$(CO)(PEt_3)ClIr(\mu\text{-}PCy_2)_2IrCl(PEt_3)(CO)$, a Phosphido-bridged Bimetallic Iridium(II) Complex

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Abstract

The reaction of $(CO)_4Fe(\mu\text{-}PCy_2)Ir(1,5\text{-}COD)$ (COD = cyclooctadiene) with 2 equivalents of PEt_3 under CO yields $(CO)_3(PEt_3)Fe(\mu\text{-}PCy_2)Ir(PEt_3)(CO)_2$. Upon attempted recrystallization of this complex, in CH_2Cl_2 over a five week period, a decomposition reaction occurred to produce $Fe(PEt_3)(CO)_4$ and $(CO)(PEt_3)ClIr(\mu\text{-}PCy_2)_2IrCl(PEt_3)(CO)$. The latter product is a rare example of an Ir(II) complex and was fully characterized by single crystal X-ray crystallography. It crystallizes in the space group *Pbca* with $a = 10.075(3)$, $b = 19.801(8)$, $c = 23.056(13)$ Å, $V = 4600(4)$ Å^3 and $Z = 4$. The structure was refined to final $R = 0.0747$ and $R_w = 0.0791$ for 1870 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Ir atoms have trigonal bipyramidal geometry with the P atoms in the plane and the Cl atom and CO groups axial. The Ir–Ir distance is 2.762(1) Å. This is shown to be consistent with the expected single bond required between d^7, Ir(II) centres.

Introduction

The diorganophosphide group (PR_2) is very useful for the preparation and stabilization of bimetallic complexes and is particularly suited for the stepwise formation of heterobimetallic complexes via the 'bridge-assisted' synthetic method [1–5]. We have recently employed the sterically demanding dicyclohexylphosphido ligand (PCy_2) to generate sites of coordinative unsaturation in heterobimetallic complexes via steric crowding [6, 7]. This is, of course, analogous to the use of bulky trialkylphosphines to produce sites of coordinative unsaturation in reactive mononuclear complexes [8].

During our investigation of the reaction chemistry of the complexes $(CO)_4Fe(\mu\text{-}PCy_2)M(1,5\text{-}COD)$ (M = Rh, Ir; COD = cyclooctadiene) [7], we found these complexes reacted with two equivalents of PEt_3 under CO(g), to give $(CO)_3(PEt_3)Fe(\mu\text{-}PCy_2)M(PEt_3)(CO)_2$. Although the $\mu\text{-}PCy_2$ bridge is usually stable under a variety of reaction conditions, we observed that during prolonged periods of dissolution in dichloromethane the complex $(CO)_3(PEt_3)Fe(\mu\text{-}PCy_2)Ir(PEt_3)(CO)_2$ decomposed. The products were the monomeric iron phosphine complex $Fe(PEt_3)(CO)_4$, detectable by $^{31}P\{^1H\}$ NMR, and $(CO)(PEt_3)ClIr(\mu\text{-}PCy_2)_2IrCl(PEt_3)(CO)$, a rare example of an Ir(II) complex [9] and the first such species containing phosphido-bridging ligands.

Experimental

X-ray Data Collection and Reduction

Red crystals of the title compound were obtained by prolonged dissolution (5 weeks) of $(CO)_3(PEt_3)Fe(\mu\text{-}PCy_2)Ir(PEt_3)(CO)_2$ in dichloromethane at −20 °C, during attempts to recrystallize this complex. Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrix was obtained from 15 machine-centered reflections selected from rotation photographs. Partial rotation photographs around each axis were consistent with an orthorhombic crystal system. Ultimately, 30 high-angle reflections ($22° < 2\theta < 25°$) were used to obtain the final lattice parameters and orientation matrix. Machine parameters, crystal data and intensity collection parameters are summarized in Table 1. The observed extinctions were consistent with space group *Pbca*. Intensity data ($+h$, $+k$, $+l$) were collected in two shells ($4.5° < 2\theta < 40°$ and $40° < 2\theta < 45°$). The intensities of three standard reflections (0 0 6, 1 4 3, 3 $\bar{4}$ 1) were recorded every 97 reflections and showed no statistically significant changes over the duration of the data collection. The data were processed using the SHELX-76 program package on the computing facilities shared with the University of Manitoba. A total of 3419 reflections was collected and 1870 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in refinement. The data were absorption corrected

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TABLE 1. Summary of Crystal Data, Intensity Collection and Structure Refinement for (CO)(PEt$_3$)ClIr(μ-PCy$_2$)$_2$IrCl(PEt$_3$)(CO)

Formula	$C_{38}H_{74}Cl_2Ir_2P_4O_2$
Crystal color, form	red blocks
a (Å)	10.075(3)
b (Å)	19.801(8)
c (Å)	23.056(13)
Crystal system	orthorhombic
Space group	*Pbca*
Volume (Å^3)	4600(4)
ρ(calc.) (g/cm^{-1})	1.65
Z	4
Crystal dimensions (mm)	0.32 × 0.24 × 0.23
Absorption coefficient (cm^{-1})	59.33
Radiation, λ (Å)	Mo Kα (0.71069)
Temperature (°C)	24
Scan speed (°/min)	2.0–5.0 (θ–2θ scan)
Scan range (°)	1.0 below Kα_1, 1.0 above Kα_2
Background/scan time ratio	0.5
Data collected	3419; 2θ of 4.5 to 45° ($+h, +k, +l$)
Unique data ($F_o^2 > 3\sigma F_o^2$)	1870
No. variables	136
R (%)	7.47
R_w (%)	7.91

(μ = 59.33 cm^{-1}) empirically by interpolation in 2θ and ϕ between ψ-scans of reflections 0 12 6, 0 10 6, and 0 8 4.

Structure Solution and Refinement

The molecule is positioned on a crystallographic centre of symmetry and as a result only half of the atoms were required to define the structure. The Ir atom position was determined using the Patterson method and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Refinement was carried out using full-matrix least-squares techniques on F minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors [10] and anomalous dispersion terms [11] were taken from the usual sources. In the final cycles of refinement, the Ir, P, Cl, O and carbonyl C atoms were assigned anisotropic thermal parameters. Fixed H atom contributions were included with C–H distances of 0.95 Å and thermal parameters 1.1 times the isotropic thermal parameters of the bonded C atoms. No H atoms were refined, but all values were updated as refinement continued. This resulted in $R = \Sigma||F_o| - |F_c|/\Sigma|F_o|| = 0.0747$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2)/\Sigma wF_o^2)^{1/2} = 0.0791$ at final convergence.

The Δ/σ values for any parameters in the final cycles were less than 0.05. A final difference Fourier map calculation showed no peaks of chemical significance. However, a rather large residual of 2.76 electrons/Å^3 remained and was associated with the iridium atom. Atomic positional parameters are summarized in Table 2 and selected bond distances and angles in Table 3. See also 'Supplementary Material'.

Results and Discussion

A perspective view of (CO)(PEt$_3$)ClIr(μ-PCy$_2$)$_2$IrCl(PEt$_3$)(CO) giving the atom numbering scheme is shown in Fig. 1 and a representation of the inner coordination sphere of the molecule is shown in Fig. 2 with some relevant bonding parameters. The unit cell contains two discrete molecules each having a crystallographically imposed centre of symmetry. The closest intermolecular non-bonded contact is 2.30 Å between H(10A) and H(7A)'. Complete listings of interatomic distances and angles may be found in Table 3.

TABLE 2. Positional Parameters[a]

Atom	x	y	z	Atom	x	y	z
Ir	0.5952(1)	0.4505(1)	−0.0071(1)	Cl	0.4304(6)	0.3607(3)	−0.0022(2)
P1	0.7422(6)	0.3608(3)	−0.0142(3)	P2	0.5222(5)	0.4946(3)	0.0838(2)
O1	0.827(2)	0.5384(8)	−0.0241(8)	C1	0.737(2)	0.5047(12)	−0.0122(10)
C2	0.747(2)	0.3036(11)	0.0467(9)	C3	0.831(3)	0.3370(15)	0.0982(11)
C4	0.919(2)	0.3867(11)	−0.0267(10)	C5	1.010(3)	0.3230(13)	−0.0302(12)
C6	0.709(3)	0.2998(12)	−0.0715(10)	C7	0.738(3)	0.3281(15)	−0.1349(11)
C8	0.422(2)	0.4396(11)	0.1306(10)	C9	0.499(2)	0.3835(12)	0.1614(10)
C10	0.413(3)	0.332(2)	0.1930(15)	C11	0.293(3)	0.3654(14)	0.2233(13)
C12	0.223(3)	0.4177(15)	0.1924(12)	C13	0.321(2)	0.4710(12)	0.1654(10)
C14	0.635(3)	0.5406(14)	0.1342(12)	C15	0.768(4)	0.536(2)	0.1286(16)
C16	0.861(3)	0.5700(13)	0.1692(11)	C17	0.813(3)	0.6297(15)	0.1979(13)
C18	0.673(4)	0.633(2)	0.208(2)	C19	0.577(3)	0.5988(13)	0.1631(11)

[a] e.s.d.s in the least significant figure(s) are given in parentheses in this and all subsequent Tables.

TABLE 3. Selected Bond Distances and Angles

Distances (Å)			
Ir–Ir	2.762(1)	C8–C9	1.53(3)
Ir–Cl	2.435(5)	C8–C13	1.44(3)
Ir–P1	2.318(6)	C9–C10	1.53(3)
Ir–P2	2.387(5)	C10–C11	1.55(4)
Ir'–P2	2.389(5)	C11–C12	1.44(4)
Ir–C1	1.79(2)	C12–C13	1.57(3)
P1–C2	1.81(2)	C14–C15	1.35(4)
P1–C4	1.87(2)	C14–C19	1.45(3)
P1–C6	1.82(2)	C15–C16	1.48(4)
P2–C8	1.84(2)	C16–C17	1.44(3)
P2–C14	1.86(2)	C17–C18	1.43(4)
C1–O1	1.15(3)	C4–C5	1.56(3)
C2–C3	1.60(3)	C6–C7	1.59(3)
Angles (Å)			
Cl–Ir–P1	83.1(2)	Ir–C1–O1	109.5(16)
Cl–Ir–P2	90.9(2)		
Cl–Ir–P2'	91.7(2)	P1–C2–C3	110.4(15)
Cl–Ir–C1	169.9(8)	P1–C4–C5	110.4(15)
P1–Ir–P2	122.6(2)	P1–C6–C7	113.5(17)
P1–Ir–P2'	127.8(2)		
P2–Ir–P2'	109.4(2)	P2–C8–C9	115(2)
P1–Ir–C1	86.8(8)	C8–C9–C10	115(2)
P2–Ir–C1	94.8(7)	C9–C10–C11	112(2)
P2'–Ir–C1	94.3(7)	C10–C11–C12	118(3)
		C11–C12–C13	112(2)
Ir–P1–C2	116.4(8)	C12–C13–C8	112(2)
Ir–P1–C4	114.1(7)		
Ir–P1–C6	116.2(8)	P2–C14–C15	121(2)
C2–P1–C4	105.3(11)	C14–C15–C16	122(3)
C2–P1–C6	98.8(11)	C15–C16–C17	117(3)
C4–P1–C6	104.1(11)	C16–C17–C18	116(3)
		C17–C18–C19	119(3)
Ir–P2–C8	117.9(8)	C18–C19–C14	114(3)
Ir–P2–C14	122.6(9)		
Ir–P2–Ir	70.7(2)		
Ir'–P2–C8	115.6(8)		
Ir'–P2–C14	122.8(9)		
C8–P2–C14	105.1(12)		

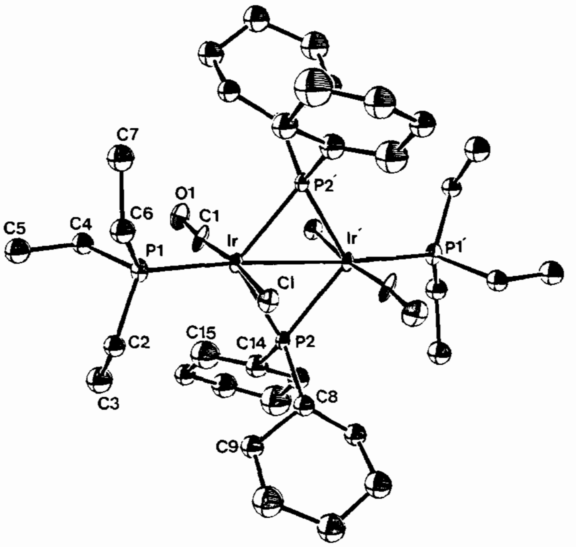

Fig. 1. Perspective ORTEP drawing of $(CO)(PEt_3)ClIr(\mu\text{-}PCy_2)_2IrCl(PEt_3)(CO)$ showing the numbering scheme. The numbering of cyclohexyl ring carbon atoms starts at the atom bound to phosphorus: 20% thermal ellipsoids are shown.

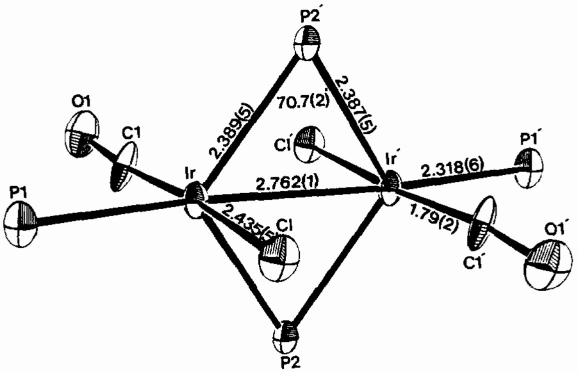

Fig. 2. Perspective ORTEP drawing of $(CO)(PEt_3)ClIr(\mu\text{-}PCy_2)_2IrCl(PEt_3)(CO)$ showing the inner coordination sphere. Some relevant bonding parameters are shown.

The geometry at the Ir atoms is trigonal bipyramidal. Each metal centre is bonded to two μ-PCy_2 groups (P(2) and P(2)'), a terminal PEt_3 ligand (P(1)), a Cl atom and a carbonyl C atom (C(1)). The three phosphorus atoms (P(1), P(2) and P(2)') form a trigonal plane with Ir–P distances of 2.318(6), 2.387(5) and 2.389(5) Å respectively. The P–Ir–P angles in the plane are 122.6(2)°, 127.8(2)° and 109.4(2)° for P(1)–Ir–P(2), P(1)–Ir–P(2)' and P(2)–Ir–P(2)' respectively. A least-squares plane calculation for the IrP_3 fragment shows the largest deviation from planarity to be 0.053(5) Å for the Ir atom. The Cl atom and the CO group are in axial positions. The Ir–Cl and Ir–C(1) distances are 2.435(5) and 1.79(2) Å respectively and the Cl–Ir–C(1) angle is 169.9(8)° with these groups tilted slightly away from the large PCy_2 bridging ligands. The average Cl–Ir–P angle is 88.8(3)° and the average C(1)–Ir–P angle is 91.6(13)° consistent with the positioning of these ligands axial to the trigonal plane. The major distortion from ideal trigonal bipyramidal geometry is the constraining of the angle at Ir between the two PCy_2 groups to 109.4(2)°, in order to form the planar Ir_2P_2 core with reasonable bonding distances for these four atoms.

Since each of the iridium atoms is formally Ir(II) there must be a single bond between these two d^7 metal centres in order to give each an electron count of 18. Indeed, this is exactly what is observed. The Ir–Ir distance is 2.762(1) Å and this is in the range of *ca.* 2.6 to 2.8 Å normally found for a single bond between iridium atoms [12–16]. Direct comparison with other bis-phosphido bridged structures is not possible however, since this is the first Ir(II) complex bridged by PR_2 groups to be structurally characterized. Further support for this interpretation can be found by comparison to the Ir(I) complexes $Ir_2(\mu\text{-}PtBu_2)_2(CO)_4$ and $Ir_2(\mu\text{-}PPh_2)_2(PPh_3)_2(CO)_2$ which have a formal Ir=Ir double bond with Ir–Ir distances of 2.545(1) and 2.551(1) Å [12, 13]; $Ir_3(\mu\text{-}PtBu_2)_3(CO)_5$ which has three Ir–Ir single bonds of 2.785(2), 2.729(2) and 2.812(2) Å [12]; and $Ir_2(\mu\text{-}AstBu_2)_2(CO)_4$ which has no Ir–Ir interaction at a distance of 3.891(1) Å [12]. This also shows that the presence of two bridging phosphido groups does not dictate the metal–metal distance since the Ir–Ir distance has been shown to vary with bond order.

The formation of $(CO)(PEt_3)ClIr(\mu\text{-}PCy_2)_2IrCl(PEt_3)(CO)$ from the heterobimetallic complex $(CO)_3(PEt_3)Fe(\mu\text{-}PCy_2)Ir(PEt_3)(CO)_2$ is probably the result of a reaction with trace amounts of HCl in the CH_2Cl_2 solution over the long period of time required for recrystallization. The actual reaction pathway could involve oxidative addition of HCl to the FeIr complex with subsequent elimination of $H_2(g)$ and $Fe(PEt_3)(CO)_4$, and formation of the dimeric Ir complex with retention of the chloride ligand. Although the common result from decomposition of this type of complex is a monomeric species, for example *trans*-$IrCl(CO)(PR_3)_2$, the formation of homobimetallic complexes has been observed [17]. Research in our laboratory is currently under way to develop a rational synthesis to Ir(II) complexes of this type and further investigate their reaction chemistry.

Supplementary Material

Tables S-I–S-III listing thermal parameters, hydrogen atom positions, and observed and calculated structure factors (27 pages) have been deposited with Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW.

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