

SYNTHESIS, CHARACTERIZATION, CRYSTAL STRUCTURE AND CARBONYLATION OF THE PERFLUOROPHENOXYIRIDIUM(I) COMPLEX, *trans*-(C₆F₅O)Ir(CO)(PPh₃)₂

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Summary

trans-(C₆F₅O)Ir(CO)(PPh₃)₂ is readily prepared by reaction of NaOC₆F₅ with *trans*-Ir(CO)(PPh₃)₂Cl. Reaction of *trans*-(C₆F₅O)Ir(CO)(PPh₃)₂ with CO does not lead to carbonylation of the Ir–O bond, consistent with expectations of OC₆F₅[–] loss from the coordination sphere. To further define the bonding of OC₆F₅[–] to the iridium we have determined the structure. *trans*-(C₆F₅O)Ir(CO)(PPh₃)₂ crystallizes in the centrosymmetric triclinic space group $P\bar{1}(C_i^1; \text{No. } 2)$ with a 11.901(3), b 12.823(4), c 14.153(5) Å, α 74.223(24), β 88.044(25), γ 66.267(23)°, V 1895.8(10) Å³ and $Z = 2$. Diffraction data (Mo- K_α , 2θ 4.5–50.0°) were collected with a Syntex P2₁ automated four-circle diffractometer and the structure was refined to R_F 4.0% for all 6727 independent data (R_F 3.3% for those 5870 data with $|F_0| > 6\sigma(|F_0|)$). The d^8 iridium(I) atom has the expected square-planar coordination geometry with Ir–P 2.320(1) and 2.321(1) Å, Ir–CO 1.798(6) Å and Ir–OC₆F₅ 2.058 (3) Å. Molecular dimensions are very similar to those of *trans*-PhOIr(CO)(PPh₃)₂ except for the Ir–O–C₆F₅ angle of 135.4(3)°, a value $8.9 \pm 0.4^\circ$ greater than the Ir–O–C₆H₅ angle of 126.5(3)°. This is interpreted as due to increased donation of p -electron density from oxygen to the electronegative C₆F₅ (vis à vis C₆H₅) group.

Introduction

Carbonylation of metal–oxygen bonds is an important part of several catalytic reactions [1–7]. Stoichiometric carbonylation of transition metal alkoxides has been the subject of several studies [8–13]. Our studies of the carbonylation of *trans*-ROIr(CO)(PPh₃)₂ (R = Me, n-Pr, t-Bu and Ph) indicated a mechanism of alkoxide displacement leading to formation of the cation, Ir(CO)₃(PPh₃)₂⁺, with carboalkoxy product formed by nucleophilic attack of alkoxide on the cation [8,9]. The reaction showed a dependence on the nucleophilicity of the alkoxido ligand [9]. To further

examine the influence of the nucleophilicity of the OR^- ligand we have prepared $\text{trans}-(\text{C}_6\text{F}_5\text{O})\text{Ir}(\text{CO})(\text{PPh}_3)_2$, examined the carbonylation reaction and studied its bonding by an X-ray structural determination.

Experimental

Iridium trichloride, $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$, was loaned by Johnson–Matthey Inc. All solvents were dried and degassed prior to use. All syntheses were accomplished under a nitrogen or argon atmosphere. Infrared spectra were recorded on a Beckman 4240.

Preparation of $\text{trans}-(\text{C}_6\text{F}_5\text{O})\text{Ir}(\text{CO})(\text{PPh}_3)_2$. A suspension of 0.50 g of $\text{trans}-(\text{C}_6\text{F}_5\text{O})\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ and 0.25 g NaOC_6F_5 is stirred in 50 ml of THF in an inert atmosphere glove box for 48 h. The solvent is removed and the solid purified by refluxing with 20 ml of hexane, followed by hexane removal and extraction into 40 ml of hot cyclohexane. Crystals were obtained by slow evaporation of the cyclohexane (3 days). The yield is 0.45 g (77%) of yellow crystals. The infrared spectrum shows one absorption at 1965 cm^{-1} in cyclohexane. Microanalysis: Found: C, 55.56, H, 3.40, P, 6.68, F, 10.30. $\text{C}_{43}\text{H}_{30}\text{F}_5\text{IrO}_2\text{P}_2$ calcd.: C, 55.65, H, 3.24, P, 6.69, F, 10.25%.

Carbonylation of $\text{trans}-(\text{C}_6\text{F}_5\text{O})\text{Ir}(\text{CO})(\text{PPh}_3)_2$. A solution of 0.10 g $\text{trans}-(\text{C}_6\text{F}_5\text{O})\text{Ir}(\text{CO})(\text{PPh}_3)_2$ in 30 ml of C_6H_6 is placed in a pressure bottle and sealed in an inert atmosphere glove box. The bottle is flushed and then charged (45 psi) with CO. The solution was monitored by IR for 48 h. The infrared spectrum indicated sharp absorptions at $2074(\text{w})$ and $2015(\text{s})\text{ cm}^{-1}$ and absorptions at $2000(\text{s})$, $1955(\text{m})$ and $1940(\text{s})\text{ cm}^{-1}$.

Collection of the X-ray diffraction data for $\text{trans}-(\text{C}_6\text{F}_5\text{O})\text{Ir}(\text{CO})(\text{PPh}_3)_2$. A pale yellow crystal of approximate dimensions $0.3 \times 0.3 \times 0.5\text{ mm}^3$ was sealed into a thin-walled glass capillary and mounted, with its extended direction close to the ϕ -axis, on a Syntex P2₁ automated four-circle diffractometer. Subsequent set-up operations (i.e., determination of the crystal's orientation matrix and accurate unit cell parameters) and data collection were carried out as described previously [14]; details are given in Table 1*. The diffraction symmetry was $\bar{1}$ and there were no systematic absences. The crystal thus belongs to the triclinic system, possible space groups being the noncentrosymmetric $P1$ (C_1^1 ; No. 1) or the centrosymmetric $\bar{P}1$ (C_i^1 ; No. 2). The latter is more probable with $Z = 2$ and was confirmed by intensity statistics and by the successful solution of the crystal structure in this higher space group.

All data were corrected for the effects of absorption by an empirical method (based upon interpolation in 2θ and ϕ between normalized ψ -scans of a set of fairly strong close-to-axial reflections) and for Lorentz and polarization factors. Data were converted to unscaled $|F_0|$ values, equivalent data were averaged ($R(I) = 1.3\%$, $R(wI) = 1.5\%$) and the data set was placed on an approximately absolute scale by means of a Wilson plot.

* Supplementary Material Available: A table of observed and calculated structure factor amplitudes is available upon the request from M.R.C.

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF *trans*-(C₆F₅O)-Ir(CO)(PPh₃)₂

(A) Unit cell data

<i>a</i> 11.901(3) Å	crystal system: triclinic
<i>b</i> 12.823(4) Å	space group: <i>P</i> $\bar{1}$ (<i>C</i> ₁ ^h ; No.2)
<i>c</i> 14.153(5) Å	<i>Z</i> = 2
α 74.223(24)°	formula: C ₄₃ H ₃₀ F ₅ IrO ₂ P ₂
β 88.044(25)°	mol. wt. 927.9
γ 66.267(23)°	<i>D</i> (calc'd) 1.63 g/cm ³
<i>V</i> 1895.8(10) Å ³	<i>T</i> 24°C (297 K)

(B) Collection of X-ray diffraction data

Diffractometer: Syntex P2₁Radiation: Mo-K α (λ 0.710730 Å)monochromator: highly orientated (pyrolytic) graphite; equatorial mode with $2\theta(m) = 12.160^\circ$; assumed to be 50% perfect/50% ideally mosaic for polarization correction.reflections measured: $+h, \pm k, \pm l$ for $2\theta: 4.5^\circ \rightarrow 50^\circ$; yielding 6727 unique data (File IRPF-209)scan type: coupled θ (crystal)- 2θ (counter)scan width: $[2\theta(K\alpha_1) - 1.0]^\circ$ through $[2\theta(K\alpha_2) + 1.0]^\circ$ scan speed: 4.0 deg/min (2θ)backgrounds: stationary crystal, stationary-counter at the two extremes of the 2θ scan; each for one-quarter of the total scan time

standard refinements: three mutually orthogonal reflections collected before each set of 97 data point. No decay observed.

absorption correction: $\mu(\text{Mo-K}\alpha) 38.9 \text{ cm}^{-1}$; corrected empirically by interpolation (in 2θ and ϕ) for 6 close-to-axial (ψ -scan) reflections.

Solution and refinement of the structure of trans-(C₆F₅O)Ir(CO)(PPh₃)₂. All calculations were carried out using our locally-modified version of the Syntex XTL interactive program package [15]. Calculated structure factors were based upon the analytical expression for the form factors [16a] of the neutral atoms; both the real and the imaginary components of anomalous dispersion [16b] were included for all non-hydrogen atoms. The function minimized during the least-squares refinement process was $\sum w(|F_0| - |F_c|)^2$ where $1/w = [\sigma(|F_0|)]^2 + [0.015|F_0|]^2$. Discrepancy indices used below are defined as follows:

$$R_F(\%) = 100 \sum | |F_0| - |F_c| | / \sum |F_0|$$

$$R_{wF}(\%) = 100 \left[\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2 \right]^{1/2}$$

$$\text{GOF} = \left[\sum w(|F_0| - |F_c|)^2 / (\text{NO} - \text{NV}) \right]^{1/2}$$

(where NO is the number of observations and NV is the number of variables).

The location of the iridium atom was quickly determined from a Patterson map. The positions of all non-hydrogen atoms were found from difference-Fourier syntheses. Hydrogen atoms of the phenyl rings were all included in calculated positions based upon $d(\text{C-H})$ 0.95 Å [17] and the assumptions of idealized (externally-bisecting) trigonal geometry about their attached carbon atoms; these positions were continuously up-dated, but were not refined. Convergence was reached with R_F 4.1%. Examination of intense low-angle data indicated that correction for secondary extinction was necessary. The applied correction was of the

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TABLE 2

ATOMIC COORDINATES FOR *trans*-(C₆F₅O)Ir(CO)(PPh₃)₂

Atom	x	y	z	B _{iso}
Ir	0.01562(2)	0.14727(2)	0.22039(1)	
P(1)	0.19026(11)	0.17450(11)	0.25266(9)	
P(2)	-0.15997(11)	0.12477(11)	0.18266(9)	
C(1)	0.07132(48)	0.12020(47)	0.10591(39)	
O(1)	0.10597(46)	0.10477(44)	0.03089(33)	
O(2)	-0.04003(32)	0.16942(30)	0.35552(24)	
C(2)	-0.11659(44)	0.25660(43)	0.38665(35)	
C(3)	-0.13692(51)	0.23687(48)	0.48751(39)	
C(4)	-0.22022(58)	0.32469(59)	0.52438(42)	
C(5)	-0.28617(61)	0.43492(59)	0.46455(55)	
C(6)	-0.26725(67)	0.45922(52)	0.36530(49)	
C(7)	-0.18415(55)	0.37240(48)	0.32988(41)	
F(3)	-0.07532(38)	0.12849(32)	0.54846(24)	
F(4)	-0.23540(41)	0.29876(39)	0.62241(27)	
F(5)	-0.36875(43)	0.51979(40)	0.50102(37)	
F(6)	-0.33214(53)	0.56805(35)	0.30434(37)	
F(7)	-0.17015(40)	0.40214(30)	0.23109(25)	
C(11)	0.17474(46)	0.25822(43)	0.34191(37)	3.053(88)
C(12)	0.16411(51)	0.20497(48)	0.43926(42)	3.78(10)
C(13)	0.14595(59)	0.26542(56)	0.50997(48)	4.78(12)
C(14)	0.13742(67)	0.37943(64)	0.48375(56)	5.64(15)
C(15)	0.14833(70)	0.43364(66)	0.38832(58)	6.08(16)
C(16)	0.16669(57)	0.37380(54)	0.31563(47)	4.55(12)
C(21)	0.32628(43)	0.03767(41)	0.30361(35)	2.741(82)
C(22)	0.33143(48)	-0.06882(45)	0.29390(40)	3.422(95)
C(23)	0.43830(53)	-0.17219(49)	0.32693(43)	3.99(11)
C(24)	0.53803(51)	-0.16983(47)	0.37099(42)	3.79(10)
C(25)	0.53356(50)	-0.06527(47)	0.38367(41)	3.64(10)
C(26)	0.42738(47)	0.03888(44)	0.35048(39)	3.271(93)
C(31)	0.23878(46)	0.25197(43)	0.14149(38)	3.079(89)
C(32)	0.36038(68)	0.22267(64)	0.12352(56)	5.82(15)
C(33)	0.39202(79)	0.28083(75)	0.03361(66)	7.11(19)
C(34)	0.30145(68)	0.36784(63)	-0.03519(54)	5.62(15)
C(35)	0.18200(63)	0.39798(59)	-0.01792(51)	5.14(13)
C(36)	0.15059(57)	0.34004(54)	0.07012(47)	4.51(12)
C(41)	-0.22444(46)	0.20614(43)	0.05535(38)	3.172(90)
C(42)	-0.26315(55)	0.15804(51)	-0.00609(45)	4.19(11)
C(43)	-0.31408(68)	0.22698(65)	-0.10160(56)	5.80(15)
C(44)	-0.32540(71)	0.34011(67)	-0.13516(58)	6.16(16)
C(45)	-0.28665(70)	0.38983(66)	-0.07540(58)	6.08(16)
C(46)	-0.23390(61)	0.32168(57)	0.02014(50)	4.96(13)
C(51)	-0.28620(43)	0.17914(41)	0.25744(36)	2.783(83)
C(52)	-0.26970(47)	0.11726(44)	0.35801(39)	3.297(93)
C(53)	-0.35747(50)	0.15946(48)	0.42029(41)	3.72(10)
C(54)	-0.46212(57)	0.26147(53)	0.38527(46)	4.48(12)
C(55)	-0.47944(62)	0.32162(58)	0.28584(49)	5.05(13)
C(56)	-0.39184(54)	0.28110(50)	0.22238(44)	4.15(11)
C(61)	-0.14093(46)	-0.02810(43)	0.19740(38)	3.115(89)
C(62)	-0.02423(54)	-0.11653(51)	0.20484(44)	4.16(11)
C(63)	-0.00902(64)	-0.23237(60)	0.21262(52)	5.35(14)
C(64)	-0.10989(63)	-0.25737(59)	0.21099(51)	5.22(13)
C(65)	-0.22488(62)	-0.17284(58)	0.20484(50)	5.06(13)
C(66)	-0.24226(56)	-0.05621(52)	0.19841(45)	4.29(11)

TABLE 2 (continued)

Atom	x	y	z	B _{iso}
H(12)	0.1693	0.1260	0.4576	6.0
H(13)	0.1394	0.2278	0.5764	6.0
H(14)	0.1238	0.4212	0.5320	6.0
H(15)	0.1434	0.5124	0.3711	6.0
H(16)	0.1735	0.4118	0.2493	6.0
H(22)	0.2621	-0.0713	0.2647	6.0
H(23)	0.4422	-0.2447	0.3189	6.0
H(24)	0.6106	-0.2407	0.3929	6.0
H(25)	0.6024	-0.0643	0.4148	6.0
H(26)	0.4235	0.1108	0.3596	6.0
H(32)	0.4233	0.1630	0.1717	6.0
H(33)	0.4761	0.2595	0.0209	6.0
H(34)	0.3228	0.4072	-0.0954	6.0
H(35)	0.1193	0.4587	-0.0658	6.0
H(36)	0.0660	0.3618	0.0813	6.0
H(42)	-0.2552	0.0783	0.0163	6.0
H(43)	-0.3411	0.1936	-0.1436	6.0
H(44)	-0.3603	0.3856	-0.2003	6.0
H(45)	-0.2955	0.4698	-0.0987	6.0
H(46)	-0.2044	0.3546	0.0610	6.0
H(52)	-0.1980	0.0462	0.3831	6.0
H(53)	-0.3453	0.1174	0.4883	6.0
H(54)	-0.5218	0.2904	0.4286	6.0
H(55)	-0.5522	0.3914	0.2608	6.0
H(56)	-0.4045	0.3236	0.1544	6.0
H(62)	0.0458	-0.0985	0.2046	6.0
H(63)	0.0713	-0.2936	0.2190	6.0
H(64)	-0.0989	-0.3359	0.2142	6.0
H(65)	-0.2939	-0.1922	0.2048	6.0
H(66)	-0.3230	0.0034	0.1947	6.0

TABLE 3

ANISOTROPIC THERMAL PARAMETERS ^a FOR *trans*-(C₆F₅O)Ir(CO)(PPh₃)₂

Atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Ir	2.3282(84)	2.8021(87)	2.0213(83)	-0.8905(59)	0.0425(53)	-0.5825(57)
P(1)	2.377(49)	2.822(51)	2.422(52)	-0.849(41)	-0.076(40)	-0.490(41)
P(2)	2.671(51)	3.051(52)	2.167(50)	-1.147(42)	-0.000(40)	-0.575(41)
C(1)	3.40(23)	4.05(25)	2.97(24)	-1.68(20)	0.64(19)	-1.12(19)
O(1)	6.79(27)	7.47(28)	3.98(22)	-3.07(22)	2.12(19)	-2.90(20)
O(2)	3.55(16)	3.66(16)	2.13(14)	-1.21(13)	0.46(12)	-0.68(12)
C(2)	2.99(21)	3.42(22)	2.39(20)	-1.58(18)	0.33(16)	-1.02(17)
C(3)	3.96(25)	4.13(25)	2.94(23)	-2.03(21)	0.38(19)	-1.01(20)
C(4)	5.18(30)	6.22(34)	3.30(26)	-3.43(27)	1.65(23)	-2.74(25)
C(5)	4.97(32)	4.87(32)	6.53(40)	-1.46(26)	1.11(28)	-3.71(30)
C(6)	6.88(38)	3.34(26)	4.42(32)	-0.85(25)	-0.11(28)	-1.39(23)
C(7)	5.06(29)	3.43(24)	3.06(24)	-1.42(21)	0.40(21)	-1.05(19)
F(3)	7.86(23)	5.40(18)	2.63(14)	-1.64(17)	0.59(15)	-0.14(13)
F(4)	8.45(25)	8.61(25)	4.04(18)	-4.34(21)	2.92(17)	-3.56(17)
F(5)	7.87(26)	7.47(24)	9.18(30)	-1.59(20)	2.75(22)	-5.99(23)
F(6)	12.67(39)	3.78(18)	7.74(29)	1.20(21)	-0.09(26)	-1.22(18)
F(7)	9.40(26)	3.83(16)	3.08(16)	-1.00(16)	0.57(16)	-0.08(12)

^a The anisotropic thermal parameters are in standard Syntex XTL format and enter the expression for the calculated structure factor in the form: $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

form $|F_{0,\text{corr}}| = |F_{0,\text{uncorr}}| (1.0 + gI_0)$, with $g = 5.7 \times 10^{-8}$. Refinement converged with R_F 4.0%, R_{wF} 4.0% and GOF 1.69 for all 6727 reflections; for those 6223 data with $|F_0| > 3\sigma(|F_0|)$, R_F 3.5%, R_{wF} 4.0% and GOF 1.73; for those 5870 data with $|F_0| > 6\sigma(|F_0|)$, R_F 3.3%, R_{wF} 3.9% and GOF 1.75.

A final difference-Fourier synthesis had no features greater than $0.26 \text{ e}^-/\text{\AA}^3$; the structure is thus both correct and complete. Atomic coordinates are collected in Table 2; anisotropic thermal parameters are listed in Table 3.

Results and discussion

trans-Carbonyl(pentafluorophenoxido)bis(triphenylphosphine)iridium(I) can be prepared in high yield from NaOC_6F_5 and *trans*- $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$. This reaction is similar to that used in synthesizing other previously reported alkoxides. In order to examine the binding of the OC_6F_5 group and compare it to that of the OC_6H_5 group [9] we have determined the structure of *trans*-($\text{C}_6\text{F}_5\text{O}$) $\text{Ir}(\text{CO})(\text{PPh}_3)_2$.

Description of the molecular structure of trans-(C₆F₅O)Ir(CO)(PPh₃)₂. The crystal contains an ordered arrangement of discrete molecular units; there are no abnormally short intermolecular distances. The overall molecular geometry and the atomic labelling scheme are illustrated in Fig. 1. A stereoscopic view of the molecule is provided by Fig. 2. Interatomic distances and angles are collected in Tables 4 and 5.

The central d^8 iridium(I) is in a square planar coordination environment, associated with the *trans* angles $\text{P}(1)\text{--Ir--P}(2)$ $177.97(5)^\circ$ and $\text{C}(1)\text{--Ir--O}(2)$ $176.76(21)$ and with *cis* angles of $88.96(19)\text{--}92.36(11)^\circ$. The two mutually *trans*- PPh_3

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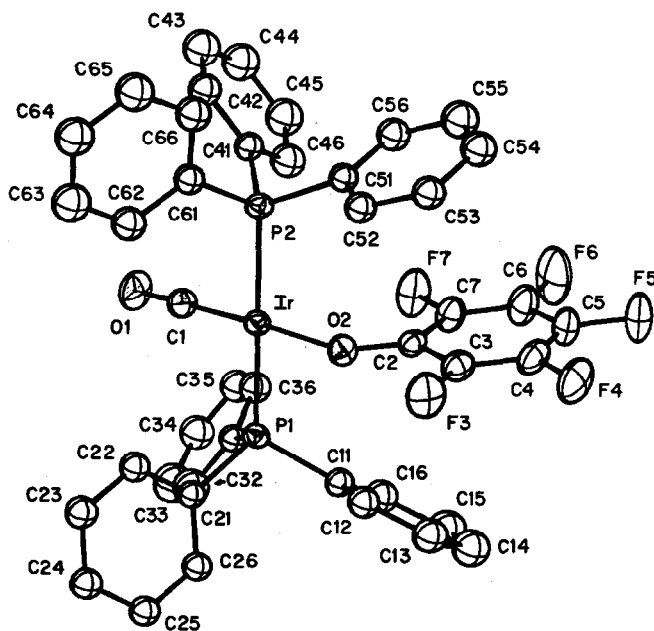


Fig. 1. Labelling of atoms in the *trans*-($\text{C}_6\text{F}_5\text{O}$) $\text{Ir}(\text{CO})(\text{PPh}_3)_2$ molecule (ORTEP-II diagram; 30% probability envelopes for the vibration ellipsoids).

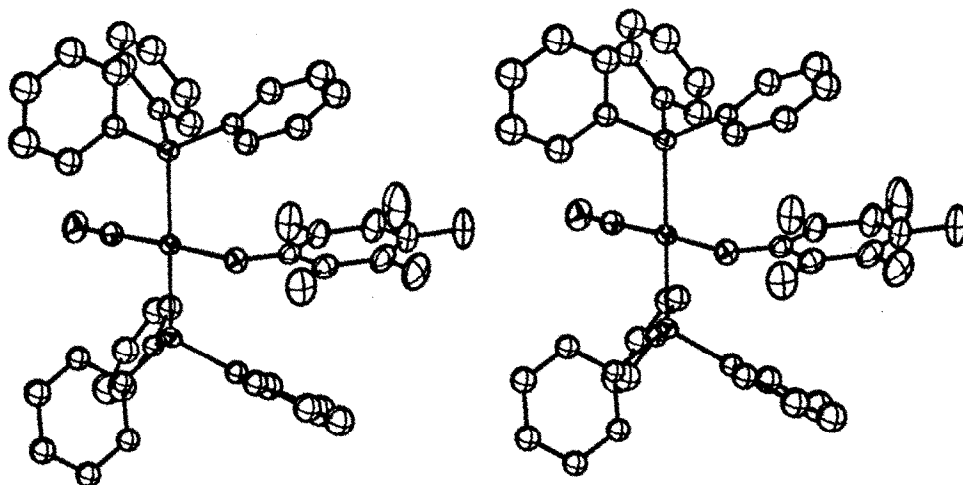


Fig. 2. A stereoscopic view of the $\text{trans}-(\text{C}_6\text{F}_5\text{O})\text{Ir}(\text{CO})(\text{PPh}_3)_2$ molecule.

TABLE 4. INTERATOMIC DISTANCES (Å) FOR $\text{trans}-(\text{C}_6\text{F}_5\text{O})\text{Ir}(\text{CO})(\text{PPh}_3)_2$

(A) Iridium – ligand distances:

Ir–P(1)	2.321(1)	Ir–O(2)	2.058(3)
Ir–P(2)	2.320(1)	Ir–C(1)	1.798(6)

(B) Phosphorus – carbon distances:

P(1)–C(11)	1.829(5)	P(2)–C(41)	1.831(5)
P(1)–C(21)	1.823(5)	P(2)–C(51)	1.820(5)
P(1)–C(31)	1.829(6)	P(2)–C(61)	1.833(6)

(C) Oxygen – carbon and fluorine – carbon distances:

O(1)–C(1)	1.164(7)	F(5)–C(5)	1.352(9)
O(2)–C(2)	1.302(6)	F(6)–C(6)	1.346(8)
F(3)–C(3)	1.336(7)	F(7)–C(7)	1.369(7)
F(4)–C(4)	1.360(7)		

(D) Carbon – carbon distances:

C(2)–C(3)	1.411(7)	C(21)–C(22)	1.386(8)
C(3)–C(4)	1.382(9)	C(22)–C(23)	1.393(8)
C(4)–C(5)	1.354(10)	C(23)–C(24)	1.374(9)
C(5)–C(6)	1.385(10)	C(24)–C(25)	1.380(8)
C(6)–C(7)	1.361(9)	C(25)–C(26)	1.394(8)
C(7)–C(2)	1.390(8)	C(26)–C(21)	1.401(8)
C(11)–C(12)	1.388(8)	C(31)–C(32)	1.374(10)
C(12)–C(13)	1.386(9)	C(32)–C(33)	1.412(12)
C(13)–C(14)	1.369(10)	C(33)–C(34)	1.367(12)
C(14)–C(15)	1.369(11)	C(34)–C(35)	1.347(12)
C(15)–C(16)	1.405(10)	C(35)–C(36)	1.390(10)
C(16)–C(11)	1.390(9)	C(36)–C(31)	1.377(9)
C(41)–C(42)	1.377(8)	C(51)–C(52)	1.405(7)
C(42)–C(43)	1.397(10)	C(52)–C(53)	1.379(8)
C(43)–C(44)	1.349(12)	C(53)–C(54)	1.373(9)
C(44)–C(45)	1.375(12)	C(54)–C(55)	1.385(9)
C(45)–C(46)	1.400(10)	C(55)–C(56)	1.385(10)
C(46)–C(41)	1.387(9)	C(56)–C(51)	1.379(8)
C(61)–C(62)	1.380(9)	C(64)–C(65)	1.348(11)
C(62)–C(63)	1.395(10)	C(65)–C(66)	1.402(10)
C(63)–C(64)	1.364(12)	C(66)–C(61)	1.389(9)

TABLE 5

INTERATOMIC ANGLES (in Deg.) FOR *trans*-(C₆F₅O)Ir(CO)(PPh₃)₂

<i>(A) Angles about the iridium atom</i>			
P(1)–Ir–P(2)	177.97(5)	P(2)–Ir–C(1)	88.96(19)
P(1)–Ir–C(1)	89.75(19)	P(2)–Ir–O(2)	92.36(11)
P(1)–Ir–O(2)	89.01(11)	C(1)–Ir–O(2)	176.76(21)
<i>(B) Ir–P–C and C–P–C angles</i>			
Ir–P(1)–C(11)	114.79(18)	Ir–P(2)–C(41)	112.26(18)
Ir–P(1)–C(21)	114.70(17)	Ir–P(2)–C(51)	114.17(17)
Ir–P(1)–C(31)	112.32(18)	Ir–P(2)–C(61)	115.82(18)
C(11)–P(1)–C(21)	103.33(24)	C(41)–P(2)–C(51)	104.77(25)
C(11)–P(1)–C(31)	106.24(25)	C(41)–P(2)–C(61)	105.46(25)
C(21)–P(1)–C(31)	104.43(24)	C(51)–P(2)–C(61)	103.25(24)
<i>(C) Ir–O–C, O–C–C and Ir–C–O angles</i>			
Ir–O(2)–C(2)	135.4(3)	O(2)–C(2)–C(3)	119.6(5)
Ir–C(1)–O(1)	178.8(5)	O(2)–C(2)–C(7)	126.6(5)
<i>(D) P–C–C angles:</i>			
P(1)–C(11)–C(12)	117.7(4)	P(2)–C(41)–C(42)	123.2(5)
P(1)–C(11)–C(16)	123.0(5)	P(2)–C(41)–C(46)	117.6(5)
P(1)–C(21)–C(22)	119.8(4)	P(2)–C(51)–C(52)	117.2(4)
P(1)–C(21)–C(26)	120.9(4)	P(2)–C(51)–C(56)	123.7(4)
P(1)–C(31)–C(32)	122.8(5)	P(2)–C(61)–C(62)	119.6(4)
P(1)–C(31)–C(36)	119.2(5)	P(2)–C(61)–C(66)	121.2(4)
<i>(E) F–C–C angles:</i>			
F(3)–C(3)–C(2)	118.4(5)	F(5)–C(5)–C(6)	120.6(7)
F(3)–C(3)–C(4)	119.3(6)	F(6)–C(6)–C(5)	119.8(7)
F(4)–C(4)–C(3)	118.9(6)	F(6)–C(6)–C(7)	120.5(6)
F(4)–C(4)–C(5)	120.1(6)	F(7)–C(7)–C(2)	118.9(5)
F(5)–C(5)–C(4)	120.6(7)	F(7)–C(7)–C(6)	116.8(6)
<i>(F) C–C–C angles:</i>			
C(7)–C(2)–C(3)	113.8(5)	C(16)–C(11)–C(12)	119.2(5)
C(4)–C(3)–C(2)	122.2(6)	C(11)–C(12)–C(13)	120.9(6)
C(5)–C(4)–C(3)	121.0(6)	C(12)–C(13)–C(14)	119.8(7)
C(6)–C(5)–C(4)	118.8(7)	C(13)–C(14)–C(15)	120.4(7)
C(7)–C(6)–C(5)	119.7(7)	C(14)–C(15)–C(16)	120.6(7)
C(2)–C(7)–C(6)	124.3(6)	C(15)–C(16)–C(11)	119.2(6)
C(26)–C(21)–C(22)	119.3(5)	C(36)–C(31)–C(32)	117.9(6)
C(21)–C(22)–C(23)	119.9(5)	C(31)–C(32)–C(33)	120.3(7)
C(22)–C(23)–C(24)	120.4(6)	C(32)–C(33)–C(34)	119.9(8)
C(23)–C(24)–C(25)	120.6(4)	C(33)–C(34)–C(35)	120.3(8)
C(24)–C(25)–C(26)	119.6(5)	C(34)–C(35)–C(36)	119.9(7)
C(25)–C(26)–C(21)	120.2(5)	C(35)–C(36)–C(31)	121.7(6)
C(46)–C(41)–C(42)	119.2(6)	C(56)–C(51)–C(52)	118.9(5)
C(41)–C(42)–C(43)	119.7(6)	C(51)–C(52)–C(53)	120.1(5)
C(42)–C(43)–C(44)	121.1(7)	C(52)–C(53)–C(54)	120.9(6)
C(43)–C(44)–C(45)	120.3(8)	C(53)–C(54)–C(55)	119.2(6)
C(44)–C(45)–C(46)	119.5(8)	C(54)–C(55)–C(56)	120.8(7)
C(45)–C(46)–C(41)	120.2(7)	C(55)–C(56)–C(51)	120.2(6)
C(66)–C(61)–C(62)	119.2(5)	C(63)–C(64)–C(65)	121.3(7)
C(61)–C(62)–C(63)	120.1(6)	C(64)–C(65)–C(66)	119.8(7)
C(62)–C(63)–C(64)	119.8(7)	C(65)–C(66)–C(61)	119.8(6)

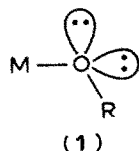
ligands have equivalent iridium–phosphorus bond lengths, with Ir–P(1) 2.321(1) and Ir–P(2) 2.320(1) Å. (These values are slightly shorter than those of 2.328(1) and 2.344(1) Å found in *trans*-PhOIr(CO)(PPh₃)₂ [9], but slightly longer than those of 2.300(1) Å (twice) found in *trans*-MeIr(CO)(PPh₃)₂ [18].)

Distances and angles within the Ir(PPh₃)₂ moiety show the usual pattern, with phosphorus–carbon distances of 1.820(5)–1.833(6) Å, all Ir–P–C angles increased from the regular tetrahedral value (range 112.26(18)–115.82(18)°) and all C–P–C angles reduced from the regular tetrahedral value (range 103.25(24)–106.24(25)°). The carbon atom skeletons of the phenyl groups of the PPh₃ ligands show the usual slight distortion from *D*_{6h} towards *C*_{2v} symmetry [19,20]. In particular, each of the C(α)–C(*ipso*)–C(α') angles is reduced from the ideal *sp*² angle of 120°, individual values being C(16)–C(11)–C(12) 119.2(5)°, C(26)–C(21)–C(22) 119.3(5)°, C(36)–C(31)–C(32) 117.9(6)°, C(46)–C(41)–C(42) 119.2(6)°, C(56)–C(51)–C(52) 118.9(5)° and C(66)–C(61)–C(62) 119.2(5)°.

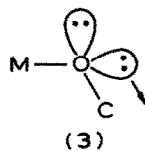
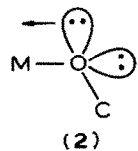
The Ir–C(1)–O(1) system is essentially linear with Ir–C(1)–O(1) 178.8(5)°, Ir–C(1) 1.798(6) Å and C(1)–O(1) 1.164(7) Å. (Cf. values of 176.8(5)°, 1.795(5) and 1.162(7) Å in *trans*-PhOIr(CO)(PPh₃)₂ [9].)

The perfluorophenoxide ligand is bonded to iridium with an Ir–O(2)–C(2) angle of 135.4(3)°, an Ir–O(2) bond length of 2.058(3) Å and an O(2)–C(2) bond length of 1.302(6) Å. Equivalent parameters for the non-fluorinated analogue, *trans*-PhOIr(CO)(PPh₃)₂, are, respectively, 126.5(3)°, 2.049(4) and 1.324(6) Å [9]. The most significant structural change is the increased Ir–O–C₆F₅ angle of 135.4(3)°, some 8.9 ± 0.4° greater than the Ir–O–C₆H₅ angle of 126.5(3)°.

The bonding to the oxygen atom in the perfluorophenoxide complex thus has more π -character than that in the phenoxide complex. The basic σ -bonding to a phenoxide (or alkoxide) is that shown in 1. More π -character to the bonding at



oxygen can be introduced by (a) donation of electron density from oxygen to the metal atom (as in 2) or (b) donation of electron density from oxygen to the carbon atom (as in 3).



Oxygen–metal π -bonding is strongly indicated from crystal structure analyses of the mononuclear tungsten(VI)-phenoxide (and alkoxide) species W(C₃Et₃)[O-2,6-C₆H₃(i-Pr)₂]₃ [21], W(C₃Et₃)[OCH(CF₃)₂]₃ [22] and W[C(t-Bu)CHC(t-Bu)]-[OCH(CF₃)₂]₃ [23]. However, these species have *d*⁰ tungsten(VI) atoms with available empty *d*-orbitals. This is not the case with the present *d*⁸ iridium(I) complex; here the appropriate *d* orbitals (*d*_{xx}, *d*_{yz} or *d*_{xy}) are already occupied. (Furthermore, we note that the alkoxide lies with the Ir–O–C(phenoxide) plane

TABLE 6

SELECTED LEAST-SQUARES PLANES ^a IN THE *trans*-(C₆F₅O)Ir(CO)(PPh₃)₂ MOLECULE

Atom	Dev. (Å)	Atom	Dev. (Å)
(A) The OIr(C)(P) ₂ coordination plane			
Equation: $-0.0838X + 0.9010Y - 0.4257Z - 0.9898 = 0$			
Ir*	-0.0011(2)		
P(1)*	0.029(1)		
P(2)*	0.030(1)		
C(1)*	-0.077(6)	O(1)	-0.101(5)
O(2)*	-0.021(4)	C(2)	0.870(5)
(B) The (OC)Ir-OC Plane			
Equation: $-0.9423X - 0.3126Y - 0.1200Z + 2.1660 = 0$			
Ir*	0.0000(2)	P(1)	-2.2982(14)
C(1)*	-0.012(6)	P(2)	2.2869(15)
O(1)*	-0.019(6)		
O(2)*	-0.015(4)		
C(2)*	-0.004(6)		
(C) The C ₆ ring of the C ₆ F ₅ ligand			
Equation: $-0.9269X - 0.3328Y - 0.1733Z + 2.5524 = 0$			
C(2)*	0.013(6)	O(2)	0.054(4)
C(3)*	-0.008(6)	F(3)	0.003(5)
C(4)*	-0.005(8)	F(4)	-0.017(5)
C(5)*	0.012(8)	F(5)	0.035(5)
C(6)*	0.002(8)	F(6)	0.024(6)
C(7)*	-0.014(7)	F(7)	-0.019(5)
Ir	0.1904(2)	P(1)	-2.106(1)
C(1)	0.284(6)	P(2)	2.479(1)
O(1)	0.345(6)		
(D) Dihedral angles (in degrees)			
A/B	98.72		
A/C	98.53		
B/C	3.38		

^a Atoms marked with an asterisk were used in calculating the plane.

essentially perpendicular to the square coordination plane about the iridium atom; hence only overlap with the d_{xy} orbital would be possible.) We can therefore be assured that increased π -character at the oxygen atom occurs by mechanism 3, with increased donation of some p -orbital electron density from oxygen to the electronegative perfluorophenyl group. This indicates that the C₆F₅O ligand is a poorer donor ligand to the metal atom than a C₆H₅O ligand.

Other geometric aspects of the perfluorophenoxide ligand are normal. The C-C distances are 1.354(10)–1.411(7) Å and C-F distances are 1.336(7)–1.369(7) Å. The C₆F₅ system has C_{2v} symmetry with C(7)–C(2)–C(3), the internal angle at the *ipso*-carbon, being reduced to 113.8(5)°; this decrease is far more dramatic than that found in *trans*-PhOIr(CO)(PPh₃)₂, in which the corresponding angle in the phenoxide system is 117.7(5)°.

The plane of the perfluorophenoxide ligand lies close to perpendicular to the coordination plane of the iridium(I) atom. Quantitative data are given in Table 6.

The carbonylation of *trans*-C₆F₅OIr(CO)(PPh₃)₂ does not produce a product of CO insertion into the iridium–oxygen bond, in contrast to other alkoxide complexes

[8,9]. Infrared spectra indicate the presence of $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2]^+[\text{OC}_6\text{F}_5]^-$ (sharp absorptions at 2074(w) and 2015(s) cm^{-1}) [9], $\text{C}_6\text{F}_5\text{OIr}(\text{CO})_2(\text{PPh}_3)_2$ (2000(s) and 1940(s) cm^{-1}) [18] and *trans*- $\text{C}_6\text{F}_5\text{OIr}(\text{CO})(\text{PPh}_3)_2$ (1955 cm^{-1}). That OC_6F_5^- is not sufficiently nucleophilic to attack a carbon in $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2]^+$ is further shown by failure to form $\text{C}_6\text{F}_5\text{OC}(\text{O})\text{Ir}(\text{CO})_2(\text{PPh}_3)_2$ by addition of NaOC_6F_5 to a THF solution of $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2]^+[\text{BPh}_4]^-$.

The failure to carbonylate the oxygen-iridium bond of *trans*-($\text{C}_6\text{F}_5\text{O}$)- $\text{Ir}(\text{CO})(\text{PPh}_3)_2$ is consistent with the mechanism which we have suggested for carbonylation of iridium alkoxide complexes - dissociation of OR^- and subsequent nucleophilic attack on the cationic carbonyl complex. While the OC_6F_5^- can be displaced by CO, it lacks sufficient nucleophilicity to attack CO on the cation, $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2]^+$.

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