C10	0.3452 (2)	0.3880 (5)	0.1767 (3)	3.0 (2)
C11	0.3470 (2)	0.2478 (5)	0.1438 (4)	3.8 (2)
C12	0.2984 (2)	0.1524 (6)	0.1228 (4)	4.9 (2)
C13	0.2486 (2)	0.1957 (6)	0.1351 (4)	5.2 (3)
C14	0.2463 (2)	0.3337 (7)	0.1684 (4)	4.6 (2)
C15	0.2944 (2)	0.4304 (5)	0.1890 (3)	3.9 (2)
C20	0.4090 (2)	0.6416 (5)	0.2867 (3)	2.9 (2)
C21	0.4099 (2)	0.7926 (5)	0.2749 (3)	3.7 (2)
C22	0.4187 (2)	0.8864 (5)	0.3506 (4)	4.3 (2)
C23	0.4265 (2)	0.8321 (6)	0.4382 (4)	4.3 (2)
C24	0.4253 (2)	0.6819 (6)	0.4514 (4)	4.4 (2)
C25	0.4169 (2)	0.5888 (5)	0.3759 (3)	4.0 (2)
C30	0.3826 (2)	0.6170 (4)	0.0856 (3)	2.8 (2)
C31	0.3216 (2)	0.6289 (5)	0.0202 (3)	3.9 (2)
C32	0.3050 (2)	0.7111 (6)	−0.0640 (4)	4.5 (2)
C33	0.3475 (2)	0.7825 (5)	−0.0825 (3)	4.1 (2)
C34	0.4079 (2)	0.7709 (5)	−0.0189 (4)	4.2 (2)
C35	0.4249 (2)	0.6886 (5)	0.0645 (3)	3.7 (2)

Table 2. *Selected geometric parameters* (Å, °)

Cu1—P5	2.243 (1)	C20—C21	1.387 (6)
Cu1—O2	2.191 (4)	C20—C25	1.382 (6)
P5—C10	1.821 (4)	C21—C22	1.381 (6)
P5—C20	1.820 (4)	C22—C23	1.367 (7)
P5—C30	1.823 (4)	C23—C24	1.385 (7)
O2—N3	1.245 (5)	C24—C25	1.378 (6)
C10—C11	1.381 (6)	C30—C31	1.390 (6)
C10—C15	1.390 (6)	C30—C35	1.375 (6)
C11—C12	1.391 (6)	C31—C32	1.392 (6)
C12—C13	1.371 (7)	C32—C33	1.357 (7)
C13—C14	1.366 (8)	C33—C34	1.372 (6)
C14—C15	1.391 (6)	C34—C35	1.382 (6)
P5—Cu1—P5′	127.75 (7)	C13—C14—C15	119.9 (5)
P5—Cu1—O2	110.2 (1)	C10—C15—C14	120.7 (4)
P5—Cu1—O2′	115.4 (1)	P5—C20—C21	123.1 (4)
O2—Cu1—O2′	56.7 (2)	P5—C20—C25	118.2 (3)
Cu1—P5—C10	115.5 (2)	C21—C20—C25	118.1 (4)
Cu1—P5—C20	110.0 (1)	C20—C21—C22	120.5 (4)
Cu1—P5—C30	117.2 (1)	C21—C22—C23	120.5 (5)
C10—P5—C20	104.6 (2)	C22—C23—C24	119.9 (5)
C10—P5—C30	104.1 (2)	C23—C24—C25	119.3 (5)
C20—P5—C30	104.1 (2)	C20—C25—C24	121.7 (5)
Cu1—O2—N3	95.0 (4)	P5—C30—C31	122.8 (3)
O2—N3—O2′	113.2 (6)	P5—C30—C35	119.0 (3)
P5—C10—C11	117.8 (3)	C31—C30—C35	118.2 (4)
P5—C10—C15	123.4 (4)	C30—C31—C32	119.8 (4)
C11—C10—C15	118.7 (4)	C31—C32—C33	120.9 (4)
C10—C11—C12	120.0 (4)	C32—C33—C34	119.9 (4)
C11—C12—C13	120.6 (5)	C33—C34—C35	119.6 (4)
C12—C13—C14	120.0 (5)	C30—C35—C34	121.6 (4)

All calculations were performed using the *TEXSAN/TEXRAY* crystallographic software package (Molecular Structure Corporation, 1985). Structure solution: *MITHRIL* (Gilmore, 1984), *DIRDIF* (Beurskens, 1984).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(diphenylphosphino)methanetetradecacarbonylhexairidium Dichloromethane Solvate

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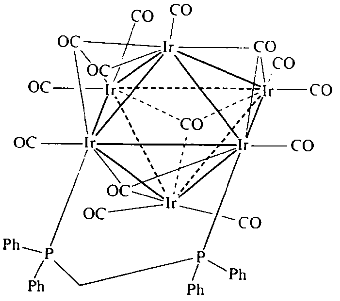
Abstract

The molecules of the title complex, μ-bis(diphenylphosphino)methane-*P*:*P′*-tetra-μ_3-carbonyl-decacarbonyl-*octahedro*-hexairidium, $[Ir_6(CO)_{14}(C_{25}H_{22}P_2)]$ are discrete monomeric units. Their coordination polyhedron is derived from that of the red $[Ir_6(CO)_{16}]$ isomer with a chelating dppm [bis(diphenylphosphino)methane] ligand replacing two equatorial terminal carbonyl groups in *cis* positions. The clusters display mirror symmetry with respect to the two P

atoms. Ten CO groups are terminal and four are face-capping. Two of the face-capping groups are asymmetric, with Ir—C bond distances ranging from 1.97 (2) to 2.43 (2) Å. The molecule is fluxional in solution down to 160 K due to rapid CO scrambling on the NMR timescale.

Comment

The reaction of $[Ir_6(CO)_{16}]$ with bis(diphenylphosphino)methane (dppm) in a 1:1 molar ratio leads to the title product (1). In contrast with $[Rh_6(CO)_{14}$(dppm)], the crystal structure of which is known (Clucas, Harding & Maginn, 1988), the ^{13}C NMR spectrum of a ^{13}CO enriched (*ca* 30%) sample of (1) exhibits a single CO resonance down to 160 K in $CD_2Cl_2/CHFCl_2$. Here we report a structural characterization of (1) in the solid state.



(1)

The cluster compound (1) is neither isostructural with $[Rh_6(CO)_{14}$(dppm)] (Clucas *et al.*, 1988) nor with $[Rh_6(CO)_{14}$(dppe)] [dppe is bis(diphenylphosphino)ethane] (Tunik *et al.*, 1992). The coordination polyhedron is derived from that of the red $[Ir_6(CO)_{16}]$ (Garlaschelli *et al.*, 1984) complex with the chelating dppm ligand replacing two equatorial terminal CO groups on adjacent Ir atoms. The molecule displays mirror symmetry with respect to the two P atoms, with ten terminal and four face-capping CO groups. The Ir—Ir bonds *trans* to the P atoms are significantly longer [2.803 (2) Å] than the other Ir—Ir bonds [mean 2.77 (1) Å] and than those of $[Ir_6(CO)_{16}]$ [mean 2.779 (1) Å]. The terminal [mean 1.12 (1) Å] and capping [mean 1.16 (3) Å] CO distances are quite comparable to the corresponding distances in $[Ir_6(CO)_{16}]$ [mean values 1.13 (1) and 1.19 (2) Å, respectively]. Two of the face-capping carbonyl groups are essentially symmetrical and two are asymmetric, with Ir—C distances ranging 1.97 (2)–2.43 (2) Å. This asymmetry is most likely due to the presence of the P donor ligand, which is a poorer π acceptor than the terminal CO groups. The fluxional behaviour in solution of the related compound $[Ir_6(CO)_{14}$(dppe)], as studied using ^{13}C NMR, is due to intramolecular CO scrambling, the process of lowest activation energy being the $\mu_3 \rightarrow \mu_2$ conversion of two face-capping CO groups which exchange with vicinal terminal CO groups (Mihokova, 1993). The asymmetry found in the solid state for two of the face-capping carbonyl ligands of (1), which are somewhat displaced towards μ_2 bending, is consistent with the ground-state geometry leading to such dynamic behaviour.

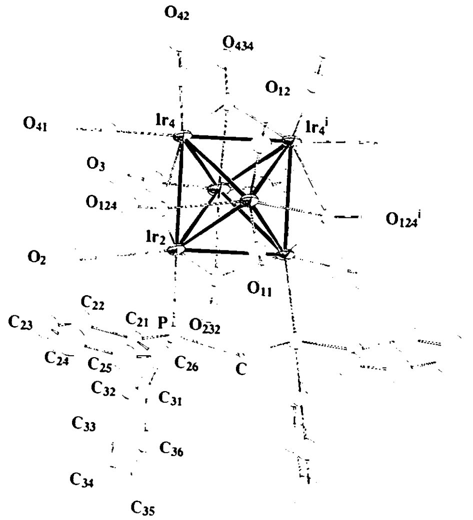


Fig. 1. *ORTEP* (Johnson, 1965) representation (60% probability ellipsoids for Ir atoms) of the cluster. The labels of the carbonyl C atoms have been omitted for clarity, but correspond to the labels of their O atoms. [Symmetry code: (i) $x, \frac{1}{2}-y, z$.]

Experimental

A solution of $[Ir_6(CO)_{16}]$ (0.35 g) and dppm (0.084 g) in THF (70 cm^3) was stirred at room temperature for 14 h under N_2. After evaporation to dryness, the dark red residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on a plate of silica gel (2 mm thickness) using CH_2Cl_2/hexane (2.5:1) as eluent. Recrystallization from CH_2Cl_2/hexane at 248 K gave (1) (0.22 g, 52%). Analysis: calculated for $C_{39}H_{22}Ir_6O_{14}P_2.CH_2Cl_2$, C 23.85, H 1.20, P 3.07%; found, C 24.13, H 1.12, P 3.22 %. The crystal comprised of {011}, {001}, {0$\bar{1}$1} pinacoids and ($\bar{1}$01), (210), (100) pedions.

Crystal data

$[Ir_6(CO)_{14}(C_{25}H_{22}P_2)].CH_2Cl_2$
M_r = 2014.4
Monoclinic
$P2_1/m$
a = 11.144 (3) Å
b = 15.667 (4) Å
c = 13.048 (5) Å
β = 96.32 (3)°
V = 2264.2 (12) Å^3
Z = 2
D_x = 2.952 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 40 reflections
θ = 7–15.5°
μ = 17.82 mm^{-1}
T = 140 (2) K
Prism
0.32 × 0.18 × 0.11 mm
Dark orange

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian by integration from crystal shape
$T_{\min} = 0.06$, $T_{\max} = 0.23$
7089 measured reflections
4179 independent reflections
2861 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.086$
$\theta_{\max} = 25.06°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 15$
3 standard reflections monitored every 97 reflections intensity decay: <75%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0951$
$wR(F^2) = 0.2013$
$S = 2.129$
4176 reflections
250 parameters
H atoms not located
$w = 1/[\sigma^2(F_o^2) + 2P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.102$
$\Delta\rho_{\max} = 6.00$ e Å^{-3}
$\Delta\rho_{\min} = -9.95$ e Å^{-3}

Extinction correction: $F_c{}^* = kF_c[1 + 0.001(F_c)^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00062 (12)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ir1	0.16870 (11)	1/4	0.44678 (13)	0.0202 (4)
Ir2	0.11221 (7)	0.16205 (6)	0.26224 (10)	0.0201 (3)
Ir3	−0.10533 (11)	1/4	0.22893 (14)	0.0242 (4)
Ir4	−0.05151 (8)	0.16229 (6)	0.41066 (10)	0.0224 (3)
C11	0.3352 (26)	1/4	0.4687 (33)	0.022 (3)
O11	0.4389 (17)	1/4	0.4969 (21)	0.022 (6)
C12	0.1630 (32)	1/4	0.5919 (35)	0.025 (9)
O12	0.1530 (22)	1/4	0.6717 (26)	0.045 (7)
C2	0.0615 (21)	0.0651 (16)	0.1902 (24)	0.027 (6)
O2	0.0239 (19)	0.0067 (15)	0.1415 (21)	0.062 (7)
C3	−0.2002 (19)	0.1627 (16)	0.1560 (25)	0.026 (2)
O3	−0.2597 (15)	0.1121 (11)	0.1229 (16)	0.032 (5)
C41	−0.1111 (18)	0.0552 (14)	0.3648 (21)	0.016 (5)
O41	−0.1471 (15)	−0.0097 (10)	0.3317 (18)	0.037 (5)
C42	−0.0737 (19)	0.1408 (17)	0.5479 (25)	0.024 (2)
O42	−0.0936 (15)	0.1307 (13)	0.6273 (18)	0.040 (5)
C124	0.1547 (17)	0.1145 (14)	0.4013 (20)	0.012 (5)
O124	0.1965 (12)	0.0539 (10)	0.4434 (15)	0.022 (1)
C232	0.0361 (29)	1/4	0.1301 (35)	0.023 (1)
O232	0.0449 (19)	1/4	0.0475 (23)	0.028 (3)
C434	−0.1949 (27)	1/4	0.3769 (31)	0.019 (8)
O434	−0.3012 (17)	1/4	0.3950 (22)	0.023 (4)
C	0.3915 (22)	1/4	0.2428 (25)	0.003 (6)
P	0.3036 (5)	0.1509 (4)	0.2105 (6)	0.016 (1)
C21	0.3989 (18)	0.0724 (15)	0.2772 (25)	0.026 (5)
C22	0.3583 (23)	−0.0130 (16)	0.2777 (28)	0.040 (5)
C23	0.4270 (24)	−0.0771 (16)	0.3258 (26)	0.037 (5)
C24	0.5396 (24)	−0.0541 (20)	0.3886 (29)	0.050 (7)
C25	0.5778 (20)	0.0299 (19)	0.3880 (23)	0.032 (4)
C26	0.5099 (18)	0.0967 (19)	0.3347 (25)	0.033 (5)
C31	0.3179 (19)	0.1255 (15)	0.0740 (22)	0.018 (5)
C32	0.2229 (22)	0.1189 (16)	0.0018 (30)	0.041 (7)
C33	0.2352 (24)	0.1026 (18)	−0.1030 (30)	0.047 (7)
C34	0.4523 (26)	0.1025 (21)	−0.0544 (30)	0.049 (9)
C35	0.3562 (23)	0.0947 (19)	−0.1288 (30)	0.050 (8)
C36	0.4372 (21)	0.1202 (17)	0.0495 (25)	0.029 (7)
Cl1	0.1329 (19)	−0.1541 (14)	0.1075 (23)	0.088 (7)
C1	−0.1456 (37)	1/4	−0.1535 (43)	0.05 (1)
Cl2	−0.2804 (29)	0.1988 (20)	−0.1143 (35)	0.18 (2)

Table 2. *Selected geometric parameters* (Å, °)

Ir1—Ir2	2.786 (2)	Ir1—C12	1.90 (4)
Ir1—Ir4	2.807 (2)	Ir2—C2	1.84 (3)
Ir2—Ir3	2.781 (2)	Ir3—C3	1.92 (3)
Ir2—Ir4	2.803 (2)	Ir4—C41	1.88 (2)
Ir2—Ir2^{i}	2.756 (2)	Ir4—C42	1.87 (3)
Ir3—Ir4	2.749 (2)	Ir1—C124	2.20 (2)
Ir4—Ir4^{i}	2.748 (2)	Ir2—C124	1.97 (2)
Ir2—P	2.313 (6)	Ir4—C124	2.43 (2)
C—P	1.859 (15)	Ir2—C232	2.30 (4)
P—C21	1.79 (2)	Ir3—C232	2.14 (4)
P—C31	1.85 (3)	Ir3—C434	2.27 (4)
Ir1—C11	1.85 (3)	Ir4—C434	2.12 (2)
Ir2—Ir1—Ir4	60.16 (5)	P—C—P^{i}	113.2 (14)
Ir2^{i}—Ir2—Ir4	89.92 (3)	C—P—Ir2	110.5 (8)
Ir4—Ir3—Ir2	60.91 (5)	Ir—C—O (term., mean)	174 (1)
Ir4^{i}—Ir4—Ir2	90.08 (3)	Ir—C—O (capping, mean)	133 (2)
P—Ir2—Ir2^{i}	94.33 (15)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

The rather strong anisotropic decay was accounted for by scaling on three check reflections. An absorption correction based on the observed morphology and using Gaussian integration improved the $R_{\rm int}$ value from 0.18 to 0.086. The structure was solved by interpreting Patterson and subsequent Fourier maps.

There is a disordered molecule of crystalline dichloromethane that seems to participate in hydrogen bonding between clusters along the *b* axis.

The structure was solved using *SHELXS*86 (Sheldrick, 1985) and all other calculations were made using *SHELX*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: NA1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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