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Iridium Carbonyl Clusters. 3.[1,2] Crystal Structure and Molecular Geometry of $Ir_4(CO)_{10}$(diars), a Derivative of $Ir_4(CO)_{12}$ with One Bridging and Two "Semibridging" Carbonyl Ligands

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[1,2-Bis(dimethylarsino)benzene]decacarbonyltetrairidium(6*Ir–Ir*), $Ir_4(CO)_{10}$(diars), has been characterized via a single-crystal X-ray diffraction study. This complex crystallizes in the centrosymmetric orthorhombic space group *Pnma* (D_{2h}^{16}, No. 62) with $a = 19.038$ (7) Å, $b = 10.584$ (3) Å, $c = 14.186$ (6) Å, $V = 2858$ (2) Å^3, $Z = 4$, and ρ(calcd) = 3.10 g cm^{-3} for mol wt 1335.1. Diffraction data were collected via a coupled θ(crystal)–2θ(counter) scan by using a Syntex $P2_1$ automated four-circle diffractometer. The structure was solved via a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement. The resulting discrepancy indices are $R_F = 7.3\%$ and $R_{wF} = 5.5\%$ for those 1746 reflections with $|F_o| > \sigma(|F_o|)$ and $4.0° < 2\theta < 45.0°$. The four iridium atoms define a tetrahedral cluster, and the molecule possesses crystallographic C_s (*m*) symmetry. The mirror plane contains (inter alia) the $C_6H_4As_2$ moiety along with atoms Ir(2) and Ir(3). The diars ligand chelates to Ir(3). The molecule contains one symmetrically bridging carbonyl group [across Ir(1)–Ir(1′)] and two symmetry-related "semibridging" carbonyl groups [across Ir(1)–Ir(3) and Ir(1′)–Ir(3)]; metal–carbonyl distances in the latter are Ir(3)–C(31B) = 2.012 (25) Å and Ir(1)···C(31B) = 2.257 (22) Å, with Ir(3)–C(31B)–O(31B) = 145.5 (20)°.

Introduction

We have recently reported the results of X-ray diffraction studies on $Ir_4(CO)_{12}$[2,3] and $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$,[1] each of which contain carbonyl ligands in terminal positions only. We now provide details of the solid-state molecular structure of $Ir_4(CO)_{10}$(diars), which we show to possess one symmetrically bridging and two asymmetrically bridging carbonyl groups. A preliminary report of this structure has appeared previously in conjunction with a discussion of the variable-temperature ^{13}C spectra of this molecule.[4]

Experimental Section

A crystalline sample of $Ir_4(CO)_{10}$(diars) was supplied by Professor J. R. Shapley of the University of Illinois. The analysis was begun by using crystal I, a crystalline parallelepiped of dimensions 0.12 × 0.16 × 0.24 mm. This crystal was mounted on a glass fiber which was fixed into an aluminum pin and mounted in a eucentric goniometer. Preliminary precession and cone-axis photographs indicated that the crystal belonged to the orthorhombic system (D_{2h} diffraction symmetry) and yielded approximate cell dimensions. The crystal was transferred to a Syntex $P2_1$ automated diffractometer. The crystal was centered optically, and an approximate orientation matrix was determined by the automatic centering of 24 reflections, the coordinates of which had been measured from an in situ random-orientation rotation photograph taken with $2\theta = \omega = \chi = 0°$.[5] Data with $20° < 2\theta < 30°$ were collected at the maximum scan rate (29.3°/min) so that strong reflections could be selected for more accurate determination of the cell parameters. An inspection of these data revealed the systematic absences $0kl$ for $k + l = 2n + 1$ and $hk0$ for $h = 2n + 1$ which are consistent with the centrosymmetric space group *Pnma* (D_{2h}^{16}, No. 62) or the noncentrosymmetric space group $Pn2_1a$ (a nonstandard setting of space group $Pna2_1$-C_{2v}^{9}, No. 33).

Accurate unit cell dimensions, based on the automatic centering of 24 reflections from crystal I with $2\theta = 21–28°$, were $a = 19.032$ (6), $b = 10.579$ (3), and $c = 14.178$ (4) Å, with $V = 2855$ (2) Å^3.

A smaller crystal, crystal II (an irregular block, which approximated to a parallelepiped of dimensions 0.10 × 0.07 × 0.20 mm), was used for data collection. This crystal was mounted and aligned as described above for crystal I.

Table I. Experimental Data from X-ray Diffraction Study on $Ir_4(CO)_{10}$(diars)

A. Crystal Parameters[a] at 24 °C

cryst system: orthorhombic
space group: *Pnma* [D_{2h}^{16}, No. 62]
$a = 19.038$ (7) Å
$b = 10.584$ (3) Å
$c = 14.186$ (6) Å
$V = 2858$ (2) Å^3
$Z = 4$
mol wt 1335.1
ρ(calcd) = 3.10 g cm^{-3}

B. Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda} = 0.710\,730$ Å)
monochromator: pyrolytic graphite (equatorial mounting)
rflctns measd: $+h, +k, +l$
2θ range: 4.0–45.0°
scan type: coupled θ(crystal)–2θ(counter)
scan speed: 2.0°/min (in 2θ)
scan width: $[2\theta(\text{Mo K}\alpha_1) - 1.1]° \rightarrow [2\theta(\text{Mo K}\alpha_2) + 1.1]°$
bkgd measurement: stationary crystal–stationary counter at beginning and end of 2θ scan, each for half the time taken for the 2θ scan
std rflctns: 3 measured every 97 reflections; no significant deviations from the mean were observed
total data collected: 2011 independent reflections
abs coeff: $\mu = 208.5$ cm^{-1}
abs cor (empirical, based on a series of ψ scans; rflctns used, their 2θ values, and max to min intensity): {503}, 13.7°, 2.39; {505}, 17.9°, 2.47; {707}, 25.2°, 2.54

[a] Based on a least-squares fit to the setting angles of the unresolved Mo Kα components of the following 24 reflections with $2\theta = 20–28°$: {10,0,1}, {107}, and {270}.

Table II. Statistics for Intensity Distribution in Diffraction Data from $Ir_4(CO)_{10}$(diars)

		theoretical	
	obsd	centric	acentric
$\langle \lvert E\rvert^2\rangle$	1.00	1.00	1.00
$\langle \lvert E\rvert\rangle$	0.800	0.798	0.886
$\langle \lvert E^2 - 1\rvert\rangle$	0.961	0.968	0.736
$\lvert E\rvert > 1.0$, %	31.18	31.73	36.79
$\lvert E\rvert > 2.0$, %	4.87	4.55	1.89
$\lvert E\rvert > 3.0$, %	0.45	0.27	0.01

Information on cell parameters and data collection appear in Table I. The intensity statistics, which strongly favor the centrosymmetric space group *Pnma*, are given in Table II.

Following correction of these data for Lorentz, polarization, and absorption effects, a three-dimensional Patterson map quickly revealed the positions of the four iridium atoms and suggested strongly that the true space group was *Pnma* with the molecule being bisected by

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(1) Part 2: Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1979**, *18*, 2451–2454.

(2) Part 1: Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528–3535.

(3) The structure of $Ir_4(CO)_{12}$ was first determined by G. R. Wilkes in the laboratories of Professor L. F. Dahl: Wilkes, G. R. Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1965.

(4) Shapley, J. R.; Stunz, G. F.; Churchill, M. R.; Hutchinson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7425–7428.

(5) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

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Table III. Final Positional Parameters (with Esd's) for $Ir_4(CO)_{10}$(diars)

atom	x	y	z	B_{iso}, Å^2
Ir(1)	0.05791 (5)	0.12274 (11)	0.14245 (6)	
Ir(2)	0.18206 (7)	0.25000 (0)	0.15107 (10)	
Ir(3)	0.09392 (7)	0.25000 (0)	0.30299 (9)	
As(1)	0.16873 (17)	0.25000 (0)	0.43645 (25)	
As(2)	−0.00085 (17)	0.25000 (0)	0.41377 (24)	
O(11B)	0.0332 (12)	0.25000 (0)	−0.0487 (18)	
O(12)	−0.0930 (9)	0.0429 (24)	0.1641 (15)	
O(13)	0.1127 (10)	−0.1150 (22)	0.0551 (18)	
O(21)	0.2152 (17)	0.25000 (0)	−0.0589 (20)	
O(22)	0.2656 (10)	0.0182 (22)	0.2109 (15)	
O(31B)	0.1080 (10)	−0.0334 (20)	0.3207 (12)	
C(11B)	0.0433 (19)	0.25000 (0)	0.0327 (25)	
C(12)	−0.0377 (14)	0.075 (3)	0.1553 (17)	
C(13)	0.0906 (15)	−0.025 (3)	0.0916 (24)	
C(21)	0.1988 (18)	0.25000 (0)	0.019 (3)	
C(22)	0.2332 (12)	0.104 (3)	0.1884 (21)	
C(31B)	0.0941 (12)	0.0612 (24)	0.2868 (15)	
Me(1)	0.2323 (14)	0.100 (3)	0.4541 (19)	
Me(2)	−0.0675 (13)	0.106 (3)	0.4167 (17)	
C(1)	0.1124 (19)	0.25000 (0)	0.5497 (22)	
C(2)	0.1409 (22)	0.25000 (0)	0.645 (3)	
C(3)	0.0988 (25)	0.25000 (0)	0.7210 (23)	
C(4)	0.025 (3)	0.25000 (0)	0.707 (3)	
C(5)	−0.0037 (25)	0.25000 (0)	0.6174 (23)	
C(6)	0.0379 (19)	0.25000 (0)	0.5396 (25)	
HMe(1A)	0.2624	0.0923	0.4010	6.9
HMe(1B)	0.2597	0.1114	0.5093	6.9
HMe(1C)	0.2047	0.0256	0.4601	6.9
HMe(2A)	−0.0896	0.0982	0.3569	6.1
HMe(2B)	−0.0427	0.0305	0.4307	6.1
HMe(2C)	−0.1020	0.1207	0.4637	6.1
HC(2)	0.1903	0.2500	0.6533	5.2
HC(3)	0.1181	0.2500	0.7827	5.6
HC(4)	−0.0055	0.2500	0.7603	6.0
HC(5)	−0.0532	0.2500	0.6100	5.0

the crystallographic mirror plane at $y = {}^1/_4$. A difference-Fourier synthesis, phased by the iridium atoms, yielded the location of all remaining nonhydrogen atoms. Refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms, with hydrogen atoms included in their idealized positions with $d(\text{C–H}) = 0.95$ Å,[6] resulted in convergence with $R_F = 7.3\%$ and $R_{wF} = 5.5\%$ for those 1746 reflections with $|F_o| > \sigma\{|F_o|\}$ and $4.0° < 2\theta < 45.0°$. Discrepancy indices for those data with $|F_o| > 3\sigma\{|F_o|\}$ were $R_F = 6.1\%$ and $R_{wF} = 5.3\%$.

A final difference-Fourier synthesis showed no unexpected features. The average value of the function $\sum w(|F_o| - |F_c|)^2$ showed no major variations as a function of $|F_o|$, $(\sin\theta)/\lambda$, identity or parity of crystallographic indices, or sequence number. The weighting scheme is thus satisfactory and the structure complete.

Final positional and thermal parameters are collected in Tables III and IV.

All calculations were performed by using a locally modified version of the Syntex XTL crystallographic program package on our in-house NOVA 1200 computer (24K memory) with associated Diablo disk unit (1.25 million word capacity). For structure factor calculations we used analytical scattering factors[7a] for neutral Ir, As, O, C, and H; both the $\Delta f'$ and $\Delta f''$ contributions were included for all nonhydrogen atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, and the "ignorance factor" used was $p = 0.02$.

Discussion

The crystal consists of discrete molecular units of $Ir_4(CO)_{10}$(diars) separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. The overall geometry of the molecule and the scheme used for labeling atoms is shown in Figures 1 and 2. The molecule is bisected by a crystallographic mirror plane which contains Ir(2), Ir(3), As(1), As(2), C(1)–C(6), H(2)–H(6), C(11B)–O(11B), and C(21)–O(21). Atoms of the basic asymmetric unit (i.e., those with $y \leq {}^1/_4$—cf. Table III) are labeled normally; those related to the basic asymmetric unit by reflection across $y = {}^1/_4$ are labeled with a prime (x', y', z' = x, ${}^1/_2 - y$, z).

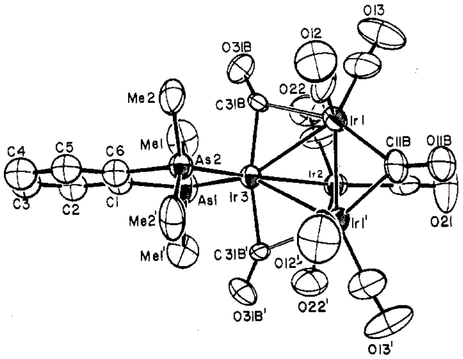

Figure 1. Geometry of the $Ir_4(CO)_{10}$(diars) molecule (ORTEP-II diagram; 30% ellipsoids; hydrogen atoms omitted). The crystallographic mirror plane is close to the direction of view and contains atoms C(1)–C(6), As(1) and As(2), and Ir(2) and Ir(3) and ligands C(11B)–O(11B) and C(21)–O(21).

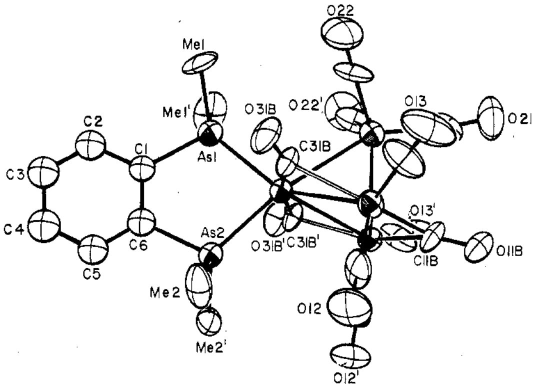

Figure 2. $Ir_4(CO)_{10}$(diars) molecule, showing the bending of the Ir(3)–C(31B)–O(31B) and Ir(3)–C(31B')–O(31B') systems. The molecule is projected onto a plane about 10° from the true crystallographic mirror plane.

Stereoscopic views of the molecule are shown in Figures 3 and 4. Interatomic distances and their estimated standard deviations (esd's) are collected in Table V, while interatomic angles are listed in Table VI.

The four iridium atoms define a tetrahedron which has precise C_s symmetry but has statistically significant deviations from full T_d symmetry. Each iridium atom is linked to three other iridium atoms, but there are three distinct ligand arrangements about the metal atoms. Atom Ir(2) is linked to three terminal carbonyl ligands and thus resembles an iridium atom in the parent $Ir_4(CO)_{12}$ molecule.[2,3] Atom Ir(3) is chelated by the diars ligand via linkages to As(1) and As(2) and is additionally linked to the carbonyl ligands C(31B)–O(31B) and C(31B')–O(31B'). [It should be noted that Ir(3) would formally possess a 19-electron outer electronic configuration if these carbonyl ligands were strictly terminal. However, as outlined below, these ligands behave as "asymmetrically bridging" or "semibridging" ligands[8] and act so as to transfer electronic charge from the formally electron-rich atom Ir(3) to the formally electron-poor atoms Ir(1) and Ir(1').] Atoms Ir(1) and Ir(1') are in electronically

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(6) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213–1214.

(7) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1973; Vol. IV: (a) pp 99–101; (b) pp 149–150.

(8) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 1233–1234.

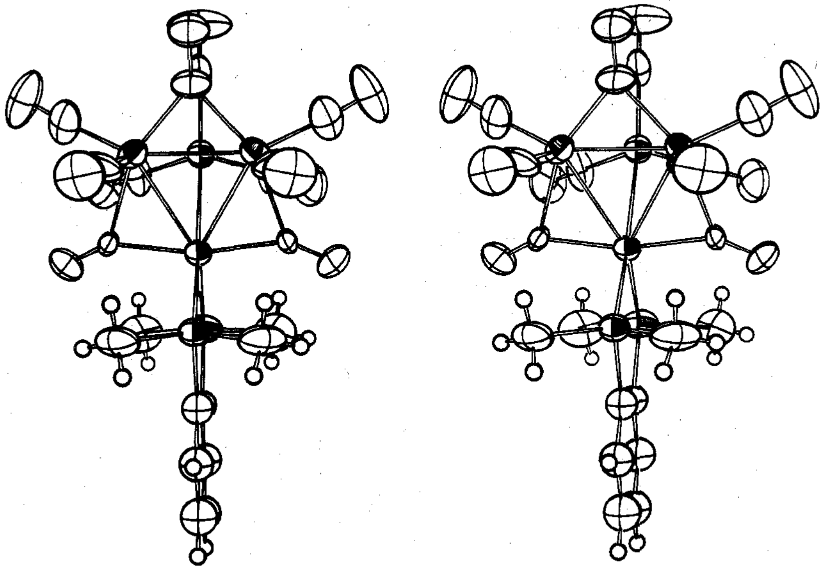


Figure 3. Stereoscopic view of the $Ir_4(CO)_{10}$(diars) molecule. The crystallographic mirror plane lies close to vertical in this view. Note the "dishing" of bridging carbonyl ligands within the $Ir_3(\mu\text{-}CO)_3(CO)_2$ system.

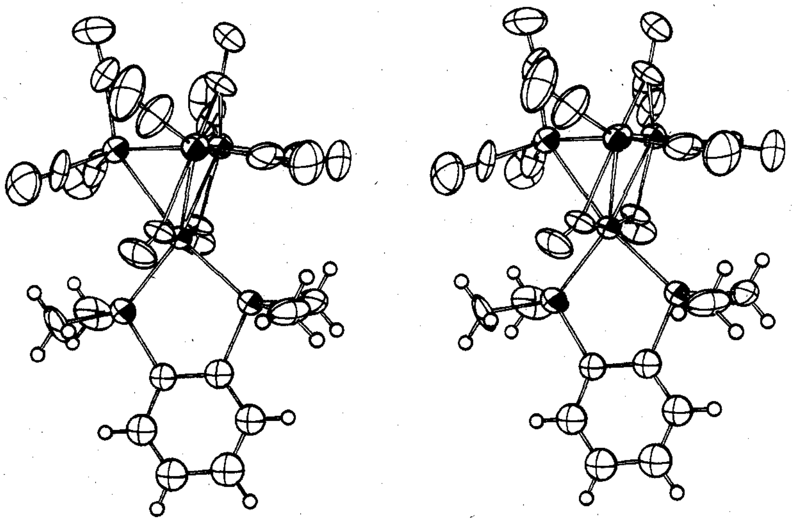
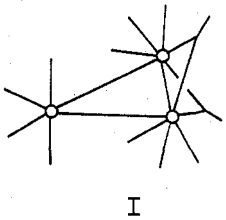


Figure 4. A stereoscopic view of the $Ir_4(CO)_{10}$(diars) molecule with hydrogen atoms included in idealized positions.

equivalent (mirror-related) sites; each is linked to two terminal carbonyl ligands and to one symmetrically bridging carbonyl group (C(11B)–O(11B)); in addition there are weak interactions of the "semibridging" type[8] of Ir(1) with ligand C(31B)–O(31B) and of Ir(1′) with the ligand C(31B′)–O(31B′).

Parameters within the symetrically bridging carbonyl group are Ir(1)–C(11B) = Ir(1′)–C(11B) = 2.077 (27) Å, ∠Ir(1)–C(11B)–O(11B) = ∠Ir(1′)–C(11B)–O(11B) = 139.6 (23)°, ∠Ir(1)–C(11B)–Ir(1′) = 80.9 (10)°, and C(11B)–O(11B) = 1.17 (4) Å. For comparison, parameters involving the asymmetrically bridging carbonyl group C(31B)–O(31B) are as follows: Ir(3)–C(31B) = 2.012 (25) Å, Ir(1)···C(31B) = 2.257 (25) Å, ∠Ir(3)–C(31B)–O(31B) = 145.5 (20)°, ∠Ir(1)···C(31B)–O(31B) = 134.9 (19)°, ∠Ir(3)–C(31B)···Ir(1) = 79.4 (8)°, and C(31B)–O(31B) = 1.14 (3) Å. The geometry of each of these systems is clearly indicated in all of the figures.

There are slight differences in iridium–iridium distances within the cluster. The symmetrically carbonyl-bridged Ir(1)–Ir(1′) bond has a length of 2.694 (2) Å and is significantly shorter than each of the other metal–metal linkages in the molecule. Thus, the nonbridged iridium–iridium bond lengths (Ir(2)–Ir(1) = 2.723 (2) Å, Ir(2)–Ir(1′) = 2.723 (2) Å, and Ir(2)–Ir(3) = 2.731 (2) Å) average 2.726 Å, while the "semibridged" iridium–iridium distances are equivalent, with Ir(3)–Ir(1) = Ir(3)–Ir(1′) = 2.733 (1) Å. (We note, parenthetically, that we expect "semibridging" carbonyl groups to have little or no effect on the length of the bridged bond because of the weakness of the M···CO component of this system.) For most polynuclear metal carbonyl cluster derivatives, the carbonyl-bridged metal–metal bonds are shorter than the nonbridged "pure-σ" metal–metal bonds. For example, in $Fe_3(CO)_{12}$ (I), the iron–iron distance within the



I

$Fe(\mu\text{-}CO)_2Fe$ system is 2.558 (1) Å in length, whereas the nonbridged iron–iron distances are 2.677 (2) and 2.683 (1) Å.[9] This pattern appears to be general for derivatives of the first-row transition metals, where bridging carbonyl ligands occur with great frequency; it is, however, less well established

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[9] Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155–4159.

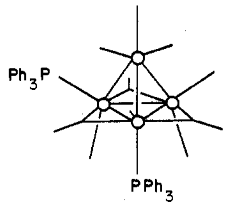
Table IV. Anisotropic Thermal Parameters (in Å^2) for $Ir_4(CO)_{10}(diars)$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ir(1)	3.17 (4)	3.28 (5)	3.01 (4)	−0.39 (4)	0.03 (4)	−0.65 (5)
Ir(2)	2.67 (6)	3.26 (8)	3.13 (6)	0.0000 (0)	0.32 (6)	0.0000 (0)
Ir(3)	2.54 (6)	2.66 (7)	2.26 (6)	0.0000 (0)	−0.17 (5)	0.0000 (0)
As(1)	2.90 (15)	5.6 (3)	2.98 (16)	0.0000 (0)	−0.35 (14)	0.0000 (0)
As(2)	2.80 (14)	3.28 (20)	2.60 (15)	0.0000 (0)	−0.19 (13)	0.0000 (0)
O(11B)	4.3 (12)	6.2 (18)	3.8 (13)	0.0000 (0)	−1.4 (11)	0.0000 (0)
O(12)	3.8 (8)	9.3 (17)	8.2 (13)	−2.7 (11)	0.6 (10)	−0.2 (13)
O(13)	5.3 (10)	5.4 (14)	12.7 (18)	0.2 (10)	1.8 (11)	−4.5 (14)
O(21)	8.0 (19)	17.5 (40)	3.5 (13)	0.0000 (0)	0.8 (15)	0.0000 (0)
O(22)	7.0 (12)	5.2 (13)	8.2 (13)	2.5 (11)	0.7 (11)	0.3 (12)
O(31B)	6.7 (10)	4.1 (11)	3.8 (9)	0.9 (10)	−1.2 (8)	1.6 (9)
C(11B)	4.5 (19)	5.8 (26)	2.7 (17)	0.0000 (0)	−1.9 (16)	0.0000 (0)
C(12)	4.9 (13)	7.2 (21)	3.1 (12)	−2.4 (15)	0.8 (11)	1.3 (14)
C(13)	5.0 (15)	4.3 (18)	7.8 (19)	−1.4 (14)	3.1 (15)	−0.9 (17)
C(21)	3.8 (17)	2.2 (19)	5.6 (22)	0.0000 (0)	2.0 (18)	0.0000 (0)
C(22)	2.5 (11)	2.7 (14)	7.7 (17)	1.2 (11)	1.5 (12)	0.5 (14)
C(31B)	4.4 (11)	1.5 (12)	2.0 (10)	0.3 (11)	−1.0 (10)	−0.3 (10)
Me(1)	5.8 (14)	8.0 (24)	5.6 (15)	4.8 (17)	−2.2 (13)	0.4 (17)
Me(2)	5.9 (14)	7.7 (21)	3.1 (11)	−4.1 (16)	0.7 (11)	−0.3 (15)
C(1)	6.1 (21)	1.4 (16)	2.1 (15)	0.0000 (0)	3.6 (15)	0.0000 (0)
C(2)	7.3 (24)	1.3 (17)	5.8 (23)	0.0000 (0)	−4.0 (23)	0.0000 (0)
C(3)	8.5 (28)	8.3 (33)	1.1 (15)	0.0000 (0)	1.7 (19)	0.0000 (0)
C(4)	8.6 (27)	4.2 (24)	3.1 (19)	0.0000 (0)	0.5 (21)	0.0000 (0)
C(5)	11.3 (31)	1.6 (18)	1.5 (15)	0.0000 (0)	−1.4 (18)	0.0000 (0)
C(6)	4.8 (19)	2.0 (18)	3.2 (18)	0.0000 (0)	0.4 (15)	0.0000 (0)

[a] The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$.

for second- and third-row transition-metal derivatives.

The effect of bridging carbonyl ligands on iridium–iridium distances in tetrahedral clusters derived from $Ir_4(CO)_{12}$ has not been analyzed in detail. Crystallographic studies on $Ir_4(CO)_{12}$[2] and $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$,[1] each of which possesses only strictly terminal ligands, revealed average Ir–Ir bond lengths of 2.693 and 2.685 Å, respectively. Distances within complexes containing carbonyl-bridged iridium–iridium bonds do not break down into any clear pattern. Thus, structural studies[10] on the neutral $Ir_4(CO)_{12}$ derivatives $Ir_4(CO)_{10}(PPh_3)_2$ (II) and $Ir_4(CO)_9(PPh_3)_3$ (III), each of which possesses three bridging carbonyl ligands around one triangular face of the tetrahedral cluster, yielded on average Ir–Ir distance of 2.73 Å and failed to indicate any "relevant differences...in bond distances between iridium atoms having bridged- or linearly-bonded carbonyl groups". Since these studies were reported some time ago (in 1967) and are not of the greatest accuracy (R_F = 11% with 700 reflections for the study of $Ir_4(CO)_{10}(PPh_3)_2$, and R_F = 13.4% with 720 reflections for the study of $Ir_4(CO)_9(PPh_3)_3$; data for each were collected photographically), these complexes should probably be reexamined. The reported average Ir–Ir distance of 2.73 Å seems long but could result from interligand repulsions.



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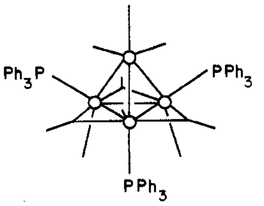

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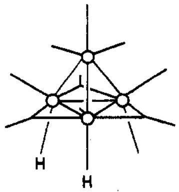
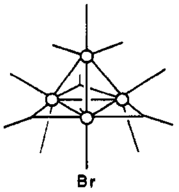
Table V. Interatomic Distances (in Å) for $Ir_4(CO)_{10}(diars)$

(A) Iridium–Iridium Distances			
Ir(1)–Ir(1′)	2.694 (2)	Ir(2)–Ir(1′)	2.723 (1)
Ir(1)–Ir(2)	2.723 (1)	Ir(2)–Ir(3)	2.731 (2)
Ir(1)–Ir(3)	2.733 (2)	Ir(3)–Ir(1′)	2.733 (2)
(B) Iridium–Arsenic Distances			
Ir(3)–As(1)	2.369 (4)	Ir(3)–As(2)	2.393 (4)
(C) Iridium–(Terminal Carbonyl) Distances			
Ir(1)–C(12)	1.897 (27)	C(12)–O(12)	1.115 (33)
Ir(1)–C(13)	1.830 (34)	C(13)–O(13)	1.164 (41)
Ir(2)–C(21)	1.903 (42)	C(21)–O(21)	1.147 (51)
Ir(2)–C(22)	1.904 (27)	C(22)–O(22)	1.141 (35)
(D) Iridium–(Bridging Carbonyl) Distances			
Ir(1)–C(11B)	2.077 (27)	Ir(3)–C(31B)	2.012 (25)
Ir(1′)–C(11B)	2.077 (27)	Ir(1)· · ·C(31B)	2.257 (22)
C(11B)–O(11B)	1.171 (44)	C(31B)–O(31B)	1.141 (32)
(E) Distances within diars Ligand			
C(1)–C(2)	1.45 (5)	C(4)–C(5)	1.38 (5)
C(2)–C(3)	1.35 (6)	C(5)–C(6)	1.36 (5)
C(3)–C(4)	1.42 (6)	C(6)–C(1)	1.43 (5)
As(1)–C(1)	1.93 (3)	As(2)–C(6)	1.93 (4)
As(1)–Me(1)	2.01 (3)	As(2)–Me(2)	1.98 (3)
As(1)–Me(1′)	2.01 (3)	As(2)–Me(2′)	1.98 (3)

Two structural studies of *anionic* derivatives have recently been reported. The species $[(PPh_3)_2N^+]_2[H_2Ir_4(CO)_{10}{}^{2-}]$,[11] has a tetranuclear anion of structure IV; here the nonbridged Ir–Ir distances range from 2.763 (2) to 2.802 (2) Å, whereas the carbonyl-bridged Ir–Ir distances are shorter, ranging from 2.703 (2) to 2.716 (2) Å. In $[PPh_4][Ir_4(CO)_{11}Br]$[12] the tetranuclear anion has the structure V; here the nonbridged Ir–Ir distances are 2.676 (2)–2.707 (2) Å, and the carbonyl-bridged Ir–Ir distances are *longer*, with a range of 2.695 (2)–2.745 (2) Å. In this latter case, however, the terminal bromide ligand



IV



V

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Table VI. Interatomic Angles (in Deg) for $Ir_4(CO)_{10}$(diars)

		(A) Angles within Iridium Tetrahedron			
Ir(1')-Ir(1)-Ir(3)	60.48 (4)	Ir(2)-Ir(3)-Ir(1)	59.78 (4)	Ir(1')-Ir(2)-Ir(1)	59.29 (4)
Ir(2)-Ir(1)-Ir(3)	60.07 (4)	Ir(1')-Ir(1)-Ir(2)	60.36 (4)	Ir(1')-Ir(3)-Ir(1)	59.05 (4)
Ir(1)-Ir(2)-Ir(3)	60.15 (4)				
		(B) Iridium-Iridium-Carbonyl Angles			
Ir(1')-Ir(1)-C(11B)	49.6 (8)	Ir(3)-Ir(1)-C(11B)	109.8 (8)	Ir(1')-Ir(2)-C(22)	149.1 (8)
Ir(1')-Ir(1)-C(12)	105.4 (9)	Ir(3)-Ir(1)-C(12)	106.9 (9)	Ir(3)-Ir(2)-C(21)	151.7 (9)
Ir(1')-Ir(1)-C(13)	148.6 (10)	Ir(3)-Ir(1)-C(13)	131.6 (10)	Ir(3)-Ir(2)-C(22)	95.4 (8)
Ir(2)-Ir(1)-C(11B)	80.2 (8)	Ir(1)-Ir(2)-C(21)	95.8 (9)	Ir(1)-Ir(3)-C(31B)	54.3 (7)
Ir(2)-Ir(1)-C(12)	163.7 (9)	Ir(1)-Ir(2)-C(22)	93.1 (8)	Ir(1')-Ir(3)-C(31B)	113.3 (7)
Ir(2)-Ir(1)-C(13)	98.3 (10)	Ir(1')-Ir(2)-C(21)	95.8 (9)	Ir(2)-Ir(3)-C(31B)	84.8 (7)
		(C) Angles in Bridging Carbonyl Systems			
Ir(1)-C(11B)-Ir(1')	80.9 (10)	Ir(1')-C(11B)-O(11B)	139.6 (23)	Ir(3)-C(31B)-O(31B)	145.5 (20)
Ir(1)-C(11B)-O(11B)	139.6 (23)	Ir(3)-C(31B)· · ·Ir(1)	79.4 (8)	Ir(1)· · ·C(31B)-O(31B)	134.9 (19)
		(D) Terminal Ir-C-O Angles			
Ir(1)-C(12)-O(12)	177.4 (26)	Ir(2)-C(21)-O(21)	173.8 (28)	Ir(2)-C(22)-O(22)	177.9 (24)
Ir(1)-C(13)-O(13)	176.4 (28)				
		(E) (OC)-Ir-(CO) Angles			
C(11B)-Ir(1)-C(12)	96.7 (12)	C(12)-Ir(1)-C(13)	98.0 (13)	C(22)-Ir(2)-C(22')	108.9 (12)
C(11B)-Ir(1)-C(13)	107.7 (13)	C(21)-Ir(2)-C(22)	100.9 (13)	C(31B)-Ir(3)-C(31B')	166.9 (10)
		(F) Angles within diars Ligand			
C(6)-C(1)-C(2)	117.6 (26)	Ir(3)-As(1)-Me(1)	117.5 (9)	Me(1)-As(1)-Me(1')	104.2 (12)
C(1)-C(2)-C(3)	121.6 (31)	Ir(3)-As(1)-C(1)	109.3 (8)	As(2)-C(6)-C(1)	118.2 (21)
C(2)-C(3)-C(4)	118.6 (32)	As(1)-Ir(3)-As(2)	85.89 (10)	As(2)-C(6)-C(5)	121.8 (23)
C(3)-C(4)-C(5)	121.0 (32)			Me(2)-As(2)-Me(2')	100.4 (11)
C(4)-C(5)-C(6)	121.3 (31)	As(1)-C(1)-C(2)	124.4 (22)	Ir(3)-As(2)-Me(2)	119.8 (8)
C(5)-C(6)-C(1)	119.9 (27)	As(1)-C(1)-C(6)	118.0 (20)	Ir(3)-As(2)-C(6)	108.6 (9)

Table VII. Deviations (in Å) of Atoms from the Ir(1)-Ir(1')-Ir(3) Plane[a]

atom	dev	atom	dev
Ir(2)	2.228 (1)	C(13)	0.805 (28)
As(1)	0.818 (3)	O(13)	1.357 (20)
As(2)	−2.181 (3)	C(13')	0.805 (28)
C(11B)	0.183 (35)	O(13')	1.357 (20)
O(11B)	0.331 (23)	C(12)	−1.795 (26)
C(31B)	0.071 (23)	O(12)	−2.840 (18)
O(31B)	0.184 (18)	C(12')	−1.795 (26)
C(31B')	0.071 (23)	O(12')	−2.840 (18)
O(31B')	0.184 (18)		

[a] Equation of plane (Cartesian (Å) coordinates): $0.9575x - 0.2883z - 0.4728 = 0$.

clearly causes some significant perturbations, since all Ir–Ir bonds involving the iridium atom bound to this ligand are anomalously short.

Our current study on the neutral species $Ir_4(CO)_{10}$(diars) and the study of $[H_2Ir_4(CO)_{13}{}^{2-}]$ provide the only documentation of the effect of bridging carbonyl ligands in relatively unperturbed $Ir_4(CO)_{12}$ derivatives. Further investigations are warranted.

As shown in Figure 3 and indicated quantitatively in Table VII, the radial ligands around the triply bridged Ir(1)-Ir(1')-Ir(3) face of the Ir_4 tetrahedron are not coplanar with the metal atoms; rather the $Ir_3(\mu\text{-}CO)_3$(radial-CO)$_2$(radial-As) system takes on a "dished" geometry with all ligands displaced toward the apical Ir(2). The greatest displacements are for As(1) (deviation (dev) 0.818 (3) Å) and the terminal carbonyl groups (dev[C(13)] = dev[C(13')] = 0.805 (38) Å, dev[O(13)] = dev[O(13')] = 1.357 (20) Å), but the bridging carbonyl ligands are also affected (dev[C(11B)] = 0.183 (35) Å, dev[O(11B)] = 0.331 (23) Å, dev[C(31B)] = dev[C(31B')] = 0.071 (23) Å, dev[O(31B)] = dev[O(31B')] = 0.184 (18) Å).

All other distances and angles in the molecule are normal: Ir–CO(terminal) = 1.830 (34)–1.904 (27) Å, C–O(terminal) = 1.115 (33)–1.164 (41) Å, ∠Ir–C–O(terminal) = 173.8 (28)–177.9 (24)°, As–C(sp^2) = 1.93 (3) and 1.93 (4) Å, As–Me = 1.98 (3)–2.01 (3) Å, and C–C(aromatic) = 1.35 (6)–1.45 (5) Å.

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Registry No. $Ir_4(CO)_{10}$(diars), 72142-36-0.

Supplementary Material Available: Tables of data processing formulas and observed and calculated structure factor amptitudes (11 pages). Ordering information is given on any current masthead page.