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CRYSTAL AND MOLECULAR STRUCTURE OF $Ir_4(CO)_8[P(CH_3)_2C_6H_5]_4 \cdot 2C_6H_6$

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Summary

The structure of $Ir_4(CO)_8(PMe_2Ph)_4$ has been determined by a single crystal X-ray investigation. The structure consists of a slightly distorted tetrahedral arrangement of Ir atoms with one phosphine ligand bonded to each metal atom. Three Ir atoms form an irregular basal triangular face symmetrically bridged by three carbonyl groups which are displaced out of the plane of the Ir atoms. The basal and apical Ir atoms have one and two terminal carbonyl groups respectively. Metal–metal bond distances are, Ir(basal)–Ir(basal) 2.726(3), 2.737(3) and 2.782(3) Å; Ir(basal)–Ir(apical) 2.734(3), 2.730(3) and 2.727(3) Å. Crystals of the compound $Ir_4(CO)_8[P(CH_3)_2C_6H_5]_4 \cdot 2C_6H_6$ have space group $P2_1/c$ with a 15.9068(21), b 10.2150(15), c 34.653(4) Å, β 94.288(10)° and $Z = 4$. Least squares refinement gave $R = 0.095$ for 3250 unique observed reflections whose intensities were measured by counter diffractometry with Mo-K_α radiation.

Introduction

In recent years there has been considerable interest in the tetranuclear carbonyl cluster complexes of iridium, and aspects of their chemistry such as ligand substitution reactions [1], fluxional processes in solution [2] and kinetic studies of dissociative carbon monoxide loss [3] have been investigated. Some years ago we prepared several complexes of the general formula $Ir_4(CO)_8L_4$, ($L = Ph_2PMe$, $PhPMe_2$, Ph_2AsMe, $(PhO)_3P$ and $\frac{1}{2}(Ph_2PCH_2)_2$), by direct interaction of the carbonyl with the ligands [4]. Although the stereochemical non-rigidity of the compounds in solution was demonstrated, the detailed structural aspects of the compounds were not established. In view of the interest in the role of steric effects on ligand

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substitution processes in these cluster complexes, it is important to know the stereochemical arrangements of the ligands in the complexes. Thus we have determined, by a single crystal X-ray diffraction study, the crystal and molecular structure of $Ir_4(CO)_8(PMe_2Ph)_4$, and comparisons have been drawn with the structure [5] of $Ir_4(CO)_8(PMe_3)_4$.

Experimental

$Ir_4(CO)_8(PMe_2Ph)_4$ was prepared as described [4]. Attempts to obtain crystals from dichloromethane/n-pentane and from toluene/n-pentane were unsuccessful. Crystals suitable for X-ray diffraction, but with occluded benzene, were obtained from benzene/n-pentane.

X-ray crystallography

Oscillation and zero- and first-layer equi-inclination Weissenberg photographs of a thin, plate-like, orange crystal of the complex gave the space group and approximate cell dimensions. The same crystal was optically centred on an Enraf-Nonius CAD4 diffractometer, 14 relatively low-angle reflections were located (program SEARCH), and their angular settings used to calculate the first unit cell and orientation matrix (INDEX). After rapid data collection in the range 9.0–11.5° (graphite-monochromated Mo-K_α X-radiation, λ_1 0.70926, λ_2 0.71354 Å), 25 reflections from this shell were accurately centred (SETANG) to generate, by least-square refinement, accurate cell dimensions and the orientation matrix used in data collection.

Crystal data

$C_{52}H_{56}O_8P_4Ir_4$, $M = 1573.8$, monoclinic, a 15.9068(21), b 10.2150(15), c 34.653(4) Å, β 94.288(10)°, U 5614 Å^3, $Z = 4$, D_c 1.861 g cm^{-3}, $F(000) = 3200$ electrons, μ(Mo-K_α) 101.38 cm^{-1}, space group $P2_1/c$ (C_{2h}^5, No.14) from systematic absences.

One quadrant of data $(+h, -k, \pm l)$ was measured in the range $\theta = 1$–$25°$ by θ–2θ scans in 96 steps. The θ scan width was given by $0.65 \pm 0.30 \tan\theta$. After a rapid pre-scan, only those reflections considered sufficiently intense $[I \geqslant 1.0\ \sigma(I)]$ were remeasured, such that their final nett intensity had $I \geqslant 33\sigma(I)$, subject to a maximum measuring time of 60 s. Two orientation and two intensity control reflections were monitored every 300 reflections and 3600 s respectively, but their subsequent analysis indicated no substantial crystal decay or movement, or source variation over approximately 132 h of data collection. The intensity data were corrected empirically for absorption effects by means of ψ scans of the (040) reflection (θ 7.98°); Lorentz and polarisation corrections were also applied. Rejection of systematic absences and merging of equivalent reflections furnished 9848 data of which 3250 with $F_o \geqslant 2.0\ \sigma(F_o)$ were used for structure solution and refinement, accomplished via automatic centrosymmetric direct methods and successive difference Fourier syntheses respectively. The former gave the positions of the four Ir atoms while the latter indicated the positions of the remaining non-hydrogen atoms. Refinement employed full-matrix least-squares and structure factors were weighted according to $w^{-1} = [\sigma^2(F_c) + 0.00124F_o^2]$, a scheme which gave no unusual variation of the root mean square deviation of a reflection of unit weight versus parity group, $(\sin\theta)/\lambda$, F_o, h, k, or l.

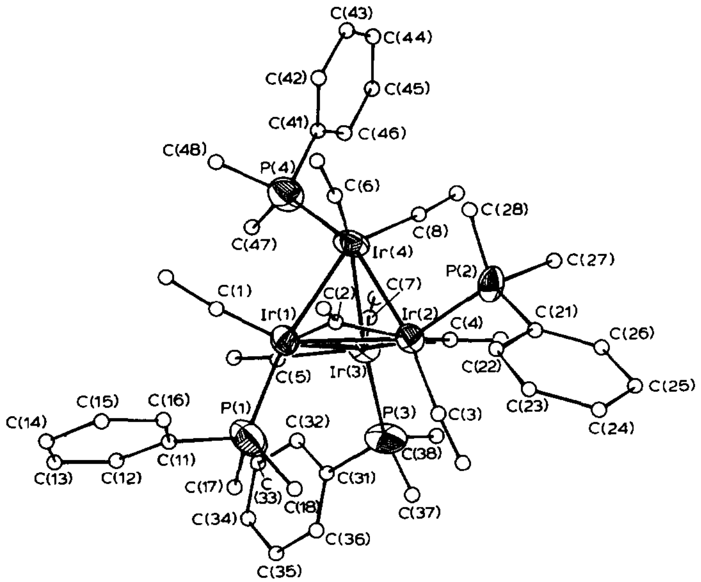

Fig. 1. ORTEP drawing of the molecule showing the numbering scheme adopted. Oxygen atoms, unlabelled in the drawing, are numbered to correspond to the carbon of attachment.

Ir and P atoms were allowed anisotropic thermal motion whilst the remaining non-hydrogen atoms were refined isotropically. Phenyl rings and benzene molecules were refined as rigid groups (AFIX) [6] with a common isotropic temperature factor for the atoms of the latter. Methyl, phenyl and benzene hydrogen atoms were refined assuming fixed, idealised geometries (AFIX) [6]. A fixed isotropic temperature factor (U 0.10 $Å^2$) * was assigned to all phenyl and benzene hydrogens while a common temperature factor was refined for all methyl hydrogens.

Refinement converged at $R = 0.095$, $R_w = 0.086$, at a data/variable ratio of better than 13/1. A final difference Fourier had no peaks > 0.84 nor trough < 0.57 e $Å^{-3}$. The largest peaks were all within 1.6 Å of the Ir atoms; apart from these, there was no peak > 0.57 e $Å^{-3}$.

The derived non-hydrogen atomic positional parameters are listed in Table 1, whilst the thermal parameters, hydrogen positional parameters, observed and calculated structure factors have been deposited **. The structure solution and refinement used programs and inlaid neutral atomic scattering factors of the SHELX-76 package [6], implemented on the University of Edinburgh ICL-2972 computer except for the scattering factor for Ir [7,8]. Molecular geometry calculations utilised XANADU [9] and XRAY 76 [10]; graphics were obtained from ORTEP II [11].

Results and discussion

The structure of $Ir_4(CO)_8(PMe_2Ph)_4$ consists of a tetrahedral arrangement of iridium atoms with terminal and bridging carbonyl groups and with one phosphine

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* The isotropic thermal parameter is defined as $\exp[-8\pi^2 U(\sin^2\theta)/\lambda^2]$.

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TABLE 1

FRACTIONAL COORDINATES OF ATOMS [a,b]

Atom	x	y	z	U_{eq}
Ir(1)	0.23633(14)	0.04644(21)	0.09941(6)	0.0386
Ir(2)	0.39470(13)	0.03157(20)	0.13509(5)	0.0334
Ir(3)	0.34428(14)	0.26078(19)	0.09957(5)	0.0346
Ir(4)	0.27592(14)	0.18461(21)	0.16586(6)	0.0393
P(1)	0.2350(10)	−0.0652(15)	0.0422(4)	0.0559
P(2)	0.4674(8)	−0.0393(13)	0.1919(4)	0.0377
P(3)	0.4195(10)	0.2951(14)	0.0462(4)	0.0544
P(4)	0.1629(11)	0.3267(18)	0.1699(4)	0.0734
O(1)	0.060(3)	−0.010(5)	0.1110(13)	0.1182
C(1)	0.135(7)	0.027(10)	0.1029(24)	0.1481
O(2)	0.2727(23)	−0.204(4)	0.1472(10)	0.0677
C(2)	0.292(4)	−0.105(6)	0.1360(15)	0.0576
O(3)	0.510(3)	−0.124(4)	0.0890(11)	0.0803
C(3)	0.462(3)	−0.060(5)	0.1063(12)	0.0369
O(4)	0.5205(21)	0.260(3)	0.1424(8)	0.0451
C(4)	0.454(3)	0.217(4)	0.1320(11)	0.0270
O(5)	0.1713(24)	0.292(4)	0.0542(10)	0.0681
C(5)	0.233(4)	0.222(5)	0.0740(14)	0.0534
O(6)	0.1986(25)	−0.011(4)	0.2160(10)	0.0704
C(6)	0.235(4)	0.061(6)	0.1965(16)	0.0691
O(7)	0.336(3)	0.545(5)	0.1156(13)	0.1096
C(7)	0.337(4)	0.437(5)	0.1081(14)	0.0542
O(8)	0.3940(24)	0.353(4)	0.2149(10)	0.0655
C(8)	0.352(3)	0.275(5)	0.1970(13)	0.0426
C(12)	0.079(3)	−0.136(3)	0.0010(10)	0.0832
C(13)	0.008(3)	−0.214(3)	−0.0063(10)	0.0773
C(14)	−0.002(3)	−0.326(3)	0.0158(10)	0.1054
C(15)	0.059(3)	−0.360(3)	0.0453(10)	0.0650
C(16)	0.130(3)	−0.281(3)	0.0526(10)	0.0772
C(11)	0.140(3)	−0.169(3)	0.0304(10)	0.0629
C(17)	0.240(4)	0.025(6)	−0.0006(15)	0.0764
C(18)	0.316(4)	−0.184(6)	0.0364(16)	0.0796
C(22)	0.4891(15)	−0.304(3)	0.1739(8)	0.0425
C(23)	0.5357(15)	−0.417(3)	0.1682(8)	0.0512
C(24)	0.6234(15)	−0.415(3)	0.1744(8)	0.0579
C(25)	0.6644(15)	−0.300(3)	0.1864(8)	0.0514
C(26)	0.6179(15)	−0.187(3)	0.1921(8)	0.0625
C(21)	0.5302(15)	−0.189(3)	0.1859(8)	0.0333
C(27)	0.540(3)	0.076(5)	0.2149(13)	0.0536
C(28)	0.405(3)	−0.094(4)	0.2306(11)	0.0288
C(32)	0.2987(23)	0.445(4)	0.0059(8)	0.0602
C(33)	0.2540(23)	0.497(4)	−0.0268(8)	0.0852
C(34)	0.2680(23)	0.448(4)	−0.0634(8)	0.0912
C(35)	0.3268(23)	0.349(4)	−0.0673(8)	0.0596
C(36)	0.3716(23)	0.297(4)	−0.0346(8)	0.0681
C(31)	0.3575(23)	0.346(4)	0.0020(8)	0.0438
C(37)	0.480(4)	0.160(6)	0.0307(16)	0.0793
C(38)	0.494(4)	0.410(6)	0.0530(15)	0.0699
C(42)	0.1500(25)	0.382(3)	0.2470(11)	0.0792
C(43)	0.1634(25)	0.454(3)	0.2810(11)	0.0587
C(44)	0.1997(25)	0.578(3)	0.2800(11)	0.1017
C(45)	0.2226(25)	0.630(3)	0.2451(11)	0.1330
C(46)	0.2092(25)	0.557(3)	0.2110(11)	0.1009

TABLE 1 (continued)

Atom	x	y	z	U_{eq}
C(41)	0.1729(25)	0.433(3)	0.2120(11)	0.0692
C(47)	0.129(6)	0.430(8)	0.1328(22)	0.1545
C(48)	0.058(6)	0.257(9)	0.1742(24)	0.1672
C(51)	−0.731(4)	−0.215(5)	−0.1087(13)	0.1505
C(52)	−0.689(4)	−0.097(5)	−0.1138(13)	0.1505
C(53)	−0.734(4)	0.021(5)	−0.1130(13)	0.1505
C(54)	−0.820(4)	0.020(5)	−0.1073(13)	0.1505
C(55)	−0.861(4)	−0.099(5)	−0.1023(13)	0.1505
C(56)	−0.817(4)	−0.216(5)	−0.1030(13)	0.1505
C(61)	0.047(4)	0.065(6)	0.2816(13)	0.1505
C(62)	−0.013(4)	0.161(6)	0.2881(13)	0.1505
C(63)	−0.011(4)	0.224(6)	0.3238(13)	0.1505
C(64)	0.051(4)	0.193(6)	0.3529(13)	0.1505
C(65)	0.111(4)	0.097(6)	0.3463(13)	0.1505
C(66)	0.109(4)	0.033(6)	0.3107(13)	0.1505

[a] Estimated standard deviations, given in parentheses, are applicable to the least significant digits.
[b] Atoms are labelled in agreement with Fig. 1. Atoms C(51)–C(56) and C(61)–C(66) are the occluded benzene molecules.

ligand attached to each iridium atom. A view of the molecule indicating the numbering scheme adopted is shown in Fig. 1. In Tables 2 and 3 are listed the internuclear separations and interbond angles respectively, for all non-hydrogen atoms except the phenyl carbon atoms which were refined (vide supra) with idealised C–C distances of 1.395 Å and CCC angles of 120°. There are no significant contacts

TABLE 2

INTERNUCLEAR BOND DISTANCES (Å) [a]

Ir(1)–Ir(2)	2.726(3)	P(1)–C(11)	1.86(4)
Ir(1)–Ir(3)	2.782(3)	P(1)–C(17)	1.75(6)
Ir(1)–Ir(4)	2.734(3)	P(1)–C(18)	1.80(6)
Ir(1)–P(1)	2.285(15)	P(2)–C(21)	1.85(3)
Ir(1)–C(1)	1.63(10)	P(2)–C(27)	1.79(5)
Ir(1)–C(2)	2.15(6)	P(2)–C(28)	1.81(4)
Ir(1)–C(5)	1.99(5)	P(3)–C(31)	1.83(4)
Ir(2)–Ir(3)	2.737(3)	P(3)–C(37)	1.79(6)
Ir(2)–Ir(4)	2.730(3)	P(3)–C(38)	1.67(6)
Ir(2)–P(2)	2.324(13)	P(4)–C(41)	1.82(4)
Ir(2)–C(2)	2.15(6)	P(4)–C(47)	1.72(8)
Ir(2)–C(3)	1.78(5)	P(4)–C(48)	1.83(9)
Ir(2)–C(4)	2.12(4)	O(1)–C(1)	1.31(11)
Ir(3)–Ir(4)	2.727(3)	O(2)–C(2)	1.14(7)
Ir(3)–P(3)	2.302(15)	O(3)–C(3)	1.20(6)
Ir(3)–C(4)	2.05(4)	O(4)–C(4)	1.18(5)
Ir(3)–C(5)	1.96(5)	O(5)–C(5)	1.36(6)
Ir(3)–C(7)	1.83(5)	O(6)–C(6)	1.18(7)
Ir(4)–P(4)	2.323(18)	O(7)–C(7)	1.13(7)
Ir(4)–C(6)	1.80(6)	O(8)–C(8)	1.19(6)
Ir(4)–C(8)	1.81(5)		

[a] E.s.d.'s, given in parentheses, are applicable to the least significant digits.

TABLE 3

INTERBOND ANGLES (°) [a]

Ir(2)–Ir(1)–Ir(3)	59.58(7)	P(3)–Ir(3)–C(5)	99.9(16)
Ir(2)–Ir(1)–Ir(4)	59.99(8)	P(3)–Ir(3)–C(7)	91.2(17)
Ir(2)–Ir(1)–P(1)	108.3(4)	C(4)–Ir(3)–C(5)	154.7(19)
Ir(2)–Ir(1)–C(1)	147(3)	C(4)–Ir(3)–C(7)	100.7(20)
Ir(2)–Ir(1)–C(2)	50.6(15)	C(5)–Ir(3)–C(7)	102.2(23)
Ir(2)–Ir(1)–C(5)	103.9(15)	Ir(1)–Ir(4)–Ir(2)	59.86(8)
Ir(3)–Ir(1)–Ir(4)	59.26(7)	Ir(1)–Ir(4)–Ir(3)	61.26(8)
Ir(3)–Ir(1)–P(1)	111.1(4)	Ir(1)–Ir(4)–P(4)	104.1(4)
Ir(3)–Ir(1)–C(1)	135(3)	Ir(1)–Ir(4)–C(6)	93.7(19)
Ir(3)–Ir(1)–C(2)	109.7(15)	Ir(1)–Ir(4)–C(8)	149.9(15)
Ir(3)–Ir(1)–C(5)	44.7(15)	Ir(2)–Ir(4)–Ir(3)	60.21(7)
Ir(4)–Ir(1)–P(1)	167.1(4)	Ir(2)–Ir(4)–P(4)	160.5(4)
Ir(4)–Ir(1)–C(1)	99(3)	Ir(2)–Ir(4)–C(6)	96.8(19)
Ir(4)–Ir(1)–C(2)	79.4(15)	Ir(2)–Ir(4)–C(8)	94.1(15)
Ir(4)–Ir(1)–C(5)	84.6(15)	Ir(3)–Ir(4)–P(4)	103.4(4)
P(1)–Ir(1)–C(1)	93.4(34)	Ir(3)–Ir(4)–C(6)	151.6(19)
P(1)–Ir(1)–C(2)	97.4(16)	Ir(3)–Ir(4)–C(8)	93.7(15)
P(1)–Ir(1)–C(5)	93.8(16)	P(4)–Ir(4)–C(6)	95.1(19)
C(1)–Ir(1)–C(2)	104(4)	P(4)–Ir(4)–C(8)	97.7(16)
C(1)–Ir(1)–C(5)	99(4)	C(6)–Ir(4)–C(8)	105.0(24)
C(2)–Ir(1)–C(5)	154.4(21)	Ir(1)–P(1)–C(11)	115.4(13)
Ir(1)–Ir(2)–Ir(3)	61.23(7)	Ir(1)–P(1)–C(17)	118.3(20)
Ir(1)–Ir(2)–Ir(4)	60.14(8)	Ir(1)–P(1)–C(18)	118.3(20)
Ir(1)–Ir(2)–P(2)	141.8(3)	C(11)–P(1)–C(17)	101.7(23)
Ir(1)–Ir(2)–C(2)	50.7(15)	C(11)–P(1)–C(18)	99.7(23)
Ir(1)–Ir(2)–C(3)	110.4(15)	C(17)–P(1)–C(18)	100.2(28)
Ir(1)–Ir(2)–C(4)	109.0(11)	Ir(2)–P(2)–C(21)	113.6(11)
Ir(3)–Ir(2)–Ir(4)	59.85(7)	Ir(2)–P(2)–C(27)	115.9(17)
Ir(3)–Ir(2)–P(2)	139.3(3)	Ir(2)–P(2)–C(28)	117.3(14)
Ir(3)–Ir(2)–C(2)	111.5(15)	C(21)–P(2)–C(27)	104.7(19)
Ir(3)–Ir(2)–C(3)	111.3(15)	C(21)–P(2)–C(28)	99.1(17)
Ir(3)–Ir(2)–C(4)	47.9(11)	C(27)–P(2)–C(28)	104.1(21)
Ir(4)–Ir(2)–P(2)	99.3(3)	Ir(3)–P(3)–C(31)	115.8(13)
Ir(4)–Ir(2)–C(2)	79.6(15)	Ir(3)–P(3)–C(37)	116.6(20)
Ir(4)–Ir(2)–C(3)	168.9(15)	Ir(3)–P(3)–C(38)	113.5(20)
Ir(4)–Ir(2)–C(4)	80.3(11)	C(31)–P(3)–C(37)	103.6(23)
P(2)–Ir(2)–C(2)	96.6(15)	C(31)–P(3)–C(38)	104.4(23)
P(2)–Ir(2)–C(3)	91.8(15)	C(37)–P(3)–C(38)	101.2(28)
P(2)–Ir(2)–C(4)	97.3(12)	Ir(4)–P(4)–C(41)	113.6(14)
C(2)–Ir(2)–C(3)	99.0(21)	Ir(4)–P(4)–C(47)	122.6(29)
C(2)–Ir(2)–C(4)	157.1(19)	Ir(4)–P(4)–C(48)	118.5(29)
C(3)–Ir(2)–C(4)	98.7(19)	C(41)–P(4)–C(47)	104(3)
Ir(1)–Ir(3)–Ir(2)	59.19(7)	C(41)–P(4)–C(48)	101(3)
Ir(1)–Ir(3)–Ir(4)	59.49(7)	C(47)–P(4)–C(48)	94(4)
Ir(1)–Ir(3)–P(3)	118.4(4)	Ir(1)–C(1)–O(1)	167(8)
Ir(1)–Ir(3)–C(4)	109.1(12)	Ir(1)–C(2)–Ir(2)	78.7(19)
Ir(1)–Ir(3)–C(5)	45.8(15)	Ir(1)–C(2)–O(2)	137(5)
Ir(1)–Ir(3)–C(7)	136.9(17)	Ir(2)–C(2)–O(2)	144(5)
Ir(2)–Ir(3)–Ir(4)	59.94(7)	Ir(2)–C(3)–O(3)	176(4)
Ir(2)–Ir(3)–P(3)	109.8(4)	Ir(2)–C(4)–Ir(3)	82.1(15)
Ir(2)–Ir(3)–C(4)	50.1(12)	Ir(2)–C(4)–O(4)	135(3)
Ir(2)–Ir(3)–C(5)	104.7(15)	Ir(3)–C(4)–O(4)	142(3)
Ir(2)–Ir(3)–C(7)	142.0(17)	Ir(1)–C(5)–Ir(3)	89.6(21)
Ir(4)–Ir(3)–P(3)	169.5(4)	Ir(1)–C(5)–O(5)	133(4)
Ir(4)–Ir(3)–C(4)	81.5(12)	Ir(3)–C(5)–O(5)	136(4)
Ir(4)–Ir(3)–C(5)	85.5(15)	Ir(4)–C(6)–O(6)	171(5)
Ir(4)–Ir(3)–C(7)	96.4(17)	Ir(3)–C(7)–O(7)	175(5)
P(3)–Ir(3)–C(4)	90.1(12)	Ir(4)–C(8)–O(8)	168(4)

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[a] E.s.d.'s, given in parentheses, are applicable to the least significant digits.

TABLE 4

DEVIATIONS OF BRIDGING CARBONYLS FROM PLANE DEFINED BY Ir(1), Ir(2) AND Ir(3) [a]

Atom	Deviation (Å)
C(2)	0.2492
O(2)	0.3950
C(4)	0.1237
O(4)	0.1477
C(5)	−0.1837
O(5)	−0.1468

[a] Equation of plane; $-6.567X+3.283Y+30.518Z=1.634$; X, Y, Z are in fractional coordinates.

either between the tetrairidium clusters or between these and the occluded benzene molecules.

Three iridium atoms, Ir(1), Ir(2) and Ir(3), form an irregular basal triangular face which has a bridging carbonyl group along each edge, an equatorial phosphine attached to Ir(2) and axial phosphines attached to Ir(1) and Ir(3). The distances between the basal iridium atoms are not equivalent, thus two are similar viz. Ir(1)–Ir(2) 2.726(3) and Ir(2)–Ir(3) 2.737(3) Å whilst Ir(1)–Ir(3) 2.782(3) Å. The bond Ir(1)–Ir(3), the longest intermetallic bond in the complex, is between metal atoms carrying axial phosphines and which also has the phosphine on the apical iridium atom positioned above the bond. This bond-lengthening structural feature has also been noted [5] for the analogous compound $Ir_4(CO)_8(PMe_3)_4$, in which it was attributed to interligand repulsion. The Ir–Ir distances between the basal iridium atoms and the apical atom are very similar to one another viz. Ir(1)–Ir(4) 2.734(3), Ir(2)–Ir(4) 2.730(3) and Ir(3)–Ir(4) 2.727(3) Å. Although the cone angle of PMe_2Ph (122°) [12] is slightly larger than that of PMe_3 (118°) [12], there is no significant difference between the Ir–Ir distances in the present compound compared with those found in $Ir_4(CO)_8(PMe_3)_4$. This presumably arises because the bulky phenyl groups are able to orientate themselves away from each other and from the Ir_4 cluster. The Ir–P distances vary from 2.285(15) to 2.324(13) Å with a mean value of 2.308(18) Å, which are very close to the values found in $Ir_4(CO)_8(PMe_3)_4$.

The bridging carbonyl groups are not coplanar with the iridium atoms forming the basal face (Table 4.) Groups CO(4) and CO(2) are displaced away from the axial phosphines on Ir(1) and Ir(3), but CO(5) is displaced towards the axial phosphines. The displacement of CO(5) presumably arises from repulsion with the apical phosphine which lies above this carbonyl group. The apparent effect of the apical phosphine on CO(5) suggests that it may also be involved in a repulsive interaction which contributes to the lengthening of the Ir(1)–Ir(3) bond.

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