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Structure of a Tetrairidium Cluster with a Bridging diop Ligand: 2,3- μ -[(+)-4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane]-(*P,P'*)-2,3;3,4;4,2-tri- μ -carbonyl-1,1,1,2,3,4,4-heptacarbonyl-tetrahedro-tetrairidium

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Abstract

The crystal structure of Ir₄(CO)₁₀{(+)-diop}, C₄₁H₃₂Ir₄O₁₂P₂, has been determined. The cluster crystallizes in the space group *P2₁2₁2₁*, with *a* = 12.009 (3), *b* = 16.943 (6) and *c* = 20.823 (8) Å. The structure was refined to *R*₁ = 0.045 and *R*₂ = 0.052 for 1875 reflections. The diop ligand adopts an unusual configuration and bridges two Ir atoms, forming an eight-membered ring $\square\text{Ir}-\text{Ir}-\text{P}-\text{C}_4-\text{P}\square$. Ir atoms edge-bridged by carbonyl ligands have a mean Ir–Ir distance of 2.764 (2) Å, which is significantly longer than the mean Ir–Ir distance of 2.723 (2) Å for non-carbonyl-bridged atoms.

Introduction

Many transition-metal complexes involving diop [4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane] have been used as catalysts for asymmetric synthesis (Balavoine, Brunie & Kagan, 1980; Balavoine, Dang, Eskenazi & Kagan, 1980; Botteghi *et al.*, 1977; Consiglio, 1976, 1977; Glaser & Blumenfeld, 1977). The configuration of this ligand in several mononuclear transition-metal complexes has been determined by X-ray methods (Balavoine, Brunie & Kagan, 1980; Brunie, Mazam, Langlois & Kagan, 1976; Gramlich & Consiglio, 1979; Knowles, Vineyard, Sabacky & Stults, 1979). In all of these, diop acts as a chelating ligand and exhibits only slight conformational changes, with the $\square\text{metal}-\text{P}-\text{C}_4-\text{P}\square$

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ring adopting the pseudo boat-chair forms of cycloheptane. Recently, $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$ and $\{\text{Ir}_4(\text{CO})_{11}\}_2\{(+)\text{-diop}\}$ have been prepared (Lieto, Rafalko, Minkiewicz, Rafalko & Gates, 1979). In the latter complex, diop bridges two tetranuclear Ir clusters. In this work, the X-ray structure determination of $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$ was undertaken, with the following objectives: (1) to resolve which bonding mode, chelating or bridging, diop adopts in this cluster, and (2) to provide a comparison between diop's conformations in cluster and mononuclear complexes.

Crystallographic data collection

$\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$ was prepared from $\text{Ir}(\text{CO})_2(p\text{-toluidine})\text{Cl}$ and (+)-diop according to literature methods (Lieto *et al.*, 1979; Stuntz & Shapley, 1976). The frequencies of the infrared carbonyl stretching bands and the positions of the ^{31}P peaks matched the reported values (Lieto *et al.*, 1979).

Orange crystals of this compound were grown from an acetone-hexane solution. A parallelepiped crystal of approximate dimensions $0.17 \times 0.19 \times 0.2$ mm was used for precession and Weissenberg photographs. Systematic absences indicated that the space group was $P2_12_12_1$. However, some satellite reflections due to small crystallites rendered the space-group determination doubtful. The above space group was later confirmed by the complete structural analysis.

This crystal was examined on a Nonius CAD-4 computer-controlled diffractometer using Ag $K\alpha$ radiation monochromatized with a graphite crystal ($\lambda_{\text{Ag } K\alpha} = 0.5608 \text{ \AA}$). The broad ω -scan profiles that were observed from some strong reflections suggested poor crystallinity of the compounds. Several crystals were checked and, finally, a very small crystal with an approximately parallelepiped shape (about $0.1 \times 0.12 \times 0.09$ mm) was found with acceptable mosaicity. The widths at half height of several intense reflections were less than 0.3° .

The unit-cell dimensions were determined by a least-squares refinement of the setting angles for 25 reflections in the range $15^\circ < \theta < 18^\circ$. The calculated density is 2.018 g cm^{-3} for a molecular weight of 1515 and $Z = 4$. Intensity data were collected at room temperature using the ω -scan method with a scan range $\Delta\omega (^\circ) = 1.65 + 0.1 \tan \theta$. About 5200 reflections were measured in the upper half of the reflection sphere up to $2\theta = 36^\circ$. The usual Lorentz-polarization and absorption corrections were applied assuming the crystal used had a parallelepiped shape ($\mu = 61.42 \text{ cm}^{-1}$). After the non-unique reflections had been averaged, there were 1875 with $I > 3\sigma(I)$. The intensities of three standard noncoplanar reflections, monitored after every 120 reflections, remained nearly constant.

Table 1. Final positional coordinates and equivalent isotropic thermal parameters, with *e.s.d.*'s in parentheses

For Ir, P and O atoms $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B_{\text{iso}} (\text{\AA}^2)$
Ir(1)	0.9286 (1)	0.96497 (8)	0.46273 (8)	4.2 (4)
Ir(2)	0.8727 (1)	1.01916 (8)	0.58103 (8)	4.6 (3)
Ir(3)	0.7147 (1)	0.96030 (10)	0.50561 (9)	6.4 (5)
Ir(4)	0.8701 (2)	0.88258 (8)	0.56472 (9)	5.6 (4)
P(1)	1.1088 (8)	0.9700 (5)	0.4236 (5)	3.9 (2)
P(2)	1.0298 (10)	1.0489 (5)	0.6378 (5)	4.2 (2)
O(1)	0.833 (2)	0.979 (2)	0.335 (1)	7.9 (4)
O(2)	0.928 (2)	1.121 (1)	0.472 (1)	6.6 (4)
O(3)	0.948 (3)	0.815 (1)	0.439 (1)	7.6 (4)
O(4)	0.793 (3)	0.934 (2)	0.693 (1)	8.1 (4)
O(5)	0.661 (3)	0.853 (2)	0.409 (2)	11.2 (6)
O(6)	0.532 (3)	0.944 (2)	0.597 (2)	11.9 (7)
O(7)	0.643 (3)	1.090 (3)	0.449 (2)	9.7 (6)
O(8)	0.724 (3)	1.122 (2)	0.630 (2)	9.1 (6)
O(9)	0.693 (3)	0.777 (1)	0.583 (2)	11.4 (8)
O(10)	1.052 (3)	0.809 (2)	0.633 (2)	8.5 (6)
O(11)	1.261 (2)	1.135 (1)	0.574 (1)	5.4 (5)
O(12)	1.324 (2)	1.121 (1)	0.471 (1)	6.8 (7)
C(1)	0.874 (3)	0.975 (2)	0.385 (2)	3.4 (7)
C(2)	0.916 (3)	1.062 (2)	0.491 (2)	3.1 (7)
C(3)	0.931 (3)	0.864 (2)	0.470 (2)	5.2 (9)
C(4)	0.828 (3)	0.944 (2)	0.642 (2)	3.5 (8)
C(5)	0.685 (3)	0.899 (2)	0.440 (2)	4.4 (9)
C(6)	0.606 (4)	0.956 (2)	0.565 (2)	6.2 (10)
C(7)	0.674 (3)	1.041 (2)	0.465 (2)	4.0 (8)
C(8)	0.787 (3)	1.083 (2)	0.613 (2)	4.2 (9)
C(9)	0.757 (3)	0.815 (2)	0.579 (2)	4.6 (9)
C(10)	0.986 (4)	0.839 (3)	0.604 (2)	7.9 (13)
C(11)	1.215 (3)	0.909 (2)	0.447 (2)	4.5 (9)
C(12)	1.201 (3)	0.873 (2)	0.504 (2)	6.0 (11)
C(13)	1.285 (4)	0.826 (2)	0.522 (2)	7.9 (13)
C(14)	1.380 (5)	0.817 (3)	0.487 (3)	8.8 (14)
C(15)	1.391 (4)	0.854 (2)	0.429 (2)	8.0 (13)
C(16)	1.309 (3)	0.901 (2)	0.410 (2)	5.4 (10)
C(17)	1.103 (3)	0.951 (2)	0.335 (2)	4.7 (9)
C(18)	1.098 (3)	0.887 (2)	0.313 (2)	5.2 (10)
C(19)	1.092 (3)	0.874 (2)	0.248 (2)	5.6 (10)
C(20)	1.088 (4)	0.925 (3)	0.205 (2)	8.1 (14)
C(21)	1.095 (4)	0.990 (2)	0.225 (2)	7.2 (12)
C(22)	1.102 (3)	1.003 (2)	0.291 (2)	5.9 (11)
C(23)	1.046 (3)	1.137 (2)	0.662 (2)	4.7 (9)
C(24)	0.994 (3)	1.187 (2)	0.628 (2)	4.2 (9)
C(25)	1.009 (4)	1.254 (2)	0.647 (2)	6.3 (11)
C(26)	1.076 (4)	1.270 (2)	0.699 (2)	6.3 (11)
C(27)	1.127 (4)	1.220 (2)	0.734 (2)	7.0 (12)
C(28)	1.114 (2)	1.153 (2)	0.715 (2)	6.9 (12)
C(29)	1.042 (3)	1.004 (2)	0.712 (2)	3.4 (8)
C(30)	1.117 (3)	0.951 (2)	0.718 (2)	3.9 (8)
C(31)	1.124 (4)	0.915 (2)	0.778 (2)	5.8 (10)
C(32)	1.057 (4)	0.934 (2)	0.828 (2)	6.6 (11)
C(33)	0.982 (4)	0.987 (2)	0.821 (2)	6.3 (11)
C(34)	0.974 (3)	1.022 (2)	0.763 (2)	5.6 (10)
C(35)	1.161 (3)	1.031 (1)	0.593 (1)	2.5 (7)
C(36)	1.185 (3)	1.050 (2)	0.425 (2)	3.6 (8)
C(37)	1.185 (3)	1.089 (2)	0.545 (2)	4.0 (9)
C(38)	1.252 (3)	1.064 (2)	0.487 (2)	4.1 (9)
C(39)	1.318 (4)	1.174 (2)	0.527 (2)	7.2 (12)
C(40)	1.248 (4)	1.233 (2)	0.504 (2)	6.8 (12)
C(41)	1.436 (4)	1.180 (3)	0.546 (2)	8.2 (13)

Solution and refinement of the structure

The crystal structure of the compound was solved by heavy-atom methods. The four Ir atoms were found in the Patterson map at the vertices of a tetrahedron. Three cycles of least-squares refinement of the Ir atoms resulted in agreement factors $R_1 = \sum |F_o| - |KF_c| / \sum F_o = 0.35$ and $R_2 = [\sum w(|F_o| - |KF_c|)^2 / \sum wF_o^2]^{1/2} = 0.39$. At this stage, the structure analysis was straightforward and was completed by the usual Fourier techniques. Attempts were made to locate the H atoms from difference Fourier maps, but not all of them could be located unambiguously. Therefore, H atoms were excluded from calculations. Finally, only nonhydrogen atoms were included in least-squares calculations and only noncarbon atoms were refined anisotropically. Final R factors were $R_1 = 0.045$ and $R_2 = 0.052$.

In order to ensure the correct chirality, a second crystal structure model obtained by inverting the positional parameters was refined. The goodness of fit of the first model compares favorably with that of the second. Therefore, the crystal structure described below is assumed.

Table 2. Bond distances (Å) in $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$

Ir(1)—Ir(2)	2.772 (2)	C(9)—O(9)	1.09 (3)
Ir(1)—Ir(3)	2.721 (2)	C(10)—O(10)	1.15 (4)
Ir(1)—Ir(4)	2.775 (2)	C(37)—O(11)	1.43 (3)
Ir(2)—Ir(3)	2.729 (2)	C(38)—O(12)	1.46 (3)
Ir(2)—Ir(4)	2.745 (2)	C(39)—O(11)	1.43 (3)
Ir(3)—Ir(4)	2.720 (2)	C(39)—O(12)	1.58 (4)
Ir(1)—C(1)	1.75 (3)	C(11)—C(12)	1.38 (4)
Ir(1)—C(2)	2.03 (3)	C(12)—C(13)	1.43 (5)
Ir(1)—C(3)	2.02 (3)	C(13)—C(14)	1.37 (5)
Ir(1)—P(1)	2.315 (8)	C(14)—C(15)	1.41 (5)
Ir(2)—C(8)	1.77 (3)	C(15)—C(16)	1.41 (5)
Ir(2)—C(2)	2.12 (3)	C(16)—C(11)	1.38 (4)
Ir(2)—C(4)	2.03 (4)	C(17)—C(18)	1.36 (4)
Ir(2)—P(2)	2.305 (8)	C(18)—C(19)	1.38 (4)
Ir(3)—C(5)	1.87 (3)	C(19)—C(20)	1.36 (5)
Ir(3)—C(6)	1.80 (4)	C(20)—C(21)	1.37 (5)
Ir(3)—C(7)	1.89 (3)	C(21)—C(22)	1.41 (5)
Ir(4)—C(9)	1.93 (4)	C(17)—C(22)	1.39 (4)
Ir(4)—C(10)	1.84 (5)	C(23)—C(24)	1.36 (4)
Ir(4)—C(3)	2.14 (3)	C(24)—C(25)	1.41 (4)
Ir(4)—C(4)	2.08 (3)	C(25)—C(26)	1.37 (4)
P(1)—C(11)	1.83 (3)	C(26)—C(27)	1.37 (4)
P(1)—C(17)	1.89 (3)	C(27)—C(28)	1.41 (4)
P(1)—C(36)	1.83 (3)	C(23)—C(28)	1.42 (4)
P(2)—C(23)	1.83 (3)	C(29)—C(30)	1.40 (3)
P(2)—C(29)	1.79 (3)	C(30)—C(31)	1.43 (4)
P(2)—C(35)	1.87 (3)	C(31)—C(32)	1.37 (4)
C(1)—O(1)	1.16 (3)	C(32)—C(33)	1.39 (4)
C(2)—O(2)	1.25 (3)	C(33)—C(34)	1.39 (4)
C(3)—O(3)	1.19 (3)	C(29)—C(34)	1.38 (4)
C(4)—O(4)	1.16 (3)	C(35)—C(37)	1.55 (4)
C(5)—O(5)	1.17 (5)	C(36)—C(38)	1.54 (4)
C(6)—O(6)	1.15 (4)	C(37)—C(38)	1.55 (4)
C(7)—O(7)	1.09 (3)	C(39)—C(40)	1.51 (5)
C(8)—O(8)	1.14 (3)	C(39)—C(41)	1.48 (5)

Scattering factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974).

The positional and thermal parameters are listed in

Table 3. Bond angles (°) in $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$

Ir(1)—Ir(4)—Ir(2)	60.29 (5)	P(1)—C(17)—C(18)	121.4 (24)
Ir(1)—Ir(4)—Ir(3)	59.34 (5)	Ir(2)—Ir(1)—Ir(3)	59.56 (5)
Ir(1)—Ir(4)—C(3)	46.3 (9)	Ir(2)—Ir(1)—Ir(4)	59.31 (4)
Ir(1)—Ir(4)—C(4)	107.6 (8)	Ir(2)—Ir(1)—P(1)	121.5 (2)
Ir(1)—Ir(4)—C(9)	135.2 (9)	Ir(2)—Ir(1)—C(1)	132.9 (9)
Ir(1)—Ir(4)—C(10)	115.3 (13)	Ir(2)—Ir(1)—C(2)	49.6 (8)
Ir(2)—Ir(4)—Ir(3)	59.91 (5)	Ir(2)—Ir(1)—C(3)	109.0 (10)
Ir(2)—Ir(4)—C(3)	106.4 (9)	Ir(3)—Ir(1)—Ir(4)	59.32 (6)
Ir(2)—Ir(4)—C(4)	47.4 (8)	Ir(3)—Ir(1)—P(1)	178.4 (2)
Ir(2)—Ir(4)—C(9)	132.8 (9)	Ir(3)—Ir(1)—C(1)	87.3 (9)
Ir(2)—Ir(4)—C(10)	114.0 (13)	Ir(3)—Ir(1)—C(2)	82.3 (7)
Ir(3)—Ir(4)—C(3)	85.3 (9)	Ir(3)—Ir(1)—C(3)	87.5 (10)
Ir(3)—Ir(4)—C(4)	81.2 (8)	Ir(4)—Ir(1)—P(1)	122.1 (2)
Ir(3)—Ir(4)—C(9)	89.2 (9)	Ir(4)—Ir(1)—C(1)	132.7 (9)
Ir(3)—Ir(4)—C(10)	173.0 (13)	Ir(4)—Ir(1)—C(2)	108.8 (8)
C(3)—Ir(4)—C(4)	153.8 (13)	Ir(4)—Ir(1)—C(3)	49.9 (10)
C(3)—Ir(4)—C(9)	105.4 (13)	P(1)—Ir(1)—C(1)	91.2 (9)
C(3)—Ir(4)—C(10)	93.6 (15)	P(1)—Ir(1)—C(2)	97.6 (8)
C(4)—Ir(4)—C(10)	97.0 (15)	P(1)—Ir(1)—C(3)	93.1 (10)
C(9)—Ir(4)—C(10)	97.7 (15)	C(1)—Ir(1)—C(2)	97.3 (12)
Ir(1)—P(1)—C(11)	121.7 (10)	C(1)—Ir(1)—C(3)	101.2 (13)
Ir(1)—P(1)—C(17)	107.5 (10)	C(2)—Ir(1)—C(3)	158.4 (12)
Ir(1)—P(1)—C(35)	120.0 (9)	Ir(1)—Ir(2)—Ir(3)	59.28 (4)
C(11)—P(1)—C(17)	99.0 (14)	Ir(1)—Ir(2)—Ir(4)	60.40 (5)
C(11)—P(1)—C(35)	102.8 (13)	Ir(1)—Ir(2)—P(2)	111.0 (2)
C(17)—P(1)—C(35)	102.3 (13)	Ir(1)—Ir(2)—C(2)	46.7 (7)
Ir(2)—P(2)—C(23)	118.0 (11)	Ir(1)—Ir(2)—C(4)	109.2 (8)
Ir(2)—P(2)—C(29)	112.7 (9)	Ir(1)—Ir(2)—C(8)	138.9 (10)
Ir(2)—P(2)—C(36)	112.7 (8)	Ir(3)—Ir(2)—P(2)	167.3 (3)
C(23)—P(2)—C(29)	103.4 (14)	Ir(3)—Ir(2)—Ir(4)	59.6 (6)
C(23)—P(2)—C(36)	103.2 (12)	Ir(3)—Ir(2)—C(2)	80.5 (7)
C(29)—P(2)—C(36)	105.5 (12)	Ir(3)—Ir(2)—C(4)	81.8 (8)
P(2)—C(36)—C(37)	109.4 (16)	Ir(3)—Ir(2)—C(8)	96.7 (10)
P(1)—C(35)—C(38)	116.0 (20)	Ir(4)—Ir(2)—P(2)	109.2 (2)
C(36)—C(37)—O(11)	108.9 (23)	Ir(4)—Ir(2)—C(2)	107.0 (7)
C(36)—C(37)—C(38)	111.2 (21)	Ir(4)—Ir(2)—C(4)	48.9 (9)
C(38)—C(37)—O(11)	101.4 (21)	Ir(4)—Ir(2)—C(8)	138.9 (10)
C(35)—C(38)—O(12)	105.4 (22)	P(2)—Ir(2)—C(2)	98.6 (7)
C(35)—C(38)—C(37)	116.3 (22)	C(2)—Ir(2)—C(4)	155.5 (11)
C(35)—C(38)—O(12)	104.2 (22)	C(2)—Ir(2)—C(8)	100.5 (2)
O(11)—C(39)—O(12)	99.3 (25)	Ir(1)—Ir(3)—Ir(2)	61.16 (5)
O(11)—C(39)—C(40)	112.2 (30)	Ir(1)—Ir(3)—Ir(4)	61.34 (5)
O(11)—C(39)—C(41)	108.4 (34)	Ir(1)—Ir(3)—C(5)	87.8 (10)
O(12)—C(39)—C(40)	108.5 (31)	Ir(1)—Ir(3)—C(6)	155.7 (11)
O(12)—C(39)—C(41)	101.6 (31)	Ir(1)—Ir(3)—C(7)	93.8 (9)
C(40)—C(39)—C(41)	123.5 (36)	Ir(2)—Ir(3)—Ir(4)	60.50 (5)
P(1)—C(11)—C(12)	119.5 (26)	Ir(2)—Ir(3)—C(5)	146.6 (10)
P(1)—C(11)—C(16)	119.7 (24)	Ir(2)—Ir(3)—C(6)	97.5 (11)
C(12)—C(11)—C(16)	120.7 (30)	Ir(2)—Ir(3)—C(7)	94.0 (9)
C(11)—C(12)—C(13)	119.1 (33)	Ir(4)—Ir(3)—C(5)	96.1 (9)
C(12)—C(13)—C(14)	121.8 (37)	Ir(4)—Ir(3)—C(6)	99.0 (11)
C(13)—C(14)—C(15)	117.7 (42)	Ir(4)—Ir(3)—C(7)	150.2 (9)
C(14)—C(15)—C(16)	121.4 (40)	C(5)—Ir(3)—C(6)	109.4 (14)
C(15)—C(16)—C(11)	119.2 (31)	C(5)—Ir(3)—C(7)	100.4 (13)
		C(6)—Ir(3)—C(7)	99.5 (14)
P(1)—C(17)—C(22)	118.9 (24)	C(26)—C(27)—C(28)	119.5 (34)
C(18)—C(17)—C(22)	119.6 (28)	C(27)—C(28)—C(23)	119.9 (32)
C(17)—C(18)—C(19)	120.3 (30)	P(2)—C(29)—C(30)	120.2 (21)
C(18)—C(19)—C(20)	120.5 (32)	P(2)—C(29)—C(34)	119.4 (21)
C(19)—C(20)—C(21)	121.2 (38)	C(30)—C(29)—C(34)	120.3 (26)
C(20)—C(21)—C(22)	118.2 (37)	C(29)—C(30)—C(31)	119.2 (26)
C(21)—C(22)—C(17)	120.1 (32)	C(30)—C(31)—C(32)	119.3 (31)
P(2)—C(23)—C(24)	121.0 (24)	C(31)—C(32)—C(33)	120.9 (33)
P(2)—C(23)—C(28)	118.7 (24)	C(32)—C(33)—C(34)	120.1 (33)
C(24)—C(23)—C(28)	120.3 (29)	C(33)—C(34)—C(29)	120.1 (30)
C(23)—C(24)—C(25)	119.6 (30)	C(37)—O(11)—C(39)	111.7 (20)
C(24)—C(25)—C(26)	120.5 (32)	C(38)—O(12)—C(39)	108.6 (23)
C(25)—C(26)—C(27)	121.0 (33)		
Ir(1)—C(1)—O(1)	175.5 (27)	Ir(3)—C(5)—O(5)	166.8 (31)
Ir(1)—C(2)—O(2)	142.3 (22)	Ir(3)—O(6)—O(6)	168.9 (36)
Ir(2)—C(2)—O(2)	133.9 (21)	Ir(3)—C(7)—O(7)	169.9 (31)
Ir(1)—C(3)—O(3)	141.6 (27)	Ir(2)—C(8)—O(8)	174.5 (30)
Ir(4)—C(3)—O(3)	134.4 (25)	Ir(4)—C(9)—O(9)	175.6 (33)
Ir(2)—C(4)—O(4)	142.7 (25)	Ir(4)—C(10)—O(10)	172.9 (37)
Ir(4)—C(4)—O(4)	133.5 (24)		

Table 1.* Bond distances and angles are given in Tables 2 and 3, respectively.

Results and discussion

The structure of $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$ is displayed in Fig. 1 and an unobstructed view of the central atoms around the Ir tetrahedron is shown in Fig. 2. The packing diagram is shown in Fig. 3. Three of the ten carbonyls edge-bridge Ir atoms and lie in a basal plane, as is common for many tetranuclear clusters. There is a slight asymmetry in the bridging species (Table 2).

The Ir—C distances in the terminal carbonyls qualitatively reflect π -backbonding effects. The mean Ir—C distances for the terminal carbonyls on Ir(1) and Ir(2) (each also having two bridging carbonyls and a P atom bonded to it), for the two on Ir(4) (it also has two bridging carbonyls bonded to it), and for the three on Ir(3) are 1.76 (3), 1.88 (3) and 1.85 (3) Å, respectively. These values reflect the π -acceptor capability of the ligands, with bridging CO > terminal CO > diarylalkylphosphine.

The two P atoms are bonded to different Ir atoms in the basal plane. Both P atoms are in axial positions, in contrast to those in $\text{Ir}_4(\text{CO})_{10}(\text{PPh}_3)_2$, in which one P atom is in an axial position and the other in a radial position (Albano, Bellon & Scatturin 1976). The angles formed with the apical Ir, the two basal Ir, and the two P atoms are nearly linear: Ir(3)—Ir(1)—P(1) =

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36777 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

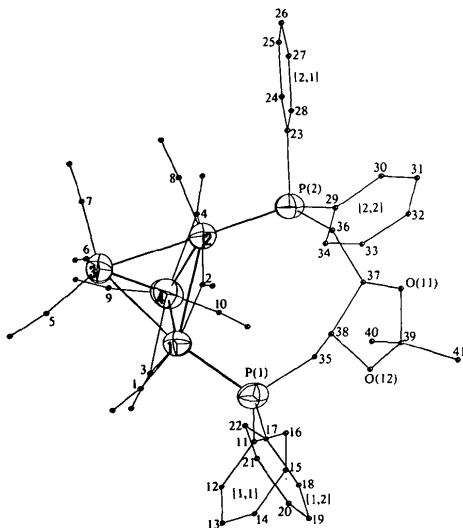


Fig. 1. Structure of $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$ (complete representation).

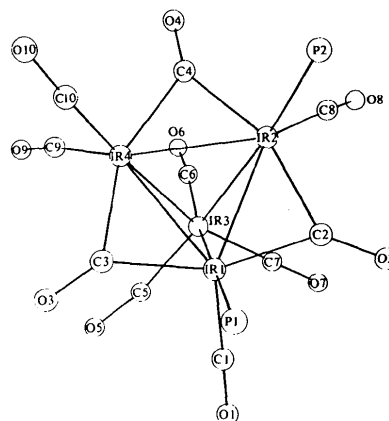


Fig. 2. Partial representation of the structure of $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$, showing the cluster framework.

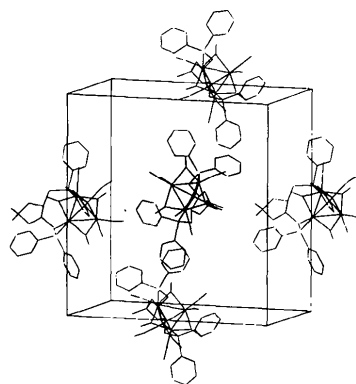


Fig. 3. Packing diagram of $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$.

178.4 (2) and Ir(3)—Ir(2)—P(2) = 167.3 (3)°. Apparently, the bonding geometry is constrained by diop's conformation and the bonding orbitals of the Ir atoms.

The Ir—Ir bond distances show some differences. A clear distinction is observed between the distances of two Ir atoms that are edge-bridged by carbonyls and those that are not. The nonbridged distances of 2.721 (2), 2.729 (2) and 2.720 (2) Å are shorter than the bridged distances of 2.772 (2), 2.775 (2) and 2.745 (2) Å. This is remarkable, since, within a particular compound, carbonyl-bridged metal—metal distances have always been found to be shorter than noncarbonyl-bridged metal—metal distances (Colton & McCormick, 1980). Evidently, diop, which cobridges two Ir atoms with a carbonyl, imposes geometric constraints on the Ir atoms in the basal plane.

The structure determination of $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$ provides the first configurational data characterizing a diop that acts as a bridging rather than a chelating ligand. Such behavior was observed with bis(diphenylphosphino)methane in $\text{Rh}_4(\text{CO})_8(\text{Ph}_2\text{P}-\text{CH}_2-\text{PPh}_2)_2$ (Cotton & Troup, 1974). The formation of the bridging

mode in the Ir cluster further illustrates the ability of a particular diphosphine to adopt either bridging or chelating configurations.

The absolute configuration of the cluster is *RR*. The effect of the asymmetric centers C(38) and C(37) is ultimately transmitted by the alignment of the phenyl groups on the P atoms. The two P atoms are not equivalent and are in the *cis* position with respect to the five-membered ring $\text{—C(37),C(38),O(12),C(39),O(11)—}$.

The angles formed between the two phenyl rings bonded to the same P atom are listed in Table 4 for $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$ and for some other complexes in which diop is a chelating ligand. If an average plane passing through the eight atoms Ir(1), Ir(2), P(2), C(36), C(37), C(38), C(35), and P(1) is calculated, the angles between this plane and the phenyl rings are 72, 67, 85, and 78° for rings (1,1), (1,2), (2,1) and (2,2), respectively. Comparable angles between average planes in seven-membered rings and the phenyl groups in the Ir and Ni complexes are 86, 36, 53, and 50° and 52, 11, 36, and 41°, respectively (Brunie *et al.*, 1976).

Unfortunately, direct correlations cannot be made between diop's conformations and optical yields in catalysis, because it is not known whether the original conformations are maintained in the intermediates in the catalytic cycles. Furthermore, there is NMR evidence that diop in $\text{Pt}(\text{diop})_2$ undergoes conformational changes in solution (Brown & Chaloner, 1978).

The polymer-supported Ir clusters $\text{P}^{\oplus}\text{—diop—}\{\text{Ir}_4(\text{CO})_{10}\}_2$ (Lieto *et al.*, 1979), $\text{P}^{\oplus}\text{—PPh}_2\}_x\text{Ir}_4(\text{CO})_{12-x}$ ($x = 1, 2, \text{ or } 3$) (Lieto, Rafalko & Gates, 1980) (where P^{\oplus} represents cross-linked polystyrene) have been shown to be effective catalysts for ethylene hydrogenation. Both $\text{P}^{\oplus}\text{—diop}\{\text{Ir}_4(\text{CO})_{10}\}_2$ and $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$ were

tested for asymmetric hydrogenation leading to products such as alanine and phenylalanine. Unfortunately, the clusters decomposed after 20 min of contact with the amino acids. Further studies of the stabilization and asymmetric catalytic properties of $\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$ are in progress.

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Table 4. Dihedral angles (°) of the phenyl groups

Compound	Angles between the planes of adjacent phenyl rings	
	$\varphi(1,1) - \varphi(1,2)$	$\varphi(2,1) - \varphi(2,2)$
$\text{Ir}_4(\text{CO})_{10}\{(+)\text{-diop}\}$	65	66
$\text{PdCl}\{(-)\text{-diop}\}$	76	76
(Gramlich & Consiglio, 1979)		
$\text{PtCl}_2\{(-)\text{-diop}\}$	77	74
(Gramlich & Consiglio, 1979)		
$\text{NiCl}_2\{(-)\text{-diop}\}$	85	83
(Gramlich & Consiglio, 1979)		
$\text{Ir}(1,4\text{-cyclooctadiene})\{(+)\text{-diop}\}\text{Cl}$	47	87
(Brunie <i>et al.</i> , 1976)		
$\text{Fe}(\text{cyclopentadienyl})\{(-)\text{-diop}\}$	67	79
(Balavoine, Brunie & Kagan, 1980)		