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An accurate X-ray diffraction study of Vaska's compound, *trans*-IrCl(CO)(PPh$_3$)$_2$, including resolution of the carbonyl/chloride disorder problem

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Abstract

Vaska's compound, *trans*-IrCl(CO)(PPh$_3$)$_2$, crystallizes in the centrosymmetric triclinic space group $P\bar{1}$, (C_i^1; No. 2) with a 9.2076(10), b 9.6458(16), c 10.4601(11) Å, α 72.290(11), β 89.597(10), γ 69.568(11)°, V 824.17(18) Å^3 and $Z = 1$. A complete shell of data for 2θ 4.5–50.0° (Mo-$K_{\bar{\alpha}}$ radiation) was collected on a Syntex P2$_1$ automated four-circle diffractometer and the structure was solved and refined to R_F 1.7% and R_{wF} 2.1% for 2920 independent data. The *trans*-IrCl(CO)(PPh$_3$)$_2$ molecule lies at a site of $C_i(\bar{1})$ symmetry and thereby suffers from disorder of CO and Cl ligands; the crystal is isomorphous with *trans*-Ir(CH$_3$)(CO)(PPh$_3$)$_2$ and presumably with *trans*-RhCl(CO)(PPh$_3$)$_2$. The chloride ligand and atoms of the CO ligand have been clearly resolved; metal–ligand distances are Ir–P 2.330(1) Å, Ir–Cl 2.382(3) Å and Ir–CO 1.791(13) Å, with C–O 1.161(18) Å and Ir–C–O 175.1(12)°.

Introduction

Vaska's compound, *trans*-IrCl(CO)(PPh$_3$)$_2$, occupies a position of pivotal importance in the discovery of oxidative-addition reactions of transition metal complexes [1,2]. Despite this, no structural study of Vaska's compound has appeared in the primary literature, although several closely related iridium(I) species have been studied, viz; *trans*-IrCl(CO)[P(C$_6$H$_4$-*o*-CH$_3$)$_3$]$_2$ (which suffers from Cl/CO disorder [3]), *trans*-IrCl(CO)[P(C$_6$H$_4$-*p*-CH$_3$)$_3$]$_2$ (which is ordered [4]) and *trans*-Ir(CH$_3$)(CO)(PPh$_3$)$_2$ (which suffers from CH$_3$/CO disorder [5]). The analogous rhodium(I) complex, *trans*-RhCl(CO)(PPh$_3$)$_2$, has been studied. A report of a triclinic crystal form appeared in 1969 [6]. The structure was solved in the acentric space group $P1$, but the resulting model has some disturbing features and is close to centric; one assumes that the authors failed to transform the model appropriately to

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the centric space group $P\bar{1}$. Furthermore, the unit cell parameters and positional parameters closely parallel those of *trans*-$Ir(CH_3)(CO)(PPh_3)_2$, which was solved using a disordered centric model [5]. While our work was in progress, a crystallographic study of an ordered monoclinic crystal modification of *trans*-$RhCl(CO)(PPh_3)_2$ was reported [7].

We began our study of Vaska's compound with the expectation that the chloride and carbonyl ligands would be disordered. (This proved to be the case, vida infra). With predicted distances of Ir–CO ~ 1.8 Å, Ir $\cdots$ O ~ 2.9 Å and Ir–Cl ~ 2.35 Å (cf. [4]), one needs to be able to refine "atoms" separated by only (approximately) 0.45 Å. This is normally attainable with a "resolution" of $\leqslant 0.9$ Å. With a good data set to $2\theta = 50°$ (Mo-K_α), one should be able to resolve the (expected) disorder problem. This proved to be the case; our results are reported below.

Experimental

Crystals were grown by recrystallization of a sample of *trans*-$IrCl(CO)(PPh_3)_2$ from benzene/pentane.

Collection of X-ray diffraction data for trans-IrCl(CO)(PPh₃)₂

The crystal selected for the X-ray structural study was a well-formed transparent parallelepiped with approximate orthogonal dimensions of 0.3 mm × 0.3 mm × 0.5 mm. The crystal was sealed into a thin-walled glass capillary and was aligned accurately on a Syntex $P2_1$ automated four-circle diffractometer. Subsequent set-up operations and collection of the X-ray diffraction data were carried out as described previously [8]; details are collected in Table 1.

The crystal was found to belong to the triclinic crystal system (diffraction symmetry $\bar{1}$; no systematic absences). Possible space groups are the noncentrosymmetric space group $P1$ (C_1^1; No. 1) or the related centrosymmetric space group $P\bar{1}$ (C_i^1; No. 2). The observed unit cell volume of 824.17(18) $Å^3$ yields a volume of 11.4 $Å^3$/atom for $Z = 1$. There is thus either one ordered molecule per crystallographic asymmetric unit in space group $P1$ or one-half of a disordered molecule per asymmetric unit in space group $P\bar{1}$. Since the crystals are isomorphous with those of *trans*-$Ir(CH_3)(CO)(PPh_3)_2$ [5], the analysis was begun by assuming the true space group to be $P\bar{1}$.

A complete shell of data ($\pm h, \pm k, \pm l$) for 2θ 4.5–50.0° (Mo-$K_{\bar{\alpha}}$) was collected. All data were corrected for the effects of absorption by an empirical method based upon interpolation (in both 2θ and ϕ) between a set of four normalized ψ-scans of close-to-axial reflections. Symmetry-equivalent data (hkl and $\overline{hkl}$) were averaged ($R(I)$ 1.47 % and $R(wI)$ 1.75% for 2921 pair of averaged data) and corrected for Lorentz and polarization factors. All data were converted to unscaled $|F_o|$ values. (No data were deleted; all had $|F_o| > 8\sigma(|F_o|)$). A Wilson plot was used to place the data on an approximately absolute scale, which also provided the value for the overall isotropic thermal parameter of $\bar{B}$ 2.59 $Å^2$.

Solution and refinement of the structure of trans-IrCl(CO)(PPh₃)₂

All calculations were performed by use of our locally-modified version of the Syntex XTL interactive crystallographic program package [9]. Throughout the analysis, calculated structure factors were based upon the analytical expressions for

Table 1

Experimental data for the X-ray diffraction study of *trans*-$IrCl(CO)(PPh_3)_2$

A. Crystal parameters at 24 °C (297 K)

crystal system: triclinic
space group: $P\bar{1}$ (C_i^1; No. 2)
a 9.2076(10) Å
b 9.6458(16) Å
c 10.4601(11) Å
α 72.290(11)°
β 89.597(10)°
γ 69.568(11)°

V 824.17(18) Å^3
$Z = 1$
formula: $C_{37}H_{30}ClOIrP_2$
mol wt 780.3
D(calcd) 1.57 g/cm^3

B. Measurement of intensity data

Diffractometer: Syntex $P2_1$
Radiation: Mo-$K_{\bar{\alpha}}$ (λ 0.710730 Å)
Monochromator: pyrolytic graphite ($2\theta_m$ 12.2°), equatorial mode; assumed 50% perfect/50% ideally mosaic for polarization correction.
Reflections measured: $\pm h, \pm k, \pm l$ for 2θ 4.5–50.0°
Scan type: coupled θ(crystal)-2θ(counter)
Scan range: $[2\theta(K_{\alpha_1})-1.0]-[2\theta(K_{\alpha_2})+1.0]$°
Scan speed: 4.0°/min in 2θ
Background: stationary crystal and counter at each end of 2θ scan, each for 1/4 of total scan time.
Total measurements: 6025 reflections, yielding 2921 unique data ($R(I) = 1.47\%$ and $R(wI)$ 1.75% for 2921 pairs of averaged data).
Standard reflections: 3 approximately mutually orthogonal reflections collected before every 97 data points; no decay observed.
Absorption coefficient: μ 45.0 cm^{-1}; corrected empirically by interpolation (in 2θ and ϕ) between 4 pairs of close-to-axial ψ scans.
(410 and $\bar{4}\bar{1}0$, 2θ 17.86°, $T_{min}/T_{max} = 0.694$;
510 and $\bar{5}\bar{1}0$, 2θ 22.55°, $T_{min}/T_{max} = 0.712$;
620 and $\bar{6}\bar{2}0$, 2θ 26.74°, $T_{min}/T_{max} = 0.725$;
721 and $\bar{7}\bar{2}\bar{1}$, 2θ 31.76°, $T_{min}/T_{max} = 0.713$).

the scattering factors of the neutral atoms; corrections for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included for all non-hydrogen atoms [10].

The function minimized in least-squares refinement processes was $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma(|F_o|)^2 + (0.015|F_o|)^2]^{-1}$. Discrepancy indices referred to below are defined in eq. 1–3. In eq. 3, NO = number of observations and NV = number of variables.

$$R_F(\%) = 100\Sigma\,||F_o| - |F_c||/\Sigma|F_o| \tag{1}$$

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

$$\text{GOF} = \left[\Sigma w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})\right]^{1/2} \tag{3}$$

The structure is an unusual case of the "self-phasing" variety. Reflections were phased by introducing the iridium atom at the origin (0,0,0). A difference-Fourier map was used to provide the location of the P and Cl atoms and all carbon atoms of the phenyl rings. The C and O atoms were input in calculated positions (strictly *trans* to the Ir–Cl vector, with Ir–CO 1.8 Å, C–O 1.2 Å and angle Ir–C–O 180°).

Full-matrix least-squares refinement of positional and thermal parameters (firstly isotropic and secondly anisotropic) for all non-hydrogen atoms proceeded smoothly to convergence (with no problems of coalescence of C, O and Cl atoms) yielding R_F 2.2%, R_{wF} 2.9% and GOF 1.439. A difference-Fourier map, based upon those 891 data with $\sin \theta/\lambda < 0.4$, provided the locations off all 15 independent hydrogen atoms as the strongest peaks on the map. The contributions from these atoms were now included in the model. Continued refinement, now including positional and isotropic thermal parameters for all hydrogen atoms, led to final convergence (maximum value of shift/esd for any parameter 0.03) with R_F 1.7%, R_{wF} 2.1% and GOF 1.090 for 265 parameters refined against 2920 independent data. (The 100

Table 2

Final positional parameters for *trans*-$IrCl(CO)(PPh_3)_2$

Atom	*x*	*y*	*z*	*B* (Å^2)
Ir	0	0	0	
P	0.01902(7)	−0.20672(8)	0.19417(6)	
Cl	−0.20919(34)	0.16106(31)	0.08613(30)	
C(1)	0.1608(15)	−0.1241(14)	−0.0592(10)	
O(1)	0.2614(13)	−0.1967(13)	−0.1067(11)	
C(11)	0.11433(30)	−0.19930(35)	0.34385(27)	
C(12)	0.1226(4)	−0.0582(4)	0.34225(35)	
C(13)	0.1933(5)	−0.0472(6)	0.4538(4)	
C(14)	0.2555(5)	−0.1758(7)	0.5661(4)	
C(15)	0.2479(6)	−0.3131(7)	0.5679(4)	
C(16)	0.1781(5)	−0.3285(5)	0.45663(34)	
C(21)	0.1269(4)	−0.40485(33)	0.19096(29)	
C(22)	0.2882(4)	−0.4508(4)	0.1854(4)	
C(23)	0.3730(6)	−0.5980(6)	0.1784(5)	
C(24)	0.2996(10)	−0.6988(6)	0.1759(6)	
C(25)	0.1415(11)	−0.6534(6)	0.1791(8)	
C(26)	0.0546(6)	−0.5070(5)	0.1865(5)	
C(31)	−0.17206(32)	−0.20982(35)	0.23991(29)	
C(32)	−0.2089(4)	−0.2406(4)	0.37202(33)	
C(33)	−0.3562(5)	−0.2427(6)	0.4000(5)	
C(34)	−0.4652(5)	−0.2148(6)	0.2967(5)	
C(35)	−0.4307(5)	−0.1850(7)	0.1660(5)	
C(36)	−0.2839(4)	−0.1802(6)	0.1369(4)	
H(12)	0.078(4)	0.034(5)	0.262(4)	5.1(8)
H(13)	0.207(6)	0.058(6)	0.443(5)	7.3(12)
H(14)	0.304(6)	−0.168(7)	0.644(5)	8.6(14)
H(15)	0.281(7)	−0.397(8)	0.633(6)	9.7(17)
H(16)	0.169(5)	−0.426(5)	0.461(4)	5.5(9)
H(22)	0.347(5)	−0.370(6)	0.174(5)	6.6(10)
H(23)	0.484(7)	−0.631(7)	0.179(6)	8.5(14)
H(24)	0.368(8)	−0.800(9)	0.164(6)	11.1(18)
H(25)	0.100(7)	−0.720(8)	0.175(6)	9.4(16)
H(26)	−0.053(5)	−0.476(5)	0.188(4)	5.9(10)
H(32)	−0.125(5)	−0.264(5)	0.449(4)	6.2(10)
H(33)	−0.379(7)	−0.272(7)	0.510(6)	9.2(14)
H(34)	−0.576(7)	−0.214(7)	0.314(6)	9.4(15)
H(35)	−0.510(7)	−0.168(7)	0.091(5)	9.4(15)
H(36)	−0.252(5)	−0.162(5)	0.048(4)	5.4(9)

Table 3

Final anisotropic thermal parameters for *trans*-IrCl(CO)(PPh$_3$)$_2$ [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ir	2.541(7)	2.296(7)	2.430(6)	−0.684(5)	0.515(4)	−0.697(4)
P	2.896(25)	2.651(25)	2.704(24)	−1.156(21)	0.307(19)	−0.634(20)
Cl	4.84(18)	4.14(15)	3.77(15)	−0.14(14)	1.99(12)	−1.35(9)
C(1)	6.0(7)	4.0(5)	2.05(28)	−1.3(5)	2.45(29)	−1.32(25)
O(1)	7.3(6)	6.5(5)	5.38(35)	1.3(4)	3.23(34)	−1.71(29)
C(11)	2.97(10)	4.05(12)	3.07(10)	−1.39(9)	0.44(8)	−1.17(9)
C(12)	3.96(13)	4.32(14)	4.64(14)	−1.12(11)	−0.06(11)	−2.21(12)
C(13)	5.20(17)	6.52(22)	6.39(21)	−1.51(16)	−0.11(15)	−4.06(18)
C(14)	5.14(17)	9.38(31)	4.64(17)	−1.95(19)	−0.00(14)	−3.77(19)
C(15)	6.68(22)	8.43(30)	3.66(16)	−2.38(21)	−0.98(15)	−0.47(18)
C(16)	6.55(20)	5.35(18)	3.45(13)	−2.43(16)	−0.70(12)	−0.07(12)
C(21)	4.47(13)	2.71(11)	3.46(11)	−1.02(10)	−0.01(9)	−0.69(9)
C(22)	4.40(14)	4.09(15)	5.33(16)	−0.00(12)	−0.35(12)	−1.67(13)
C(23)	6.93(24)	5.36(22)	6.21(21)	1.71(19)	−1.27(18)	−2.47(17)
C(24)	12.9(5)	3.98(21)	7.90(29)	1.26(26)	−2.21(29)	−3.03(20)
C(25)	13.1(5)	4.02(21)	11.5(4)	−3.22(29)	−0.4(4)	−3.20(24)
C(26)	7.35(25)	3.69(16)	8.24(25)	−2.63(16)	0.11(20)	−1.86(16)
C(31)	3.16(11)	3.53(12)	3.84(12)	−1.54(9)	0.57(9)	−1.00(9)
C(32)	4.62(14)	4.88(15)	4.34(14)	−2.48(12)	1.61(11)	−1.83(12)
C(33)	5.42(18)	7.44(23)	6.62(21)	−3.52(17)	3.00(16)	−3.29(18)
C(34)	4.19(16)	8.26(27)	8.82(28)	−3.28(18)	2.50(17)	−3.54(23)
C(35)	4.39(17)	8.99(30)	7.30(24)	−3.43(19)	−0.11(16)	−1.88(21)
C(36)	4.02(14)	7.99(24)	4.58(16)	−3.19(15)	0.17(12)	−1.13(15)

[a] Anisotropic thermal parameters are in standard XTL format and enter the expression for the calculated structure factor in the form: $\exp[-0.25(B_{11}\cdot h^2a^{\star 2}+\ldots 2B_{12}\cdot hka^{\star}b^{\star}+\ldots)]$.

reflection, with 2θ 4.74°, was removed from the data set since it had $|F_o| \ll |F_c|$, i.e., 97.2 versus 122.0, and clearly suffered from "clipping" by the Pb backstop.) All data had been subjected to a small correction for secondary extinction by use of the approximation to the Zachariasen correction [11] shown in eq. 4.

$$|F_{o,cor}| = |F_{o,uncor}|(1.0 + gI_o) \tag{4}$$

The value determined for g was 3.24×10^{-8}.

A final difference-Fourier map, based upon all data, had peaks of height up to 1.18 e$^-$/Å^3 very close to the origin (i.e., the position of the iridium atom) and up to 0.38 e$^-$/Å^3 in a general position. The structure is thus clearly both correct and complete.

Final positional parameters are provided in Table 2; anisotropic thermal parameters are collected in Table 3.

Discussion

The molecular structure and atomic labelling scheme are illustrated in Fig. 1, while Fig. 2 presents a stereoscopic view of the molecule. Interatomic distances and angles are collected in Tables 4 and 5.

The unit cell contains a single molecule of *trans*-IrCl(CO)(PPh$_3$)$_2$. In the crystal these molecules are statistically (randomly) disordered such that the chloride and

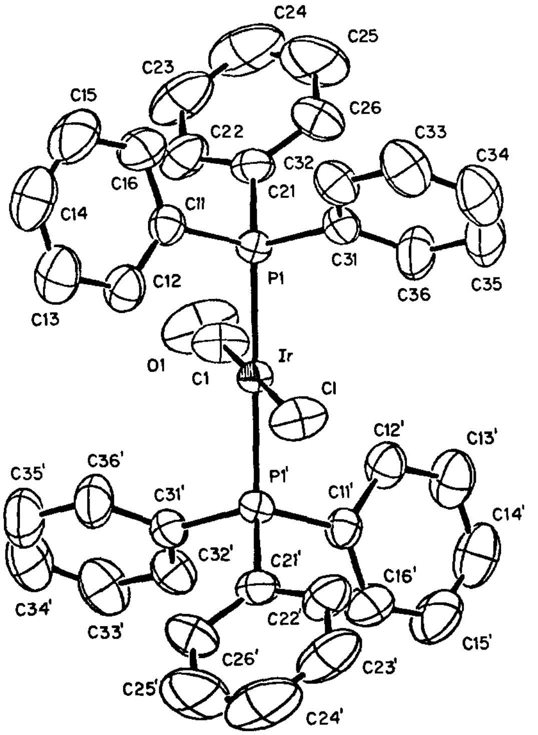


Fig. 1. Labelling of non-hydrogen atoms in *trans*-IrCl(CO)(PPh$_3$)$_2$. Atoms labelled with a prime are related to the basic asymmetric unit via the transformation $x', y', z' = -x, -y, -z$. Only one site for the chloride and carbonyl ligands is shown. The second site is related to that shown by inversion through the origin (i.e., the iridium atom). Thus atoms Cl', C(1)' and O(1)' have been omitted for clarity. (ORTEP diagram, 30% probability ellipsoids).

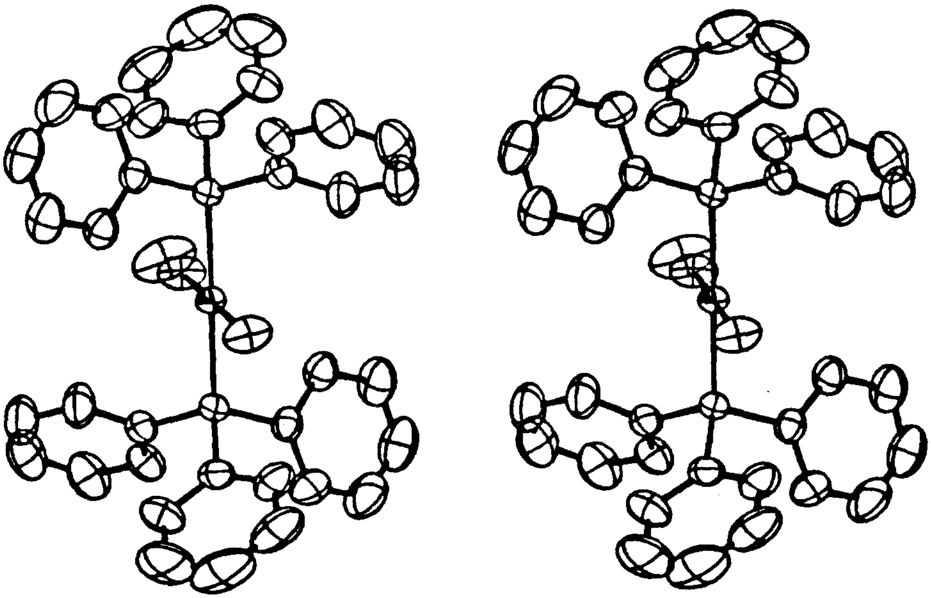


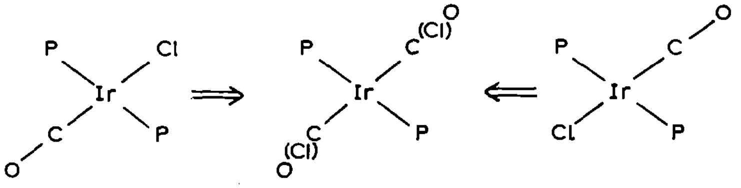
Fig. 2. A stereoscopic view of the *trans*-IrCl(CO)(PPh$_3$)$_2$ molecule.

Table 4

Interatomic distances (in Å) for *trans*-IrCl(CO)(PPh$_3$)$_2$

(A) Iridium – ligand distances			
Ir–P	2.330(1)	Ir–C(1)	1.791(13)
Ir–P($-x,-y,-z$)	2.330(1)	Ir $\cdots$ O(1)	2.949((12)
Ir–Cl	2.382(3)	Ir $\cdots$ H(12)	2.977(40)
(B) Phosphorus – carbon distances			
P–C(11)	1.832(3)	P–C(31)	1.828(3)
P–C(21)	1.831(3)		
(C) C – O and disordered (CO) $\cdots$ Cl distances			
C(1)–O(1)	1.161(18)	O(1) $\cdots$ Cl($-x,-y,-z$)	0.569(13)
C(1) $\cdots$ Cl($-x,-y,-z$)	0.595(13)		
(D) Carbon – carbon distances			
C(11)–C(12)	1.385(5)	C(21)–C(22)	1.400(5)
C(12)–C(13)	1.390(6)	C(22)–C(23)	1.386(7)
C(13)–C(14)	1.369(7)	C(23)–C(24)	1.370(10)
C(14)–C(15)	1.345(9)	C(24)–C(25)	1.369(13)
C(15)–C(16)	1.405(6)	C(25)–C(26)	1.385(8)
C(16)–C(11)	1.376(5)	C(26)–C(21)	1.379(6)
C(31)–C(32)	1.388(4)	C(34)–C(35)	1.367(7)
C(32)–C(33)	1.391(6)	C(35)–C(36)	1.397(7)
C(33)–C(34)	1.377(7)	C(36)–C(31)	1.388(5)
(E) Refined carbon – hydrogen distances			
C(12)–H(12)	0.98(4)	C(22)–H(22)	1.08(5)
C(13)–H(13)	1.04(6)	C(23)–H(23)	0.96(7)
C(14)–H(14)	0.97(6)	C(24)–H(24)	1.00(8)
C(15)–H(15)	0.84(7)	C(25)–H(25)	0.86(7)
C(16)–H(16)	0.96(5)	C(26)–H(26)	0.94(5)
C(32)–H(32)	1.04(5)	C(35)–H(35)	1.01(6)
C(33)–H(33)	1.13(6)	C(36)–H(36)	0.96(4)
C(34)–H(34)	1.04(7)		

carbonyl ligands occupy each of the possible mutually *trans* sites with 50% probability; thus, as shown below, molecule **1** and molecule **2** make up the disordered pattern **3**.



(1) (3) (2)

Although the molecular pattern is subject to disorder, there are no abnormally short intermolecular distances; clearly, the molecules pack principally by minimizing contacts between PPh$_3$ ligands.

The chloride ligand and the atoms of the carbonyl ligand have been refined independently. The Ir–Cl bond length is 2.382(3) Å and the Ir–CO bond length is

Table 5

Interatomic angles (in deg.) for *trans*-IrCl(CO)(PPh_3)$_2$

(A) Angles around the iridium atom:			
P–Ir–Cl	87.75(8)	P($-x,-y,-z$)–Ir–Cl	92.25(8)
P–Ir–C(1)	90.81(40)	P($-x,-y,-z$)–Ir–C(1)	89.19(40)
Cl–Ir–C(1)	178.08(40)	P($-x,-y,-z$)–Ir–P	180.00(–)
(B) Ir–C–O and C···Cl···O angles			
Ir–C(1)–O(1)	175.1(12)	C(1)···Cl($-x,-y,-z$)···O(1)	172.3(18)
(C) Ir–P–C angles			
Ir–P–C(11)	113.37(10)	Ir–P–C(31)	112.25(10)
Ir–P–C(21)	117.37(10)		
(D) C–P–C angles			
C(11)–P–C(21)	103.41(14)	C(21)–P–C(31)	104.13(14)
C(11)–P–C(31)	105.06(14)		
(E) P–C–C angles			
P–C(11)–C(12)	118.37(24)	P–C(21)–C(26)	122.66(30)
P–C(11)–C(16)	122.41(27)	P–C(31)–C(32)	122.93(25)
P–C(21)–C(22)	118.33(26)	P–C(31)–C(36)	117.81(27)
(F) C–C–C angles			
C(16)–C(11)–C(12)	119.23(32)	C(25)–C(24)–C(23)	119.9(7)
C(13)–C(12)–C(11)	120.26(35)	C(26)–C(25)–C(24)	120.8(7)
C(14)–C(13)–C(12)	120.27(43)	C(21)–C(26)–C(25)	120.1(5)
C(15)–C(14)–C(13)	119.62(49)	C(36)–C(31)–C(32)	119.26(33)
C(16)–C(15)–C(14)	121.60(49)	C(33)–C(32)–C(31)	119.98(36)
C(11)–C(16)–C(15)	119.02(40)	C(34)–C(33)–C(32)	120.01(45)
C(26)–C(21)–C(22)	118.92(35)	C(35)–C(34)–C(33)	120.81(50)
C(23)–C(22)–C(21)	119.98(39)	C(36)–C(35)–C(34)	119.51(49)
C(24)–C(23)–C(22)	120.3(5)	C(31)–C(36)–C(35)	120.40(41)
(G) C–C–H angles			
C(11)–C(12)–H(12)	119.6(25)	C(21)–C(22)–H(22)	121.6(27)
C(13)–C(12)–H(12)	120.2(25)	C(23)–C(22)–H(22)	118.0(27)
C(12)–C(13)–H(13)	117.1(30)	C(22)–C(23)–H(23)	119.9(38)
C(14)–C(13)–H(13)	122.3(30)	C(24)–C(23)–H(23)	119.7(38)
C(13)–C(14)–H(14)	120.3(36)	C(23)–C(24)–H(24)	115.4(43)
C(15)–C(14)–H(14)	120.1(36)	C(25)–C(24)–H(24)	124.5(43)
C(14)–C(15)–H(15)	126.0(48)	C(24)–C(25)–H(25)	116.7(47)
C(16)–C(15)–H(15)	112.4(48)	C(26)–C(25)–H(25)	122.6(47)
C(11)–C(16)–H(16)	120.4(28)	C(21)–C(26)–H(26)	119.3(30)
C(15)–C(16)–H(16)	120.5(28)	C(25)–C(26)–H(26)	120.6(31)
C(31)–C(32)–H(32)	119.5(27)	C(35)–C(34)–H(34)	117.1(36)
C(33)–C(32)–H(32)	120.5(27)	C(34)–C(35)–H(35)	120.4(37)
C(32)–C(33)–H(33)	117.4(32)	C(36)–C(35)–H(35)	120.1(37)
C(34)–C(33)–H(33)	122.6(32)	C(31)–C(36)–H(36)	116.4(27)
C(33)–C(34)–H(34)	122.0(36)	C(35)–C(36)–H(36)	123.2(27)

1.791(13) Å, with C–O 1.161(18) Å and angle Ir–C–O 175.1(12)°. The chloride ligand and carbonyl ligand at a given site are associated with the interatomic separations C(1)···Cl($-x,-y,-z$) 0.595(13) Å and O(1)···Cl($-x,-y,-z$) 0.569(13) Å, somewhat greater than our original estimate. The angle C(1)···

Cl($-x, -y, -z$) $\cdots$ O(1) is 172.3(18)°, so that the Ir–CO and Ir–Cl($-x, -y, -z$) vectors are not truly coincident.

The central iridium(I) atom has a slightly irregular square-planar coordination environment. The Ir–P distances are equivalent at 2.330(1) Å. The *trans* angles are P–Ir–P($-x, -y, -z$) 180.00° and Cl–Ir–C(1) 178.08(40)°. The *cis* angles are P–Ir–Cl 87.75(8)°, P($-x, -y, -z$)–Ir–Cl 92.25(8)°, P–Ir–C(1) 90.81(40)° and P($-x, -y, -z$)–Ir–C(1) 89.19(40)°.

Within the PPh_3 ligands, phosphorus–carbon bond lengths range from 1.828(3) to 1.832(3) Å, averaging 1.830 ± 0.003 Å. The phosphorus atoms have a stereochemical environment which is distorted from T_d towards C_{3v}; the Ir–P–C(*ipso*) angles are all greater than the regular tetrahedral value of 109.47° (Ir–P–C(31) 112.25(10)°, Ir–P–C(11) 113.37(10)°, Ir–P–C(21) 117.37(10)°; average 114.33°), while the C(*ipso*)–P–C(*ipso′*) angles are all contracted from the regular tetrahedral value (viz. C(11)–P–C(21) 103.41(14)°, C(21)–P–C(31) 104.13(14)°, C(11)–P–C(31) 105.06(14)°; average 104.20°).

Carbon–carbon distances within the phenyl rings range from 1.345(9) to 1.405(6) Å, averaging 1.382 ± 0.014 Å; the refined carbon–hydrogen distances range from 0.84(7) through 1.13(6) Å, averaging 0.99 ± 0.08 Å (cf. the accepted "X-ray determined" value of ~ 0.95 Å [12]).

It is interesting to note that there are two very weak Ir $\cdots$ H interactions involving the aromatic hydrogen atoms of the PPh_3 ligands. Thus, Ir $\cdots$ H(12) = Ir $\cdots$ H(12)($-x, -y, -z$) 2.977(40) Å. Atoms H(12) and H(12)($-x, -y, -z$) lie in positions approximating, very roughly, to the fifth and sixth position for octahedral coordination about the iridium atom. (Angles of note are P–Ir $\cdots$ H(12) 63.4(8)°, P($-x, -y, -z$)–Ir $\cdots$ H(12) 116.6(8)°, Cl–Ir $\cdots$ H(12) 64.0(8)° and C(1)–Ir $\cdots$ H(12) 114.2(9)°; for H(12)($-x, -y, -z$) the appropriate angles are the supplements of those given for H(12).)

Table 6 relates interatomic distances for the three accurately determined structures in the *trans*-$MCl(CO)(PAr_3)_2$ series (M = Ir, Rh; Ar = Ph, *p*-tolyl). It is clear that, finally, a self-consistent set of geometric parameters is available for this important class of materials.

Table 6

Comparison of bond lengths from accurate structural studies on *trans*-$MCl(CO)(PAr_3)_2$ species

Complex	R_F	Bond lengths	
trans-$Ir(CO)Cl(PPh_3)_2$	1.7%	Ir–P	2.330(1)
		Ir–Cl	2.382(3)
		Ir–CO	1.791(13)
trans-$Ir(CO)Cl[P(p\text{-}tol)_3]_2$	3.5%	Ir–P	2.330(2) 2.332(2)
(ref. 4)		Ir–Cl	2.364(2)
		Ir–CO	1.817(8)
trans-$Rh(CO)(Cl(PPh_3)_2$	3.7%	Rh–P	2.327(1) 2.333(1)
monoclinic form		Rh–Cl	2.395(1)
(ref. 7)		Rh–CO	1.821(5)

Additional material available

A list of observed and calculated structure factor amplitudes is available upon request from M.R.C.

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