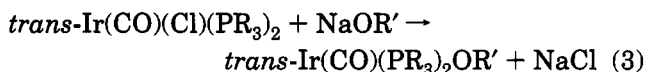


Another, recently published route, by Burk and Crabtree occurs at room temperature:<sup>6</sup>



Vaska's-type alkoxy and aryloxy complexes have been formed by a simple metathesis reaction in which the

chloro complex reacts with a sodium alkoxide forming the desired product and NaCl.<sup>5a</sup>



This route has proven to be successful in the formation of R=*p*-tolyl; R'=CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> or *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> in this work. X-ray crystallography, <sup>1</sup>H and <sup>31</sup>P NMR, IR and elemental analysis of these complexes are reported.

Another successful route in the formation of Vaska's-type complexes with varying phosphine ligands is a phosphine ligand exchange reaction, illustrated in reaction 4 for preparation of the hydroxy and methoxy complexes with tricyclohexylphosphine. This route is successful when PR'<sub>3</sub> is more electron-rich than PR<sub>3</sub>.

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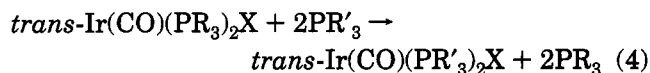
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R = p-tolyl; R' = Cy; X = OH or OCH<sub>3</sub>

Whether pi-donation from an alkoxo (or aryloxo) ligand to a late transition metal is significant remains a question. Based on relative stabilities of late-transition metal-X bonds (X = oxygen-, nitrogen- or carbon-donor ligands), Bryndza and Tam concluded that no significant pi interaction exists for bonds of alkyl, alkoxo or amido ligands to late-transition metal centers.<sup>7</sup> Using structural data<sup>8</sup> and  $\nu_{\text{CO}}$  frequencies,<sup>9</sup> Caulton and coworkers have concluded that extensive pi-donation exists for Ir-OCH<sub>2</sub>CF<sub>3</sub> and for Ru-OCH<sub>2</sub>CF<sub>3</sub>. To provide further data on the nature of late-transition metal-oxygen-donor ligand bonds we have prepared new alkoxo and hydroxo complexes and examined the structures of three complexes.

### Experimental Section

**Materials.** IrCl<sub>3</sub>·3H<sub>2</sub>O was purchased or borrowed from Johnson Matthey. Tri-p-tolylphosphine and tricyclohexylphosphine were purchased from Strem Chemical Company. These materials were used as received without further purification.

**Solvents.** Benzene and THF were refluxed in a N<sub>2</sub> atmosphere over Na/benzophenone until the solution became blue or purple. Cyclohexane was refluxed in a N<sub>2</sub> atmosphere with finely divided CaH<sub>2</sub> overnight. The solvent was then distilled into a collection flask which had been evacuated three times with subsequent N<sub>2</sub> backfilling. The purified solvents were stored in an inert atmosphere glove box. Benzyl alcohol, p-cresol, and CD<sub>2</sub>Cl<sub>2</sub> were stirred overnight with finely divided CaH<sub>2</sub>, followed by vacuum distillation. CD<sub>2</sub>Cl<sub>2</sub> was distilled into an oven-dried pressure-tube fitted with a Teflon stopcock. The purified solvent was stored in an inert atmosphere glovebox. Dry benzyl alcohol and p-cresol were stirred with Na overnight followed by removal of excess solvent forming the sodium alkoxide salts. The solvents were purchased from Aldrich Co. except CD<sub>2</sub>Cl<sub>2</sub> which was purchased from Cambridge Isotope Labs.

**Instrumental Measurements.** <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Varian VXR-400. References were set to residual solvent peaks in the <sup>1</sup>H NMR spectra. <sup>31</sup>P NMR spectra were referenced to an external sample of H<sub>3</sub>PO<sub>4</sub> at 0.0 ppm and are proton decoupled. All chemical shifts are reported in ppm and all coupling constants (J) are reported in Hz. Infrared spectra were obtained using a Mattson Polaris Fourier transform spectrometer as KBr disks. Elemental Analysis was done at E & R Microanalytical.

**Preparations.** All syntheses were accomplished under an argon or nitrogen atmosphere (unless otherwise noted) using an argon filled glovebox, Schlenk or high vacuum techniques. Square planar iridium complexes, *trans*-Ir(CO)(Cl)(P(p-tolyl)<sub>3</sub>)<sub>2</sub>, *trans*-Ir(CO)(OH)(P(p-tolyl)<sub>3</sub>)<sub>2</sub> and *trans*-Ir(CO)(OCH<sub>3</sub>)(P(p-tolyl)<sub>3</sub>)<sub>2</sub> were prepared as previously described.<sup>10</sup>

**General Preparation of Ir(CO)(P(p-tolyl)<sub>3</sub>)<sub>2</sub>X (X = OCH<sub>3</sub> or OH).** A solution of *trans*-Ir(CO)(Cl)(P(p-tolyl)<sub>3</sub>)<sub>2</sub> (0.887 g, 1.027 mmol) and NaOR (0.906 g, 6.97 mmol) in THF (50 mL) is stirred under Ar in a sealed flask

Table 1. IR and <sup>31</sup>P NMR Data

<i>trans</i> Ir(I) complex	IR <sup>a</sup> $\nu_{\text{CO}}$ (cm <sup>-1</sup> )	<sup>31</sup> P NMR <sup>b</sup> (ppm)
Ir(CO)(PCy <sub>3</sub> ) <sub>2</sub> OH	1912	35.0 (s)
Ir(CO)(PCy <sub>3</sub> ) <sub>2</sub> OCH <sub>3</sub>	1914	34.1 (s)
Ir(CO)(P(p-tolyl) <sub>3</sub> ) <sub>2</sub> OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	1953	21.5 (s)
Ir(CO)(P(p-tolyl) <sub>3</sub> ) <sub>2</sub> OC <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	1949	23.3 (s)

<sup>a</sup> KBr. <sup>b</sup> CD<sub>2</sub>Cl<sub>2</sub>.

Table 2. <sup>1</sup>H NMR Data

<i>trans</i> Ir(I) complex	<sup>1</sup> H NMR (ppm) in CD <sub>2</sub> Cl <sub>2</sub>
Ir(CO)OH(PCy <sub>3</sub> ) <sub>2</sub>	2.3–1.2 (multiple peaks), –1.0 (t) J = 7.5 Hz
Ir(CO)(OCH <sub>3</sub> )(PCy <sub>3</sub> ) <sub>2</sub>	2.3–1.2 (multiple peaks), 3.5 (s)
Ir(CO)(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )(P(p-tolyl) <sub>3</sub> ) <sub>2</sub>	7.8–6.4 (multiple peaks), 4.2 [s, 1H], 2.4 [s, 10H]
Ir(CO)(OC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )(P(p-tolyl) <sub>3</sub> ) <sub>2</sub>	7.8–6.4 (multiple peaks), 2.6 [s, 2H], 2.3 [s, 9.5H]

Table 3. Elemental Analyses

<i>trans</i> Ir(I) complex	actual % (calculated %)		
	Ir	C	H
Ir(CO)(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )(P(p-tolyl) <sub>3</sub> ) <sub>2</sub>	20.2 (21.2)	64.0 (66.4)	5.2 (5.5)
Ir(CO)(OC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )(P(p-tolyl) <sub>3</sub> ) <sub>2</sub>	20.7 (21.2)	64.4 (66.4)	5.1 (5.5)
Ir(CO)(OH)(PCy <sub>3</sub> ) <sub>2</sub>	23.8 (24.1)	55.8 (55.7)	8.4 (8.5)

overnight. The THF is removed from the cloudy yellow solution, followed by addition of cyclohexane (40 mL). The solution is stirred and a white solid containing excess NaOR and NaCl is filtered off. The cyclohexane is removed from the filtrate and the product is extracted with benzene (30 mL) followed by filtration of more white solid. The benzene is removed and the remaining solid is recrystallized in a saturated benzene solution layered with hexanes. After 18 h, yellow crystals formed (0.595 g, 0.636 mmol). IR, NMR and elemental analysis data are included in Tables 1–3.

**General Preparation of *trans*-Ir(CO)(PCy<sub>3</sub>)<sub>2</sub>X (X = OCH<sub>3</sub> or OH).** A solution of *trans*-Ir(CO)(P(p-tolyl)<sub>3</sub>)<sub>2</sub>X (1.005 g, 1.188 mmol) and PCy<sub>3</sub> (1.668 g, 5.95 mmol) in benzene (40 mL) is stirred under Ar in a sealed flask overnight. The benzene is removed and the light yellow product is washed with cyclohexane (20 mL) resulting in a yellow powder (0.643 g, 0.806 mmol, 67.8% yield). Recrystallization is effected with a saturated benzene solution (the solution is heated to prepare the saturated solution) layered with hexanes overnight in a sealed flask under an Ar atmosphere. IR and NMR data and elemental analyses are included in Tables 1–3.

**Collection of X-ray Diffraction Data.** All three data sets were collected on an upgraded Nicolet/Siemens P2<sub>1</sub>/R3 diffractometer using molybdenum radiation ( $\lambda(\text{MoK}\alpha) = 0.71073\text{\AA}$ ) at ambient temperature (298 ± 1K). The experimental method has been described previously;<sup>11</sup> details are provided in Table 4. All data were merged and corrected for both absorption and for Lorentz and polarization effects.

It should be noted that crystals of Ir(CO)(OC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(P(p-tolyl)<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH were of relatively poor quality and yielded a much "weaker" data set than those obtained for the other two species.

**Solution of Crystal Structures.** All calculations were performed under the Siemens SHELXTL-PLUS system<sup>12</sup> on a VAXstation 3100 computer. The analytical scattering factors for the neutral atoms<sup>13a</sup> were corrected for anomalous dispersion.<sup>13b</sup> Structures were solved by a combination of direct methods and difference-Fourier syntheses. Hydrogen

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Table 4. Details of X-ray Structural Analyses

	Ir(CO)(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )(P(p-tolyl) <sub>3</sub> ) <sub>2</sub>	Ir(CO)(OC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )(P(p-tolyl) <sub>3</sub> ) <sub>2</sub> ·CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	Ir(CO)(OH)(PCy <sub>3</sub> ) <sub>2</sub>
molecular formula	C <sub>50</sub> H <sub>49</sub> IrO <sub>2</sub> P <sub>2</sub>	C <sub>50</sub> H <sub>49</sub> IrO <sub>2</sub> P <sub>2</sub> ·C <sub>7</sub> H <sub>8</sub> O	C <sub>37</sub> H <sub>67</sub> IrO <sub>2</sub> P <sub>2</sub>
fw	936.0	1044.2	798.0
crystal system	triclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> , Å	10.5187(16)	21.1172(28)	9.916(3)
<i>b</i> , Å	12.8320(15)	12.0167(15)	10.305(4)
<i>c</i> , Å	17.4940(19)	22.5658(31)	10.825(4)
$\alpha$ , deg	71.447(8)	90.000	114.16(3)
$\beta$ , deg	84.907(11)	117.180(10)	109.55(3)
$\gamma$ , deg	72.407(11)	90.000	90.14(3)
<i>V</i> , Å <sup>3</sup>	2133.8(5)	5094.0(12)	938.6(5)
<i>Z</i>	2	4	1
<i>d</i> (calc'd), g cm <sup>-3</sup>	1.457	1.361	1.412
crystal size (mm)	0.3 × 0.25 × 0.25	0.2 × 0.17 × 0.1	0.3 × 0.3 × 0.2
$\mu$ (mm <sup>-1</sup> )	3.227	2.712	3.655
min/max transmission	0.152/0.294	0.467/0.600	0.232/0.372
2 $\theta$ range, deg	5–45	5–45	5–45
index ranges	<i>h</i> , -11→0; <i>k</i> , -13→+13; <i>l</i> , -18→+18	<i>h</i> , 0→+22; <i>k</i> , 0→+12; <i>l</i> , -24→+24	<i>h</i> , -10→+10; <i>k</i> , -11→+11; <i>l</i> , -11→+11
total reflections collected	6061	7305	4924
independent reflections	5605	6698	2462
<i>R</i> (int), %	0.83	2.33	2.81
reflections above 6 $\sigma$	4567	3296	2462
no. of variables	497	569	196
residual electron density, e <sup>-</sup> /Å <sup>3</sup>	-0.31→+0.58	-1.05→+0.95	-1.21→+1.46
<i>R</i> ( <i>wR</i> ) 6 $\sigma$ data	2.48% (2.73%)	4.26% (4.26%)	2.40% (2.96%)
<i>R</i> ( <i>wR</i> ) all data	3.50% (3.81%)	10.71% (7.55%)	2.40% (2.96%)

atoms of the organic fragments were included in calculated positions with  $d(\text{C-H}) = 0.96\text{\AA}$ .<sup>14</sup>

Data on final *R*-factors and residuals on electron density maps are compiled in Table 4. However, certain aspects of the structural solution of Ir(CO)(OH)(PCy<sub>3</sub>)<sub>2</sub> merit a more detailed discussion. A complete sphere ( $2\theta = 4\text{--}45^\circ$ ) of data was collected; these data were merged to a unique set with  $R_{\text{int}} = 2.81\%$  for 2462 averaged pairs of reflections. The molecule crystallizes in space group *P* $\bar{1}$  with *Z* = 1 and must be disordered, since the ensemble is required to have an inversion center. In fact, there are two possible orientations for each entire molecule. The individual molecules pack, in a random fashion, such that their PCy<sub>3</sub> ligands appear to overlap precisely, while carbonyl and hydroxide ligands are observed as overlapping images at the other two coordination sites (see Figure 1a). We endeavored to refine appropriate atoms of the carbonyl ligand (C(1) and O(1)) and of the hydroxide ligand (O(2)) independently. Much to our surprise, this appears to have been successful, even though the separation of C(1) and O(2A) (or C(1A) and O(2)) is only 0.441(14)Å. We also identified a feature near O(2) which could be the hydrogen atom of the hydroxide ligand, defined as H(3) (see Figure 1b). This attribution is not entirely secure; we note that the presumed location is associated with an O(2)-H(3) distance of 1.08Å and an Ir(1)-O(2)-H(3) angle of 161°.

Final atomic coordinates for the three structures are collected in Tables 5–7.

### Description of the Molecular Structures

**(A) Ir(CO)(OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(P(p-tolyl)<sub>3</sub>)<sub>2</sub>.** This species crystallizes as discrete molecular units. The scheme for labelling atoms is shown in Figure 2. Important interatomic distances and angles are collected in Table 8.

The central d<sup>8</sup> iridium(I) atom has a slightly distorted square planar stereochemistry. The *cis* angles range from P(1)-Ir(1)-O(1) = 83.9(1) through P(2)-Ir(1)-O(1) = 96.4(1)°, while *trans* angles are P(1)-Ir(1)-P(2) = 176.9-(1)° and O(1)-Ir(1)-C(9) = 173.8(3)°. The two indepen-

dent iridium-phosphorus distances are Ir(1)-P(1) = 2.334(2) and Ir(1)-P(2) = 2.306(2)Å (average = 2.320Å).

The iridium-alkoxide linkage is defined by Ir(1)-O(1) = 2.022(4)Å and the oxygen atom has a "bent" environment with Ir(1)-O(1)-C(2) = 132.8(4)°. The O(1)-C(2) distance is 1.377(7)Å.

**(B) Ir(CO)(OC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(P(p-tolyl)<sub>3</sub>)<sub>2</sub>·CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH.** The iridium complex here crystallizes with CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-OH molecules of solvation. The relative position of these two species and the atomic labelling scheme are illustrated in Figure 3. Selected interatomic distances and angles are compiled in Table 9.

The d<sup>8</sup> iridium(I) atom again has a slightly distorted square planar stereochemistry. It is associated with *cis* angles ranging from P(2)-Ir(1)-C(1) = 89.7(6) through P(1)-Ir(1)-O(2) = 90.2(3)° and *trans* angles of P(1)-Ir(1)-P(2) = 174.4(1) and O(2)-Ir(1)-C(1) = 178.9(5)°. The iridium-phosphorus distances are Ir(1)-P(1) = 2.322(4) and Ir(1)-P(2) = 2.330(4)Å (average = 2.326Å). The iridium-phenoxide linkage is given by Ir(1)-O(2) = 2.067(7)Å and is associated with an Ir(1)-O(2)-C(2) angle of 122.5(7)° and an O(2)-C(2) bond length of 1.347(14)Å.

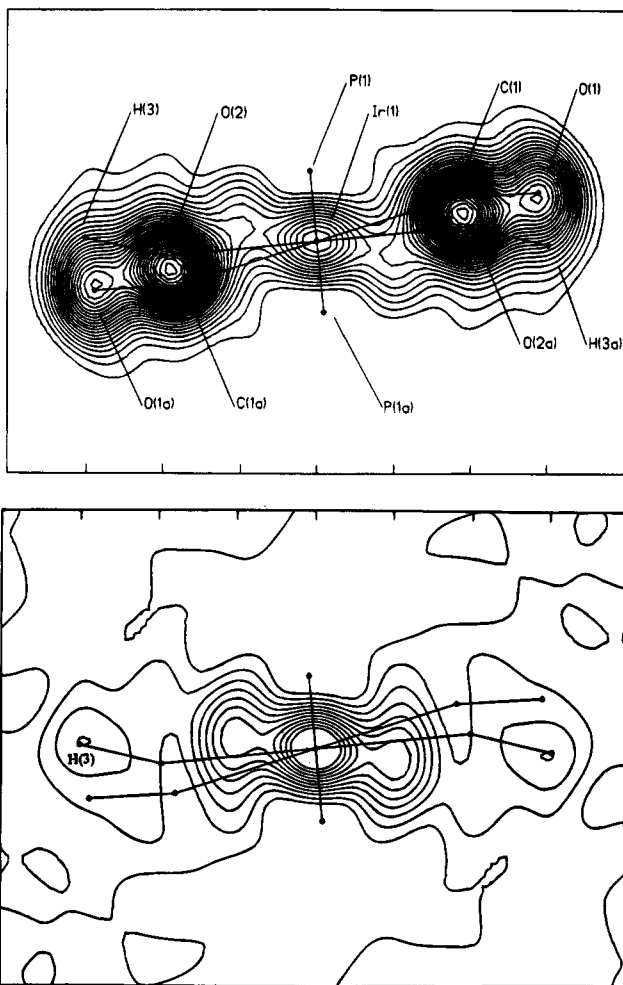
Identification of the molecule of solvation as *p*-cresol rests upon comparison of bond lengths involving the substituents (C(1S)-O(1S) = 1.372(19)Å as opposed to C(4S)-C(7S) = 1.505(23)Å) and upon the satisfactory behavior of atoms O(1S) and C(7S) under anisotropic refinement. (As shown in Figure 3, the thermal vibration ellipsoids for these atoms are chemically sensible.) The *p*-cresol moiety is hydrogen bonded to the oxygen atom of the *p*-cresolate ligand – see Figure 4. The O(2) ... O(1S)' distance is 2.659(12)Å.

**(C) Ir(CO)(OH)(PCy<sub>3</sub>)<sub>2</sub>.** This structure is disordered (see above) in a fashion similar to that observed in such species as Ir(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>,<sup>15</sup> Ir(CO)(CH<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>,<sup>4a</sup> and Ir(CO)Cl(PCy<sub>3</sub>)<sub>2</sub>.<sup>16</sup> An illustration of the deconvoluted

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**Figure 1.** Electron density maps from the X-ray diffraction study of  $\text{Ir}(\text{CO})(\text{OH})(\text{PCy}_3)_2$ . (a) Residual electron density due to the disordered CO/OH groups. Contours are at  $0.2 \text{ e}^-/\text{\AA}^3$  intervals from  $0.0 \rightarrow 6.0 \text{ e}^-/\text{\AA}^3$ . Based upon a  $\Delta F$  map, phased by all atoms other than those of the carbonyl and hydroxide ligands. (b) Residual electron density showing a possible location for the hydrogen atom of the hydroxide ligand. Contours at  $0.2 \text{ e}^-/\text{\AA}^3$  intervals, starting at  $0.0 \text{ e}^-/\text{\AA}^3$ ; orientation as above. Based upon a  $\Delta F$  map, phased by all atoms save H(3).

molecule is provided in Figure 5. Appropriate distances and angles are collected in Table 10.

The central iridium(I) atom is associated with *cis* angles ranging from  $89.1(3)$  through  $91.0(3)^\circ$  and with the *trans* angles  $\text{P}(1)\text{-Ir}(1)\text{-P}(1\text{A}) = 180.0^\circ$  (exactly) and  $\text{C}(1)\text{-Ir}(1)\text{-O}(2) = 167.2(4)^\circ$ . The two equivalent iridium-phosphorus distances are  $\text{Ir}(1)\text{-P}(1) = \text{Ir}(1)\text{-P}(1\text{A}) = 2.331(1)\text{\AA}$ . The remaining two ligands are associated with distances of  $\text{Ir}(1)\text{-C}(1) = 1.887(13)\text{\AA}$  (for the carbonyl ligand) and  $\text{Ir}(1)\text{-O}(2) = 1.978(12)\text{\AA}$  (for the hydroxide ligand). Disorder renders impossible a true assessment of the accuracy (as opposed to precision) of these two bond lengths.

**(D) Discussion of the O-Bonded Ligands.** The present study allows a comparison of bond distances and other parameters for the structural isomers  $\text{Ir}(\text{CO})(\text{OCH}_2\text{C}_6\text{H}_5)(\text{P}(\text{p-tolyl})_3)_2$  (which has an iridium-alkoxide linkage) and  $\text{Ir}(\text{CO})(\text{OC}_6\text{H}_4\text{CH}_3)(\text{P}(\text{p-tolyl})_3)_2$  (which has an iridium-phenoxide linkage). Previous studies by our research groups have involved the related species  $\text{Ir}(\text{CO})(\text{OC}_6\text{H}_5)(\text{PPh}_3)_2$ ,<sup>5a</sup>  $\text{Ir}(\text{CO})(\text{OC}_6\text{F}_5)(\text{PPh}_3)_2$ <sup>17</sup> and  $\text{Rh}$ -

**Table 5.** Atomic Coordinates ( $\times 10^4$ ) and  $U(\text{eq})$  Values ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Ir}(\text{CO})(\text{OCH}_2\text{C}_6\text{H}_5)(\text{P}(\text{p-tolyl})_3)_2$

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})^a$
Ir(1)	1691(1)	3332(1)	2109(1)	53(1)
P(1)	2254(1)	2533(1)	1055(1)	56(1)
P(2)	1254(1)	4092(1)	3167(1)	53(1)
O(1)	1443(5)	1784(3)	2733(2)	85(2)
O(9)	2045(6)	5526(4)	1021(3)	116(3)
C(2)	1167(6)	1303(5)	3529(3)	74(3)
C(3)	-58(6)	882(4)	3643(3)	62(2)
C(4)	-1264(7)	1622(5)	3321(4)	79(3)
C(5)	-2398(7)	1258(6)	3454(4)	94(3)
C(6)	-2346(8)	163(6)	3900(4)	92(4)
C(7)	-1167(8)	-569(6)	4234(4)	90(3)
C(8)	-22(7)	-219(5)	4115(4)	81(3)
C(9)	1908(7)	4674(5)	1454(3)	75(3)
C(11)	2804(5)	3482(4)	157(3)	58(2)
C(12)	1888(6)	4402(5)	-351(3)	72(3)
C(13)	2304(6)	5233(5)	-943(3)	76(3)
C(14)	3644(6)	5166(5)	-1066(3)	70(3)
C(15)	4554(6)	4219(5)	-586(3)	75(3)
C(16)	4151(5)	3373(4)	20(3)	63(2)
C(17)	4069(8)	6111(5)	-1680(4)	93(3)
C(21)	957(5)	2126(4)	682(3)	60(2)
C(22)	34(5)	1746(5)	1223(3)	67(2)
C(23)	-966(6)	1440(5)	958(4)	75(3)
C(24)	-1069(6)	1507(5)	172(4)	73(3)
C(25)	-135(6)	1865(6)	-356(4)	86(3)
C(26)	863(6)	2168(6)	-108(4)	81(3)
C(27)	-2190(7)	1184(6)	-103(5)	102(4)
C(31)	3673(5)	1237(4)	1316(3)	55(2)
C(32)	3918(6)	403(5)	939(3)	67(2)
C(33)	5012(6)	-550(5)	1137(4)	76(3)
C(34)	5910(6)	-702(5)	1724(4)	81(3)
C(35)	5691(6)	163(6)	2082(4)	84(3)
C(36)	4585(6)	1098(5)	1893(3)	70(3)
C(37)	7102(8)	-1785(7)	1955(5)	131(4)
C(41)	1412(5)	5535(4)	2974(3)	57(2)
C(42)	2612(5)	5744(5)	2657(4)	72(3)
C(43)	2796(6)	6808(5)	2503(4)	78(3)
C(44)	1818(6)	7706(5)	2661(3)	69(3)
C(45)	641(6)	7501(5)	2970(4)	80(3)
C(46)	429(6)	6441(5)	3130(4)	72(3)
C(47)	2016(8)	8874(5)	2470(4)	95(3)
C(51)	2344(5)	3307(4)	4045(3)	56(2)
C(52)	3393(5)	2348(4)	4039(3)	64(2)
C(53)	4297(6)	1811(5)	4673(4)	75(3)
C(54)	4180(6)	2196(5)	5331(4)	77(3)
C(55)	3128(6)	3137(5)	5360(3)	74(3)
C(56)	2235(5)	3696(5)	4722(3)	64(2)
C(57)	5226(8)	1648(7)	5986(5)	115(4)
C(61)	-452(5)	4229(4)	3510(3)	56(2)
C(62)	-847(5)	3752(5)	4289(3)	65(2)
C(63)	-2168(6)	3847(5)	4469(4)	74(3)
C(64)	-3150(6)	4426(5)	3890(4)	75(3)
C(65)	-2771(5)	4915(5)	3125(4)	71(3)
C(66)	-1444(5)	4820(5)	2924(3)	64(2)
C(67)	-4588(6)	4493(7)	4078(5)	106(4)

<sup>a</sup> Equivalent isotropic  $U$ , defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

$(\text{CO})(\text{OC}_6\text{H}_5)(\text{PPh}_3)_2$ .<sup>18</sup> Dimensions for all of these species are compared in Table 11.

The most obvious result is that the alkoxide derivative,  $\text{Ir}(\text{CO})(\text{OCH}_2\text{C}_6\text{H}_5)(\text{P}(\text{p-tolyl})_3)_2$  is associated with: (1) the shortest Ir-O distance ( $2.022(4)\text{\AA}$ , as opposed to Ir-O(phenoxide) distances of  $2.049(4)\text{-}2.067(7)\text{\AA}$ ); (2) the longest O-C distance ( $1.377(7)\text{\AA}$  as opposed to O-C(aromatic) distances of  $1.302(6)\text{-}1.347(14)\text{\AA}$ ); and (3) one of the larger Ir-O-C angles ( $132.8(4)^\circ$ , as opposed to values of  $122.5(7)^\circ$  for the Ir-O-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> system and

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(18) Bernard, K. A.; Churchill, M. R.; Janik, T. S.; Atwood, J. D., *Organometallics* **1990**, *9*, 12.

**Table 6. Atomic Coordinates ( $\times 10^4$ ) and  $U(\text{eq})$  Values ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Ir}(\text{CO})(\text{OC}_6\text{H}_4\text{CH}_3)(\text{P}(\text{p-tolyl})_3)_2\text{CH}_2\text{C}_6\text{H}_4\text{OH}$** 

	x	y	z	$U(\text{eq})^a$
Ir(1)	-2839(1)	8421(1)	-2165(1)	43(1)
P(1)	-3146(2)	9189(3)	-1387(2)	43(1)
P(2)	-2488(2)	7818(3)	-2952(2)	46(2)
O(1)	-4254(5)	9071(10)	-3235(5)	85(6)
O(2)	-1871(4)	7917(7)	-1407(4)	53(4)
C(1)	-3678(8)	8827(11)	-2820(8)	63(8)
C(2)	-1777(7)	6912(9)	-1114(6)	49(7)
C(3)	-1112(8)	6704(12)	-546(7)	75(7)
C(4)	-1010(9)	5667(14)	-245(8)	83(9)
C(5)	-1496(11)	4879(15)	-438(9)	83(10)
C(6)	-2142(9)	5090(12)	-980(9)	77(9)
C(7)	-2272(7)	6084(11)	-1310(7)	53(7)
C(8)	-1344(10)	3763(14)	-41(9)	129(13)
C(11)	-3744(6)	8344(10)	-1183(5)	45(5)
C(12)	-4102(7)	7429(11)	-1567(6)	57(6)
C(13)	-4521(7)	6766(12)	-1384(8)	71(8)
C(14)	-4572(8)	6968(11)	-812(8)	68(8)
C(15)	-4217(7)	7889(11)	-424(7)	62(8)
C(16)	-3825(7)	8575(10)	-614(6)	53(6)
C(17)	-4982(10)	6182(14)	-596(10)	112(12)
C(21)	-3555(7)	10575(10)	-1637(6)	50(6)
C(22)	-3281(8)	11267(11)	-1964(6)	61(7)
C(23)	-3529(8)	12317(13)	-2148(7)	75(8)
C(24)	-4068(8)	12739(11)	-2027(7)	66(8)
C(25)	-4347(7)	12063(13)	-1717(7)	66(7)
C(26)	-4108(7)	10975(11)	-1538(6)	56(7)
C(27)	-4337(8)	13915(11)	-2216(9)	93(9)
C(31)	-2402(6)	9471(9)	-574(6)	43(6)
C(32)	-2092(6)	8564(11)	-137(6)	50(6)
C(33)	-1518(7)	8749(11)	481(6)	58(7)
C(34)	-1245(7)	9766(15)	694(7)	72(8)
C(35)	-1554(9)	10676(13)	268(8)	83(9)
C(36)	-2115(8)	10495(11)	-356(7)	64(8)
C(37)	-633(8)	9980(14)	1376(7)	93(9)
C(41)	-1544(6)	7560(9)	-2658(6)	42(6)
C(42)	-1116(7)	8190(10)	-2848(7)	60(7)
C(43)	-411(7)	7987(13)	-2628(7)	67(8)
C(44)	-85(7)	7109(14)	-2178(7)	66(7)
C(45)	-509(7)	6496(12)	-1994(6)	65(7)
C(46)	-1217(6)	6711(11)	-2212(6)	55(6)
C(47)	701(7)	6843(14)	-1932(8)	96(10)
C(51)	-2898(7)	6523(11)	-3373(6)	55(6)
C(52)	-3569(8)	6262(12)	-3447(7)	67(8)
C(53)	-3912(8)	5344(13)	-3815(8)	75(9)
C(54)	-3626(8)	4621(12)	-4105(8)	73(8)
C(55)	-2946(9)	4871(12)	-4015(7)	77(9)
C(56)	-2597(7)	5801(11)	-3653(6)	58(7)
C(57)	-4018(10)	3651(14)	-4523(11)	141(14)
C(61)	-2735(6)	8801(10)	-3635(6)	47(6)
C(62)	-2774(7)	8499(12)	-4236(6)	62(7)
C(63)	-2924(8)	9270(12)	-4735(7)	75(9)
C(64)	-3037(7)	10366(13)	-4650(7)	69(7)
C(65)	-2971(9)	10679(12)	-4033(8)	84(10)
C(66)	-2806(8)	9924(11)	-3534(7)	68(8)
C(67)	-3262(10)	11212(15)	-5204(8)	120(12)
O(1S)	808(5)	10632(9)	867(5)	103(6)
C(1S)	941(8)	9576(13)	1126(9)	74(9)
C(2S)	497(11)	8723(17)	768(10)	133(13)
C(3S)	643(13)	7661(19)	1050(12)	128(15)
C(4S)	1194(11)	7442(13)	1663(11)	87(11)
C(5S)	1579(9)	8321(15)	2008(9)	89(10)
C(6S)	1468(8)	9397(14)	1762(8)	80(9)
C(7S)	1323(11)	6290(12)	1957(11)	125(16)

<sup>a</sup> Equivalent isotropic  $U$ , defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

126.5(3)° for the Ir-O-C<sub>6</sub>H<sub>5</sub> system; only the Ir-O-C<sub>6</sub>F<sub>5</sub> system has a larger value -135.4(3)°).

It should be noted that the M-O-C angle for each of the species studied (Table 8) has a value in excess of 120°. Thus, while we might expect the oxygen atom to be sp<sup>3</sup> hybridized (two bonding pairs of electrons at ~105° to each other and two lone pairs of electrons), the M-O-C angles of 122.5(7)–135.4(3)° suggest consid-

**Table 7. Atomic Coordinates ( $\times 10^4$ ) and  $U(\text{eq})$  Values ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Ir}(\text{CO})(\text{OH})(\text{PCy}_3)_2$** 

	x	y	z	$U(\text{eq})^a$
Ir(1)	0	0	0	36(1)
P(1)	-2008(1)	-291(1)	-2038(1)	37(1)
C(46)	-1438(5)	2380(4)	-2092(5)	52(2)
C(44)	-2236(5)	4627(4)	-651(5)	60(2)
C(41)	-2559(4)	1451(4)	-1982(4)	42(2)
C(42)	-2869(5)	2295(4)	-592(5)	52(2)
C(45)	-1943(5)	3809(4)	-2017(5)	58(2)
C(43)	-3351(5)	3727(4)	-536(5)	60(2)
C(11)	-1657(4)	-1115(4)	-3754(4)	43(2)
C(16)	-1006(5)	-2511(5)	-3979(5)	58(2)
C(12)	-2892(5)	-1313(5)	-5141(4)	61(2)
C(14)	-1701(6)	-3099(6)	-6635(5)	70(2)
C(15)	-507(6)	-2960(6)	-5270(5)	69(2)
C(13)	-2359(6)	-1735(6)	-6396(5)	69(2)
C(62)	-5149(5)	-1097(5)	-3170(7)	69(3)
C(61)	-3687(4)	-1287(4)	-2227(5)	46(2)
C(65)	-4906(6)	-3561(6)	-2460(8)	82(3)
C(66)	-3653(5)	-2887(5)	-2639(6)	60(2)
C(63)	-6393(5)	-1756(6)	-2980(8)	86(3)
C(64)	-6354(6)	-3338(6)	-3352(8)	90(4)
C(1)	1162(10)	810(11)	-658(11)	44(2)
O(1)	1913(7)	1010(10)	-1140(8)	76(4)
O(2)	-1297(10)	-402(10)	891(10)	72(3)

<sup>a</sup> Equivalent isotropic  $U$ , defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 8. Selected Interatomic Distances ( $\text{\AA}$ ) and Angles (deg) for  $\text{Ir}(\text{CO})(\text{OCH}_2\text{C}_6\text{H}_5)(\text{P}(\text{p-tolyl})_3)_2$** 

Ir(1)–P(1)	2.334(2)	Ir(1)–P(2)	2.306(2)
Ir(1)–O(1)	2.022(4)	Ir(1)–C(9)	1.806(6)
P(1)–C(11)	1.826(5)	P(1)–C(21)	1.834(7)
P(1)–C(31)	1.827(4)	P(2)–C(41)	1.829(6)
P(2)–C(51)	1.821(5)	P(2)–C(61)	1.816(5)
O(1)–C(2)	1.377(7)	O(9)–C(9)	1.157(8)
C(2)–C(3)	1.516(9)	C(3)–C(4)	1.373(8)
C(3)–C(8)	1.382(7)	C(4)–C(5)	1.384(11)
C(5)–C(6)	1.359(10)	C(6)–C(7)	1.356(10)
C(7)–C(8)	1.385(12)		
P(1)–Ir(1)–P(2)	176.9(1)	P(1)–Ir(1)–O(1)	83.9(1)
P(2)–Ir(1)–O(1)	96.4(1)	P(1)–Ir(1)–C(9)	90.2(2)
P(2)–Ir(1)–C(9)	89.6(2)	O(1)–Ir(1)–C(9)	173.8(3)
Ir(1)–P(1)–C(11)	112.8(2)	Ir(1)–P(1)–C(21)	117.4(2)
C(11)–P(1)–C(21)	104.4(3)	Ir(1)–P(1)–C(31)	111.9(2)
C(11)–P(1)–C(31)	103.8(2)	C(21)–P(1)–C(31)	105.4(3)
Ir(1)–P(2)–C(41)	117.1(2)	Ir(1)–P(2)–C(51)	115.7(2)
C(41)–P(2)–C(51)	100.4(3)	Ir(1)–P(2)–C(61)	111.3(2)
C(41)–P(2)–C(61)	103.5(2)	C(51)–P(2)–C(61)	107.5(2)
Ir(1)–O(1)–C(2)	132.8(4)	O(1)–C(2)–C(3)	113.4(5)
C(2)–C(3)–C(4)	120.1(5)	C(2)–C(3)–C(8)	121.6(5)
C(4)–C(3)–C(8)	118.1(6)	C(3)–C(4)–C(5)	120.4(5)
C(4)–C(5)–C(6)	121.0(6)	C(5)–C(6)–C(7)	119.1(8)
C(6)–C(7)–C(8)	120.8(6)	C(3)–C(8)–C(7)	120.5(5)
Ir(1)–C(9)–O(9)	178.6(6)	P(1)–C(11)–C(12)	120.6(4)
P(1)–C(11)–C(16)	120.6(3)	P(1)–C(21)–C(22)	118.4(5)
P(1)–C(21)–C(26)	123.5(5)	P(1)–C(31)–C(32)	122.9(4)
P(1)–C(31)–C(36)	119.3(4)	P(2)–C(41)–C(42)	118.2(4)
P(2)–C(41)–C(46)	124.6(4)	P(2)–C(51)–C(52)	120.5(4)
P(2)–C(51)–C(56)	122.1(3)	P(2)–C(61)–C(62)	126.1(4)
P(2)–C(61)–C(66)	116.3(4)		

erably more s-character in the O-M and O-C  $\sigma$ -bonds. The key question is whether this indicates the presence of pi-donation from the ligand to the metal.<sup>19</sup>

A number of alkoxo and aryloxo complexes of iridium have been prepared and structurally characterized. The two parameters most affected by possible pi-donation are the Ir-OR bond distance and the Ir-O-C bond angle. A complete lack of correlation of M-O bond distances and M-O-C angles was noted for niobium(V) and tan-

(19) Caulton, K. G., *New J. Chem.* **1994**, *18*, 25 and references therein.

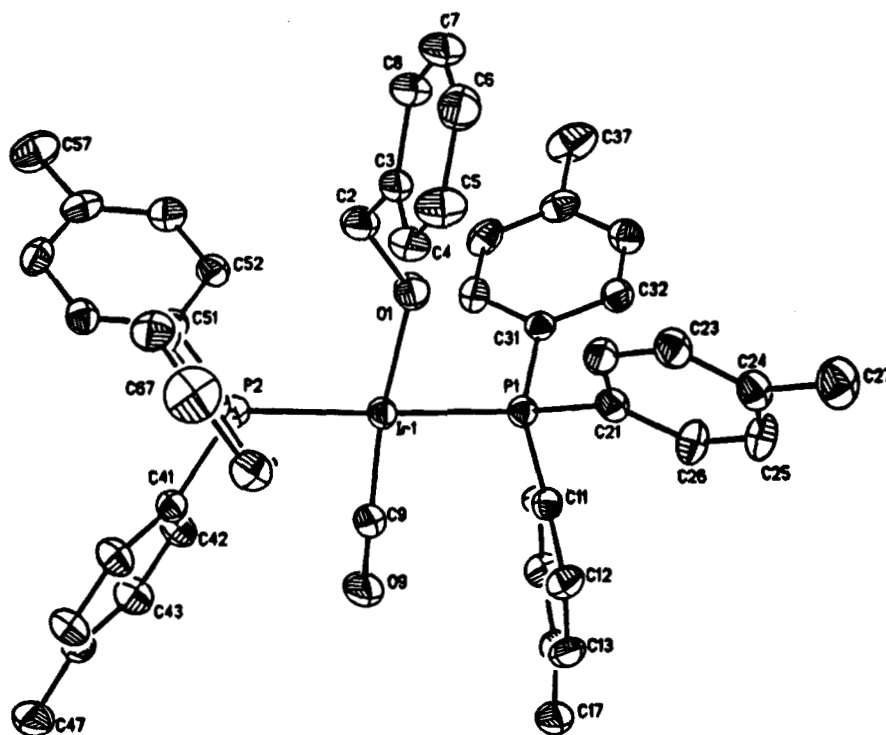


Figure 2. Labelling of atoms in  $\text{Ir}(\text{CO})(\text{OCH}_2\text{C}_6\text{H}_5)(\text{P}(\text{p-tolyl})_3)_2$ .

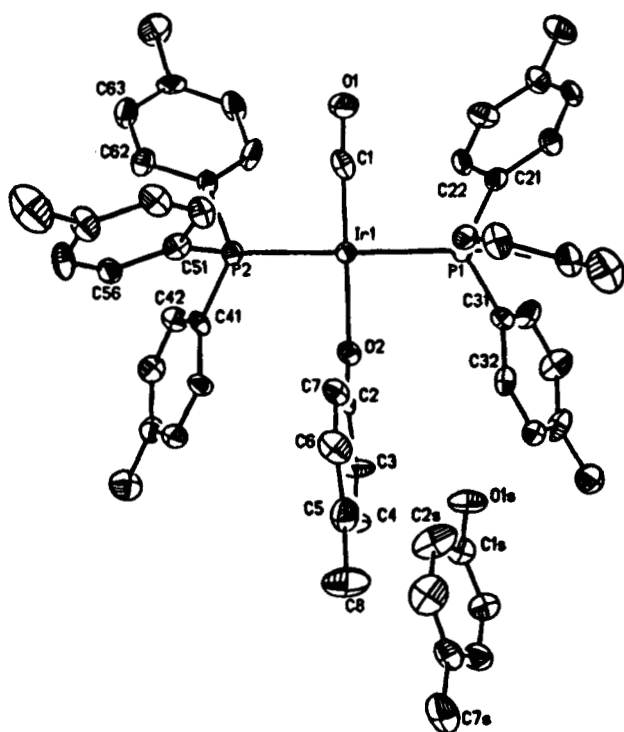


Figure 3. Labelling of atoms for  $\text{Ir}(\text{CO})(\text{OC}_6\text{H}_4\text{CH}_3)(\text{P}(\text{p-tolyl})_3)_2 \cdot \text{CH}_3\text{C}_6\text{H}_4\text{OH}$ .

talum(V) complexes.<sup>20</sup> The Ir-O bond length is affected by a number of factors. Although one might expect Ir(III)-O bond distances to be shorter than Ir(I)-O bond distances (due to the decreasing radius for iridium), the Ir(III)-O bonds are typically longer than Ir(I)-O bonds (see Table 11). While this could be attributed to change in the nature of the Ir-O bond, it could also result from

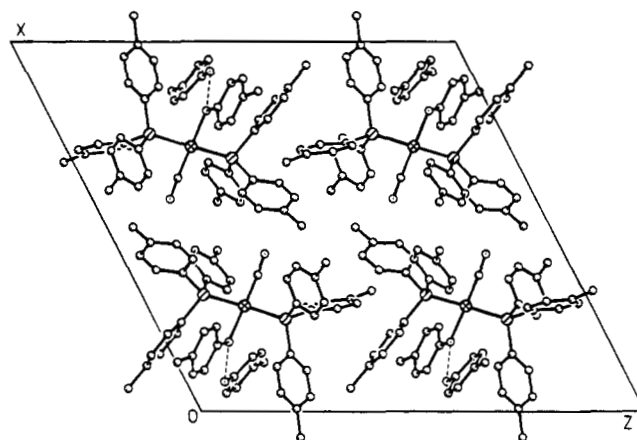


Figure 4. Packing diagram for  $\text{Ir}(\text{CO})(\text{OC}_6\text{H}_4\text{CH}_3)(\text{P}(\text{p-tolyl})_3)_2 \cdot \text{CH}_3\text{C}_6\text{H}_4\text{OH}$ , showing hydrogen bonding between the phenolic oxygen atoms of the p-cresol molecule and the p-cresolate ligand.

the larger coordination number of Ir(III) and enhanced steric interactions. The Ir-OCH<sub>2</sub>CF<sub>3</sub> bond distance of 2.169(7) Å for  $\text{Ir}(\text{CO})(\text{H})_2(\text{OCH}_2\text{CF}_3)(\text{PCy}_3)_2$  was suggested as a typical, non pi-bonded Ir-O distance.<sup>8b</sup> However, this is the longest of the well-characterized Ir-OR distances and may well not be typical. The two PCy<sub>3</sub> groups may be exerting a steric influence causing this Ir-O bond to be unusually long. The Ir-OMe bond length of 2.057(8) Å for  $\text{Ir}(\text{CO})(\text{OMe})(\text{TCNE})(\text{PPh}_3)_2$  (TCNE = tetracyanoethylene) may be a more typical Ir-OMe bond length, especially for Ir(I).<sup>21</sup> As an 18e<sup>-</sup> complex, pi donation should not be significant. The Ir(I)-OR bonds reported in this manuscript (except for the hydroxide complex) are not significantly shorter than this Ir-O distance.

(20) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P., *Polyhedron* **1990**, *9*, 963.

(21) Janik, T. S.; Bernard, K. A.; Churchill, M. R.; Atwood, J. D., *J. Organomet. Chem.* **1987**, *323*, 247.

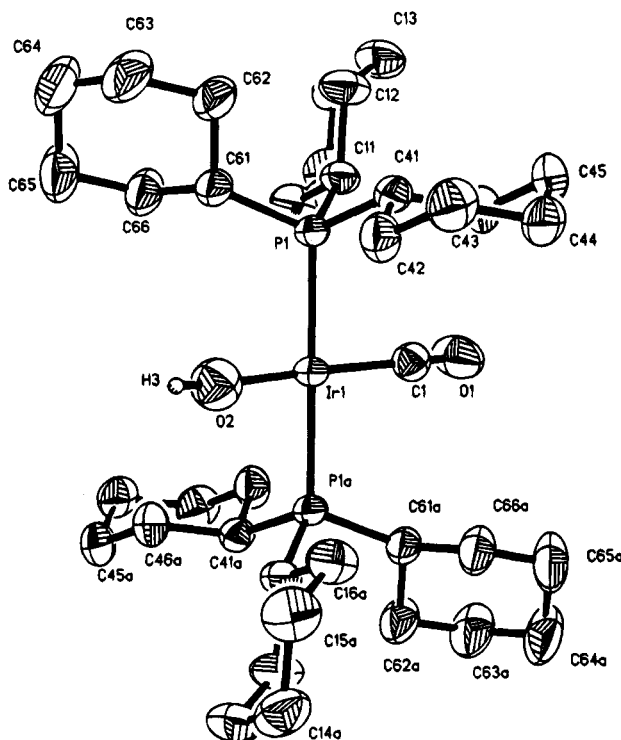
**Table 9. Selected Interatomic Distances (Å) and Angles (deg) for Ir(CO)(OC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH**

(A) Selected Distances in the Iridium Complex			
Ir(1)–P(1)	2.322(4)	Ir(1)–P(2)	2.330(4)
Ir(1)–O(2)	2.067(7)	Ir(1)–C(1)	1.781(13)
P(1)–C(11)	1.837(14)	P(1)–C(21)	1.842(12)
P(1)–C(31)	1.821(10)	P(2)–C(41)	1.817(12)
P(2)–C(51)	1.823(13)	P(2)–C(61)	1.818(13)
O(1)–C(1)	1.183(16)	O(2)–C(2)	1.347(14)
C(2)–C(3)	1.425(16)	C(2)–C(7)	1.363(18)
C(3)–C(4)	1.388(22)	C(4)–C(5)	1.315(26)
C(5)–C(6)	1.378(21)	C(5)–C(8)	1.562(25)
C(6)–C(7)	1.366(20)		
(B) Selected Angles in the Iridium Complex			
P(1)–Ir(1)–P(2)	174.4(1)	P(1)–Ir(1)–O(2)	90.2(3)
P(2)–Ir(1)–O(2)	90.1(3)	P(1)–Ir(1)–C(1)	90.2(6)
P(2)–Ir(1)–C(1)	89.7(6)	O(2)–Ir(1)–C(1)	178.9(5)
Ir(1)–P(1)–C(11)	115.6(4)	Ir(1)–P(1)–C(21)	112.5(5)
C(11)–P(1)–C(21)	107.2(6)	Ir(1)–P(1)–C(31)	115.2(5)
C(11)–P(1)–C(31)	103.0(6)	C(21)–P(1)–C(31)	102.1(5)
Ir(1)–P(2)–C(41)	116.9(5)	Ir(1)–P(2)–C(51)	114.9(6)
C(41)–P(2)–C(51)	103.0(6)	Ir(1)–P(2)–C(61)	112.1(5)
C(41)–P(2)–C(61)	105.2(6)	C(51)–P(2)–C(61)	103.2(5)
Ir(1)–O(2)–C(2)	122.5(7)	Ir(1)–C(1)–O(1)	176.1(17)
O(2)–C(2)–C(3)	117.6(11)	O(2)–C(2)–C(7)	125.2(10)
C(3)–C(2)–C(7)	117.2(11)	C(2)–C(3)–C(4)	117.8(13)
C(3)–C(4)–C(5)	124.1(13)	C(4)–C(5)–C(6)	117.9(16)
C(4)–C(5)–C(8)	120.2(14)	C(6)–C(5)–C(8)	121.9(16)
C(5)–C(6)–C(7)	121.0(15)	C(2)–C(7)–C(6)	121.9(11)
P(1)–C(11)–C(12)	121.3(11)	P(1)–C(11)–C(16)	120.5(9)
P(1)–C(21)–C(22)	116.6(11)	P(1)–C(21)–C(26)	125.6(11)
P(1)–C(31)–C(32)	118.2(8)	P(1)–C(31)–C(36)	124.7(9)
P(2)–C(41)–C(42)	123.7(9)	P(2)–C(41)–C(46)	119.6(11)
P(2)–C(51)–C(52)	118.2(12)	P(2)–C(51)–C(56)	124.3(11)
P(2)–C(61)–C(62)	122.1(10)	P(2)–C(61)–C(66)	120.2(11)
(C) Distances within the CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH Molecules of Solvation			
O(1S)–C(1S)	1.372(19)	C(1S)–C(2S)	1.376(24)
C(1S)–C(6S)	1.373(20)	C(2S)–C(3S)	1.396(30)
C(3S)–C(4S)	1.366(27)	C(4S)–C(5S)	1.343(24)
C(4S)–C(7S)	1.505(23)	C(5S)–C(6S)	1.385(25)
(D) Angles within the CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH Molecule of Solvation			
O(1S)–C(1S)–C(2S)	119.1(13)	O(1S)–C(1S)–C(6S)	120.1(14)
C(2S)–C(1S)–C(6S)	120.5(16)	C(1S)–C(2S)–C(3S)	117.6(16)
C(2S)–C(3S)–C(4S)	123.1(19)	C(3S)–C(4S)–C(5S)	116.5(17)
C(3S)–C(4S)–C(7S)	121.4(16)	C(5S)–C(4S)–C(7S)	121.9(16)
C(4S)–C(5S)–C(6S)	123.7(15)	C(1S)–C(6S)–C(5S)	118.2(14)

An expansion of the Ir–O–R angle could also indicate pi donation from the ligand to the metal. As discussed above, any angle >105° indicates some distortion. For a Ru–OCH<sub>2</sub>CF<sub>3</sub> complex an angle of 124.6° was attributed to pi donation.<sup>8a</sup> The complexes reported in this manuscript, *trans*-Ir(CO)(OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub> and *trans*-Ir(CO)(OC<sub>6</sub>H<sub>4</sub>Me)(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub> have Ir–O–R angles of 132.8(4)° and 122.5(7)°, respectively. These could be considered indicative of pi donation. However, one of the largest Ir–O–C angles (137°) was observed for Ir(CO)(OMe)(TCNE)(PPh<sub>3</sub>)<sub>2</sub> which should not be a pi-donor to the iridium.<sup>21</sup> Examining all of the Ir–O–C angles show a range from 118–138° with no clearly interpretable pattern. It is most likely that this angle is controlled by a combination of steric, electronic and packing effects.

Carbonyl stretching frequencies were also used to indicate pi donation.<sup>9</sup> For a number of *trans*-Ir(CO)-(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>X complexes (Table 12) prepared in our laboratory there are small changes in ν<sub>CO</sub>. Larger shifts are seen for complexes involving alkyl groups where pi donation is not possible. We can see no good way to differentiate σ- and π-effects on ν<sub>CO</sub>.

For the *trans*-Ir(CO)(OR)L<sub>2</sub> complexes we find no convincing evidence that pi donation from the alkoxide

**Figure 5.** The deconvoluted structure of Ir(CO)(OH)(PCy<sub>3</sub>)<sub>2</sub>.**Table 10. Selected Interatomic Distances (Å) and Angles (deg) for Ir(CO)(OH)(PCy<sub>3</sub>)<sub>2</sub>**

(A) Intramolecular Distances			
Ir(1)–P(1)	2.331(1)	Ir(1)–C(1)	1.887(13)
Ir(1)–O(2)	1.978(12)	Ir(1)–P(1A)	2.331(1)
P(1)–C(41)	1.861(4)	P(1)–C(11)	1.854(4)
P(1)–C(61)	1.860(5)	C(1)–O(1)	1.104(16)
(B) "Distances" between Disordered Images			
C(1)–O(2A)	0.441(14)	O(1)–O(2A)	1.041(16)
O(2)–C(1A)	0.441(14)	O(2)–O(1A)	1.041(16)
(C) Intramolecular Angles			
P(1)–Ir(1)–C(1)	89.1(3)	P(1)–Ir(1)–O(2)	90.1(3)
C(1)–Ir(1)–O(2)	167.2(4)	P(1)–Ir(1)–P(1A)	180.0
C(1)–Ir(1)–P(1A)	91.0(3)	O(2)–Ir(1)–P(1A)	89.9(3)
Ir(1)–P(1)–C(11)	112.9(1)	Ir(1)–P(1)–C(41)	112.9(1)
Ir(1)–P(1)–C(61)	113.8(2)	Ir(1)–C(1)–O(1)	165.6(10)

**Table 11. Geometry of the M–O–C or M–O–H Frameworks in Iridium Complexes**

	M–O (Å)	M–O–C(deg)	reference
Ir(CO)(OH)(PCy <sub>3</sub> ) <sub>2</sub>	1.978(12)		this work
Ir(CO)(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )(P( <i>p</i> -tolyl) <sub>3</sub> ) <sub>2</sub>	2.022(4)	132.8(4)	this work
Ir(CO)(OC <sub>6</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	2.049(4)	126.5(3)	5a
Ir(CO)(OC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )(P( <i>p</i> -tolyl) <sub>3</sub> ) <sub>2</sub>	2.067(7)	122.5(7)	this work
Ir(CO)(OC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	2.058(3)	135.4(3)	17
Rh(CO)(OC <sub>6</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	2.044(2)	125.5(2)	18
Ir(H) <sub>2</sub> (OCH <sub>2</sub> CF <sub>3</sub> )(PCy <sub>3</sub> ) <sub>2</sub>	2.032(10)	138.0(11)	8b
Ir(CO)(H) <sub>2</sub> (OCH <sub>2</sub> CF <sub>3</sub> )(PCy <sub>3</sub> ) <sub>2</sub>	2.169(7)	118.4(7)	8a
Ir(CO)(OCH <sub>3</sub> )(TCNE)(PPh <sub>3</sub> ) <sub>2</sub>	2.057(8)	137.4(9)	19
Ir(H)(OCH <sub>3</sub> )(PMe <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	2.118(8)	119.4(9)	20

or aryloxy to the metal is important to the Ir–OR bond. Cowan and Troglor also concluded that π-donation from an alkoxide should not be important.<sup>22</sup> We do note, however, that the Ir–OH bond for the most electron-rich iridium center and the most sterically hindered of the Ir(I) complexes, Ir(CO)(OH)(PCy<sub>3</sub>)<sub>2</sub>, appears to be substantially shorter than the Ir–alkoxide linkages; how-

(22) Cowan, R. L.; Troglor, W. C., *J. Am. Chem. Soc.* **1989**, *111*, 4750.

**Table 12. Carbonyl Stretching Frequencies (KBr) for *trans*-Ir(CO)X(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub> Complexes<sup>a</sup>**

X	$\nu_{\text{CO}}$ (cm <sup>-1</sup> )	X	$\nu_{\text{CO}}$ (cm <sup>-1</sup> )
I	1967	OC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	1949
Br	1966	OC <sub>6</sub> H <sub>5</sub>	1948
OC <sub>6</sub> F <sub>5</sub>	1962	OCH <sub>3</sub>	1940
Cl	1957	CH <sub>3</sub>	1937
OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	1953	OH	1932

<sup>a</sup> All prepared and characterized in our laboratory.

ever, we stress that disorder renders both this bond length and its esd unreliable.

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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 three structural studies (15 pages). Ordering information is given on any current masthead page.

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