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Structure of μ-Hydrido-bis(hydrido)bis(pentamethylcyclopentadienyl)bis(trimethylphosphino)diiridium Hexafluorophosphate

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Abstract. $[Ir_2(C_{10}H_{15})_2(C_3H_9P)_2H_3]PF_6$, $M_r = 955{\cdot}0$, monoclinic, $P2_1/n$, $a = 15{\cdot}2060\ (10)$, $b = 15{\cdot}0258\ (12)$, $c = 14{\cdot}6729\ (14)$ Å, $\beta = 99{\cdot}198\ (6)$°, $V = 3309{\cdot}4\ (8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}917$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 81{\cdot}95$ cm^{-1}, $F(000) = 1840$, $T = 298$ K, $R = 0{\cdot}0185$ for 4324 unique reflections. The cation consists of a singly hydride-bridged Ir dimer with an unusually long Ir—Ir distance of 2·983 (1) Å. Each Ir is further coordinated to one pentamethylcyclopentadienyl ring, one trimethylphosphine and one terminal hydride.

Introduction. The reaction of the tris(μ-hydrido)bis(pentamethylcyclopentadienyl)diiridate cation with trimethylphosphine produces the title compound (Gilbert & Bergman, 1985). The starting dimer shows an unusually short Ir—Ir distance thought to be a metal—metal triple bond (Bau, Gellert & Shibu, 1975). Reaction with phosphine does not cleave the dimer, but rather produces the singly bridged hydride compound discussed here. No Ir dimer with a single bridge has yet been structurally characterized, consequently the Ir—Ir distance is of great interest.

Experimental. Crystal provided by Mr Thomas Gilbert, well-formed orange prism, 0·2 × 0·2 × 0·3 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; 24 reflections, $24 < 2\theta < 30°$, used to determine lattice parameters; ω–2θ-scan mode, variable scan rate 0·63–6·66° min^{-1} in 2θ; 4732 reflections in quadrant $\pm h$, $\pm k$, $+l$ ($h = -16$–16, $k = 0$–16, $l = 0$–15) measured with $3 < 2\theta < 45°$; three standard reflections (843, 3,10,3, $\bar{3}38$) measured every hour of data collection showed an average decline in intensity of 2·9% over 73 h, orientation checked every 250 reflections and reoriented if angle deviated by 0·1°; data corrected for background, scan speed, Lorentz and polarization factors; analytical absorption correction applied, transmission factors 0·184 to 0·245; systematically absent reflections and redundant data rejected yielding 4324 data, 3724 of which had $I > 3\sigma(I)$; six additional reflections rejected whose (Δ/σ) values were three times higher than average values, leaving 3718 reflections used in refinement.

Ir atoms located by Patterson technique, standard Fourier methods yielded all non-H atoms and the three hydride atoms; positional and anisotropic thermal parameters for all non-H atoms refined, positional and isotropic thermal parameters refined for hydrides, methyl-H atoms placed and refined with fixed thermal parameters; secondary-extinction correction applied, based on F_o/F_c for several low-angle reflections, final value after refinement, $6{\cdot}2\ (2) \times 10^{-8}$ e^{-2}; $\sum w(|F_o| - |F_c|)^2$ minimized where $w = [4F_o^2/\sigma^2(F_o)^2]\sigma^2(F_o)^2 = \sigma_o^2(F_o^2) + (pF^2)^2$, $p = 0{\cdot}02$; final least-squares cycle

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

B_{eq}, the isotropic equivalent thermal parameter for anisotropically refined atoms, is defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B_{eq}(Å^2)
Ir(1)	0·43100 (1)	0·11065 (1)	0·20328 (1)	2·926 (4)
Ir(2)	0·46025 (1)	0·30527 (1)	0·18163 (1)	3·146 (4)
P(1)	0·57117 (9)	0·0584 (1)	0·2201 (1)	4·19 (3)
P(2)	0·5246 (1)	0·3427 (1)	0·3250 (1)	4·83 (4)
P(3)	0·4004 (1)	0·2891 (1)	0·6496 (1)	5·23 (4)
F(1)	0·4359 (3)	0·2077 (3)	0·5979 (3)	9·3 (1)
F(2)	0·4745 (4)	0·2747 (4)	0·7336 (4)	15·2 (2)
F(3)	0·3668 (3)	0·3700 (3)	0·7019 (3)	9·8 (1)
F(4)	0·3274 (4)	0·3027 (4)	0·5714 (4)	18·1 (2)
F(5)	0·3392 (4)	0·2278 (4)	0·6922 (5)	16·8 (2)
F(6)	0·4654 (4)	0·3498 (4)	0·6118 (4)	16·2 (2)
C(1)	0·6175 (4)	0·0086 (4)	0·3294 (4)	6·0 (2)
C(2)	0·5894 (5)	−0·0301 (5)	0·1410 (5)	7·7 (2)
C(3)	0·6576 (4)	0·1356 (5)	0·2060 (6)	8·0 (2)
C(4)	0·5412 (5)	0·2547 (4)	0·4099 (4)	6·1 (2)
C(5)	0·6350 (5)	0·3908 (5)	0·3370 (5)	8·3 (2)
C(6)	0·4634 (6)	0·4245 (5)	0·3804 (5)	8·8 (2)
C(7)	0·2811 (3)	0·1140 (3)	0·1940 (4)	3·8 (1)
C(8)	0·3083 (3)	0·0325 (4)	0·1632 (3)	4·0 (1)
C(9)	0·3635 (3)	−0·0111 (3)	0·2373 (4)	4·2 (1)
C(10)	0·3673 (3)	0·0469 (4)	0·3176 (3)	4·3 (1)
C(11)	0·3170 (3)	0·1227 (4)	0·2901 (4)	4·2 (1)
C(12)	0·2118 (4)	0·1753 (5)	0·1417 (5)	6·3 (2)
C(13)	0·2794 (4)	−0·0097 (5)	0·0689 (4)	7·0 (2)
C(14)	0·3931 (5)	−0·1052 (4)	0·2394 (6)	7·3 (2)
C(15)	0·4089 (4)	0·0228 (5)	0·4131 (4)	6·6 (2)
C(16)	0·2925 (4)	0·1938 (5)	0·3520 (5)	6·9 (2)
C(17)	0·5031 (4)	0·3078 (3)	0·0378 (4)	4·2 (1)
C(18)	0·5397 (4)	0·3813 (4)	0·0883 (4)	4·7 (1)
C(19)	0·4657 (4)	0·4332 (3)	0·1119 (3)	4·7 (1)
C(20)	0·3856 (4)	0·3892 (4)	0·0719 (4)	4·5 (1)
C(21)	0·4083 (4)	0·3109 (3)	0·0282 (3)	4·0 (1)
C(22)	0·5535 (5)	0·2410 (5)	−0·0108 (4)	6·9 (2)
C(23)	0·6351 (4)	0·4101 (5)	0·1027 (5)	7·8 (2)
C(24)	0·4730 (5)	0·5233 (4)	0·1514 (5)	7·6 (2)
C(25)	0·2927 (4)	0·4241 (5)	0·0716 (5)	7·1 (2)
C(26)	0·3450 (5)	0·2515 (5)	−0·0344 (4)	6·6 (2)
H(1)	0·452 (3)	0·123 (3)	0·110 (4)	7 (1)*
H(2)	0·390 (4)	0·292 (4)	0·244 (5)	9 (2)*
H(3)	0·500 (3)	0·199 (3)	0·227 (3)	6 (1)*

* Atoms refined with isotropic thermal parameters.

Table 2. *Bond distances* (Å) *and bond angles* (°)

Ir(1)—Ir(2)	2·983 (1)	P(2)—C(4)	1·806 (5)
Ir(1)—P(1)	2·248 (1)	P(2)—C(5)	1·810 (6)
Ir(1)—H(1)	1·47 (5)	P(2)—C(6)	1·812 (7)
Ir(1)—H(3)	1·69 (4)	P(3)—F(1)	1·579 (3)
Ir(2)—P(2)	2·246 (1)	P(3)—F(2)	1·547 (5)
Ir(2)—H(2)	1·52 (6)	P(3)—F(3)	1·566 (3)
Ir(2)—H(3)	1·80 (4)	P(3)—F(4)	1·477 (5)
P(1)—C(1)	1·806 (5)	P(3)—F(5)	1·514 (5)
P(1)—C(2)	1·815 (6)	P(3)—F(6)	1·514 (5)
P(1)—C(3)	1·790 (5)		

Ir(2)—Ir(1)—P(1)	101·51 (3)	Ir(2)—P(2)—C(6)	114·34 (22)
Ir(2)—Ir(1)—H(1)	73·4 (17)	C(4)—P(2)—C(5)	101·6 (3)
Ir(2)—Ir(1)—H(3)	32·3 (14)	C(4)—P(2)—C(6)	102·3 (3)
P(1)—Ir(1)—H(1)	78·6 (17)	C(5)—P(2)—C(6)	102·7 (3)
P(1)—Ir(1)—H(3)	73·1 (14)	F(1)—P(3)—F(2)	90·75 (24)
Ir(1)—Ir(2)—P(2)	101·28 (3)	F(1)—P(3)—F(3)	179·0 (3)
Ir(1)—Ir(2)—H(2)	70·9 (19)	F(1)—P(3)—F(4)	90·3 (3)
Ir(1)—Ir(2)—H(3)	30·3 (14)	F(1)—P(3)—F(5)	90·39 (25)
P(2)—Ir(2)—H(2)	73·5 (22)	F(1)—P(3)—F(6)	89·9 (3)
P(2)—Ir(2)—H(3)	78·6 (14)	F(2)—P(3)—F(3)	88·35 (25)
Ir(1)—H(3)—Ir(2)	117·4 (25)	F(2)—P(3)—F(4)	178·1 (4)
Ir(1)—P(1)—C(1)	118·10 (18)	F(2)—P(3)—F(5)	90·2 (4)
Ir(1)—P(1)—C(2)	115·12 (20)	F(2)—P(3)—F(6)	86·6 (4)
Ir(1)—P(1)—C(3)	117·50 (19)	F(3)—P(3)—F(4)	90·6 (3)
C(1)—P(1)—C(2)	100·8 (3)	F(3)—P(3)—F(5)	89·9 (3)
C(1)—P(1)—C(3)	100·4 (3)	F(3)—P(3)—F(6)	89·73 (24)
C(2)—P(1)—C(3)	102·2 (3)	F(4)—P(3)—F(5)	88·2 (4)
Ir(2)—P(2)—C(4)	117·84 (17)	F(4)—P(3)—F(6)	94·9 (4)
Ir(2)—P(2)—C(5)	116·71 (20)	F(5)—P(3)—F(6)	176·8 (5)

$R = 1·85$, $wR = 2·49\%$; max. $(\Delta/\sigma) = 0·56$; max. peak height in final difference map $= 0·637$ e Å^{-3}, associated with the PF_6^- anion; complex neutral-atom scattering factors from Cromer & Waber (1974); all calculations carried out using *SDP* (Frenz, 1980) and *ORTEP* (Johnson, 1965).

Discussion. Table 1 lists the final positional and equivalent isotropic thermal parameters. Table 2 presents bond distances and angles.† Fig. 1 gives a view of the Ir dimer with the atom-labeling scheme. Fig. 2 is a stereoscopic diagram of the unit-cell contents.

$Ir_2(\mu\text{-}H)H_2(PMe_3)_2Cp^*_2$ (Cp* = pentamethylcyclopentadienyl) is a dimer with an unusually long Ir—Ir bond distance of 2·983(1) Å. The coordination geometry about each Ir atom is approximately tetrahedral, ignoring the bridging hydride. The two Ir—P bonding

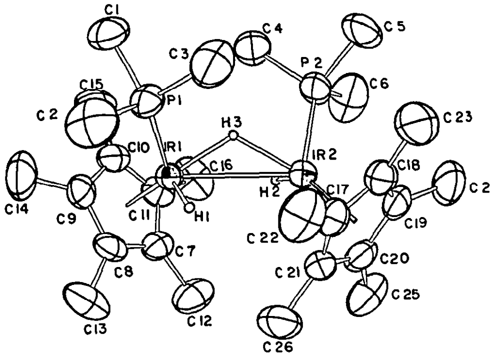

Fig. 1. *ORTEP* drawing (Johnson, 1965) and atom-numbering scheme of the $Ir_2(\mu\text{-}H)H_2[P(CH_3)_3]_2[C_5(CH_3)_5]_2^+$ molecule. Ellipsoids are scaled to represent 50% of the probability surface.

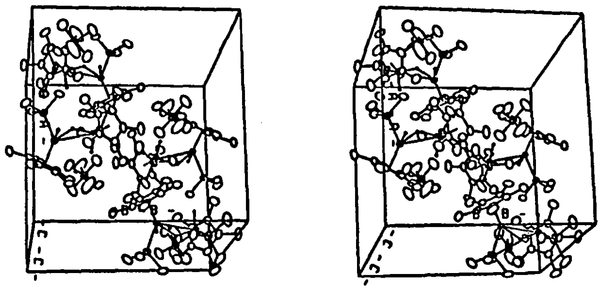

Fig. 2. Stereoscopic view of the molecules in the unit cell.

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† Lists of structure factors, anisotropic thermal parameters, calculated H-atom coordinates, bond lengths and angles within the Cp* rings, torsion angles and least-squares planes have been deposited with the British Library Docment Supply Centre as Supplementary Publication No. SUP 43431 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances are 2·248 (1) and 2·246 (1) Å. The angles Ir(2)—Ir(1)—P(1) and Ir(1)—Ir(2)—P(2) are approximately equal at 101·51 (3) and 101·28 (3)°.

The Cp* rings are essentially planar, with a maximum deviation from planarity of 0·014 Å. The methyl groups are bent out of the ring plane, away from the Ir atoms. The two ring-centroid—Ir distances are nearly equal at 1·89 Å. The angle between the Cp* planes is 57·7°. The mean C—C distance within the rings is 1·421 (7) Å and the mean ring-C to methyl-C distance is 1·499 (7) Å. The hydride bridge is symmetrical with an Ir(1)—H(3) distance of 1·69 (4) and an Ir(2)—H(3) distance of 1·80 (4) Å. A pseudo-twofold axis passes through the bridging hydride, perpendicular to the Ir—Ir vector. The Ir—Ir—terminal H angles deviate significantly from tetrahedral at 73·4 (2) and 70·9 (2)°.

Although not disordered, the PF_6^- anion shows considerable thermal motion corresponding to rotation about the F(1)—P(3)—F(3) axis.

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Structure du Bis(*N*,*N*-di-*n*-butyl diméthyl-3,3 butanamide)dinitratodioxouranium(VI)

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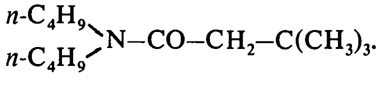
Abstract. $[U(NO_3)_2O_2(C_{14}H_{29}NO)_2]$, $M_r = 848$, monoclinic, $C2/c$, $a = 40{\cdot}731\ (12)$, $b = 9{\cdot}944\ (7)$, $c = 21{\cdot}510\ (8)$ Å, $\beta = 114{\cdot}21\ (3)°$, $V = 7945$ Å^3, $Z = 8$, $D_x = 1{\cdot}419$ g cm^{-3}, $\lambda(\text{Mo } K\overline{\alpha}) = 0{\cdot}71073$ Å, $\mu = 3{\cdot}92$ mm^{-1}, $F(000) = 3408$, $T = 295$ K, final $R_F = 0{\cdot}049$ for 1741 observed reflections. The unit cell contains two independent U atoms lying on symmetry centers, with a similar environment. The linear uranyl groups [U(1)—O 1·75 (2), U(2)—O 1·73 (2) Å] are classically coordinated in their equatorial plane to six O atoms: four from two bidentate nitrates [U(1)—O 2·51 (2); U(2)—O 2·50 (2) Å] and two from two monodentate *N*,*N*-substituted amides in opposite positions [U(1)—O 2·36 (1); U(2)—O 2·35 (1) Å].

Introduction. Les amides en général sont de bons extractants pour l'uranyle (Descouls & Musikas, 1984; Gasparini & Grossi, 1980) et forment avec celui-ci des complexes de type $UO_2(NO_3)_2L_2$, L étant un *N*,*N*-dialkylamide substitué. Nous étudions une série de mono- et diamides pour tenter de relier leur pouvoir d'extraction, leur solubilité et leur structure. Dans le cas de monoamides, l'uranyle est entouré d'un hexagone d'oxygènes appartenant à deux nitrates bidentés et opposés et à deux amides monodentés (Martin-Gil, Martin-Gil, Perales, Fayos & Martínez-Ripoll, 1983; Charpin, Folcher, Lance, Nierlich & Vigner, 1985; Charpin, Lance, Nierlich, Vigner, Descouls & Musikas, 1986). Nous décrivons la structure d'un nouveau complexe pour lequel L est le *N*,*N*-di-*n*-butyl diméthyl-3,3 butanamide:



$$\begin{matrix} n\text{-}C_4H_9 \searrow \\ n\text{-}C_4H_9 \nearrow \end{matrix} N{-}CO{-}CH_2{-}C(CH_3)_3.$$

Partie expérimentale. Par mise en contact d'une solution benzénique de *N*,*N*-di-*n*-butyl diméthyl-3,3 butanamide (L) et d'une solution aqueuse de nitrate d'uranyle, l'uranium est extrait en phase organique sous forme de complexe $UO_2(NO_3)_2L_2$; cristaux obtenus par évaporation lente du benzène; cristal jaune-vert sous forme d'aiguille, 50 × 60 × 300 μm; CAD-4 Enraf–

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