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Iridium Carbonyl Clusters. 4.[1-3] Crystal Structure and Molecular Geometry of $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$

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The heteronuclear tungsten-iridium cluster complex $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (C_i^1; No. 2) with a = 8.3137 (16) Å, b = 9.1736 (14) Å, c = 14.1420 (26) Å, α = 91.811 (14)°, β = 92.863 (15)°, γ = 103.854 (14)°, V = 1044.9 (3) Å^3, and Z = 2. Diffraction data (Mo Kα, 2θ = 3-45°) were collected with a Syntex P2$_1$ diffractometer, and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. Convergence was reached with R_F = 4.8% and R_{wF} = 4.0% for the 2737 independent reflections with $|F_o| > \sigma(|F_o|)$. The molecule consists of a tetrahedral cluster of metal atoms. The η^5-cyclopentadienyl ligand and two carbonyl groups are bonded to the tungsten atom. This $(\eta^5\text{-}C_5H_5)W(CO)_2$ fragment is linked to three $Ir(CO)_3$ moieties. Intermetallic distances are Ir-Ir = 2.697 (1) Å, 2.699 (1) Å, and 2.702 (1) Å (average = 2.699 [3] Å) and Ir-W = 2.792 (1) Å, 2.815 (1) Å, and 2.865 (1) Å (average = 2.824 [37] Å).

Introduction

The complex $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ was prepared in 70-80% yield from the reaction of $IrCl(CO)_2[NH_2C_6H_4(p\text{-}Me)]$ and $(\eta^5\text{-}C_5H_5)W(CO)_3H$ with CO in the presence of zinc.[4] The present structural study was undertaken with a view toward determining details of the molecular geometry of $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ and of its relationship to the structure of $Ir_4(CO)_{12}$.[1]

Experimental Section

A small, approximately equidimensional, crystal (0.1 × 0.1 × 0.1 mm) was selected for the structural investigation. It was mounted on a Syntex P2$_1$ diffractometer, and diffraction data were collected as described previously.[5] Details are given in Table I. Data were corrected for absorption (μ = 246.2 cm^{-1}) and for Lorentz and polarization effects. Redundant data were averaged.

The positions of the four metal atoms were determined from a three-dimensional Patterson map. Difference Fourier syntheses led to the location of all nonhydrogen atoms; hydrogen atoms were later introduced in calculated positions with C-H = 0.95 Å and appropriate geometry.[6] Least-squares refinement led to convergence with R_F = 4.77% and R_{wF} = 4.01%.[7] The refinement included the incorporation of a correction for secondary extinction.[8]

All computations were performed on a CDC 6600-Cyber 173 system with programs and scattering factors (including $\Delta f'$ and $\Delta f''$ values for nonhydrogen atoms) described previously.[9]

Positional parameters are given in Table II; anisotropic thermal parameters appear in Table III (supplementary material).

Results and Discussion

The crystal consists of discrete molecular units of $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. The overall structure of the molecule and the atomic labeling scheme are shown in Figure 1. Interatomic distances are collected in Table IV, while interatomic angles appear in Table V. The molecule has a tetrahedral WIr_3 core in which the Ir-Ir distances are equivalent [Ir(1)-Ir(2) = 2.699 (1) Å, Ir(1)-Ir(3) = 2.702 (1) Å, Ir(2)-Ir(3) = 2.697 (1) Å; average Ir-Ir = 2.699 [3] Å],[10] while the W-Ir distances show substantial variations [W-Ir(1) = 2.815 (1) Å, W-Ir(2) = 2.792 (1) Å, W-Ir(3) = 2.865 (1) Å; average W-Ir = 2.824 [37] Å]. It should be noted that the differentiation between tungsten (Z = 74) and iridium (Z = 77) is solely on the basis of their chemical sites and interatomic distances; no attempts were made to distinguish between these atoms directly (e.g., by occupancy refinement).

Table I. Details of Data Collection for $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$

(A) Crystal Parameters[a] at 24 °C

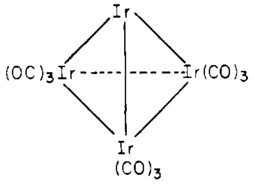
cryst syst: triclinic	γ = 103.854 (14)°
space group: $P\bar{1}$ [C_i^1; No. 2]	V = 1044.9 (3) Å^3
a = 8.3137 (16) Å	Z = 2
b = 9.1736 (14) Å	mol wt = 1133.7
c = 14.1420 (26) Å	ρ(calcd) = 3.60 g cm^{-3}
α = 91.811 (14)°	μ(calcd) = 246.4 cm^{-1} for Mo Kα
β = 92.863 (15)°	

(B) Measurement of Intensity Data

radiation: Mo Kα ($\bar{\lambda}$ = 0.710 73 Å)
monochromator: highly oriented graphite
reflctns measd: $h,\pm k,\pm l$ from 2θ = 3° to 2θ = 45°
scan type: coupled θ(crystal)-2θ(counter)
scan speed: 2.0°/min
scan range: [2θ(Kα_1) - 0.9]-[2θ(Kα_2) + 0.9]°
bkgd measmt: stationary crystal, stationary counter; measd at beginning (B1) and end (B2) of the scan, each for half the time taken for the scan
reflctns collected: 2966 total yielding 2737 independent
std reflctns: three measd every 97 reflections; no significant changes in intensity were observed

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 22 reflections with 2θ = 22-30°.

The molecular structure is closely related to that of $Ir_4(CO)_{12}$, **1** (which is disordered in the solid state),[1] but one $Ir(CO)_3$ group in the parent molecule is now replaced by an $(\eta^5\text{-}C_5H_5)W(CO)_2$ group (see **2**).



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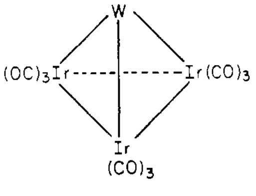

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[1] Part 1: Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528-3535.

[2] Part 2: Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1979**, *18*, 2451-2454.

[3] Part 3: Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1980**, *19*, 2765-2769.

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[6] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213-1214.

[7] $R_F = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$ (%); $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \times 100$ (%).

[8] The secondary extinction parameter (c) enters the equation for the corrected calculated structure factor amplitude in the form $F_{c,cor} = F_{c,uncor}(1 + c\beta F_{c,uncor}^2)^{-1/4}$, where $\beta = \{(1 + \cos^4 2\theta)/[(\sin 2\theta)(1 + \cos^2 2\theta)]\}(-d \ln T/d\mu)$.

[9] See ref 1, p 3530.

[10] Esd's on average values are enclosed in square brackets—see footnote *a* to Table IV.

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Table II. Positional and Isotropic Thermal Parameters for $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$[a]

atom	*x*	*y*	*z*
Ir(1)	0.00566 (7)	0.24397 (7)	0.16761 (4)
Ir(2)	0.09550 (7)	0.28079 (7)	0.35449 (4)
Ir(3)	0.21877 (7)	0.09331 (6)	0.24427 (4)
W	0.32699 (7)	0.41158 (7)	0.22656 (4)
O(11)	−0.1432 (17)	0.5097 (16)	0.1432 (12)
O(12)	0.0883 (19)	0.1932 (17)	−0.0362 (9)
O(13)	−0.3230 (16)	0.0149 (16)	0.1848 (12)
O(21)	−0.1759 (19)	0.0519 (20)	0.4441 (13)
O(22)	0.3646 (19)	0.3257 (19)	0.5140 (10)
O(23)	−0.0288 (19)	0.5637 (15)	0.3879 (10)
O(31)	−0.0716 (16)	−0.1652 (14)	0.2801 (11)
O(32)	0.4615 (16)	0.0111 (16)	0.3909 (10)
O(33)	0.3227 (18)	−0.0405 (15)	0.0619 (10)
WO(1)	0.4770 (20)	0.2939 (17)	0.0504 (11)
WO(2)	0.6236 (15)	0.3339 (16)	0.3444 (13)
C(11)	−0.0844 (21)	0.4100 (20)	0.1552 (14)
C(12)	0.0577 (20)	0.2111 (19)	0.0385 (13)
C(13)	−0.1985 (22)	0.0939 (20)	0.1799 (15)
C(21)	−0.0755 (21)	0.1366 (23)	0.4072 (14)
C(22)	0.2555 (26)	0.3087 (21)	0.4500 (13)
C(23)	0.0187 (21)	0.4546 (21)	0.3759 (13)
C(31)	0.0367 (22)	−0.0658 (18)	0.2649 (14)
C(32)	0.3753 (23)	0.0452 (21)	0.3381 (14)
C(33)	0.2892 (20)	0.0134 (17)	0.1317 (13)
WC(1)	0.4135 (26)	0.3253 (21)	0.1134 (17)
WC(2)	0.5054 (23)	0.3514 (20)	0.3023 (16)
Cp(1)	0.3348 (23)	0.6255 (17)	0.1411 (13)
Cp(2)	0.2479 (22)	0.6389 (17)	0.2226 (15)
Cp(3)	0.3615 (25)	0.6515 (20)	0.3022 (15)
Cp(4)	0.5172 (24)	0.6435 (21)	0.2676 (16)
Cp(5)	0.4963 (22)	0.6283 (20)	0.1702 (14)
HCp(1)[b,c]	0.2898	0.6148	0.0775
HCp(2)	0.1346	0.6420	0.2236
HCp(3)	0.3377	0.6606	0.3668
HCp(4)	0.6178	0.6503	0.3044
HCp(5)	0.5817	0.6196	0.1297

[a] Esd's are right adjusted to the least significant figure of the preceding number. [b] Hydrogens are in calculated positions 0.950 A from the appropriate carbon atom. [c] Isotropic thermal parameters for the hydrogens were derived from those of the corresponding carbon: $B(H) = (B(C) + 1.0)$ A^2. Resulting values (in A^2) are 5.17 for HCp(1), 5.14 for HCp(2), 6.00 for HCp(3), 6.26 for HCp(4), and 5.47 for HCp(5).

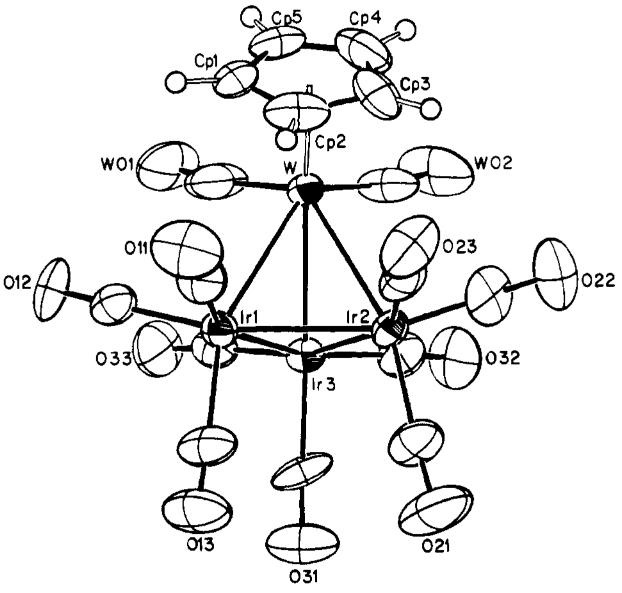


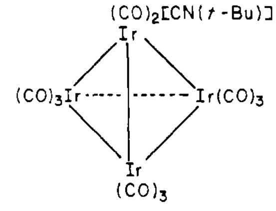
Figure 1. Labeling of atoms in the $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ molecule (ORTEP-II diagram; 30% ellipsoids).

Table IV. Interatomic Distances (A), with Esd's, for $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$

(A) Metal–Metal Bond Lengths			
Ir(1)–Ir(2)	2.6985 (10)	W–Ir(1)	2.8151 (10)
Ir(1)–Ir(3)	2.7018 (9)	W–Ir(2)	2.7920 (10)
Ir(2)–Ir(3)	2.6967 (9)	W–Ir(3)	2.8648 (10)
av Ir–Ir	2.6990 [26][a]	av W–Ir	2.8240 [372][a]
(B) Metal–Carbon and Metal···Oxygen Distances			
Ir(1)–C(11)	1.861 (17)	Ir(1)···O(11)	3.008 (13)
Ir(1)–C(12)	1.929 (18)	Ir(1)···O(12)	3.044 (13)
Ir(1)–C(13)	1.932 (18)	Ir(1)···O(13)	3.047 (13)
Ir(2)–C(21)	1.895 (18)	Ir(2)···O(21)	3.048 (14)
Ir(2)–C(22)	1.816 (21)	Ir(2)···O(22)	3.043 (14)
Ir(2)–C(23)	1.875 (19)	Ir(2)···O(23)	3.046 (12)
Ir(3)–C(31)	1.876 (17)	Ir(3)···O(31)	3.028 (13)
Ir(3)–C(32)	1.946 (20)	Ir(3)···O(32)	3.057 (12)
Ir(3)–C(33)	1.908 (19)	Ir(3)···O(33)	3.071 (13)
W–WC(1)	2.003 (22)	W···WO(1)	3.116 (13)
W–WC(2)	1.981 (21)	W···WO(2)	3.142 (12)
(C) Intramolecular M···CO Contacts (<3.2 A)			
Ir(3)···WC(1)	3.078 (19)	Ir(3)···WC(2)	2.990 (18)
(D) Carbon–Oxygen Distances			
C(11)–O(11)	1.149 (19)	C(31)–O(31)	1.152 (19)
C(12)–O(12)	1.115 (19)	C(32)–O(32)	1.113 (20)
C(13)–O(13)	1.118 (19)	C(33)–O(33)	1.165 (20)
C(21)–O(21)	1.154 (20)	WC(1)–WO(1)	1.122 (22)
C(22)–O(22)	1.228 (22)	WC(2)–WO(2)	1.170 (21)
C(23)–O(23)	1.171 (20)		
(E) W–C and C–C Distances in the $(\eta^5\text{-}C_5H_5)$W System			
W–Cp(1)	2.327 (15)	Cp(1)–Cp(2)	1.407 (24)
W–Cp(2)	2.333 (15)	Cp(2)–Cp(3)	1.417 (25)
W–Cp(3)	2.364 (17)	Cp(3)–Cp(4)	1.424 (27)
W–Cp(4)	2.363 (17)	Cp(4)–Cp(5)	1.378 (27)
W–Cp(5)	2.332 (16)	Cp(5)–Cp(1)	1.380 (24)

[a] Error estimates shown in brackets for average distances, $\bar{d}$, are the exterior estimates of the precision of the average value given by $[\Sigma_N(\bar{d} - d)^2/(N - 1)]^{1/2}$.

The average Ir–Ir distance of 2.699 [3] Å in the present $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ molecule may be compared to an average Ir–Ir bond length of 2.693 Å in $Ir_4(CO)_{12}$,[1] while the average Ir–Ir distance (between $Ir(CO)_3$ groups) in $Ir_4(CO)_{11}[\eta^1\text{-}CN(t\text{-}Bu)]$[2] (**3**) is 2.689 Å. All other simple derivatives of $Ir_4(CO)_{12}$ that have so far been subjected to X-ray structural analysis appear to have some (usually three mutually adjacent) bridging carbonyl ligands (see discussion section of ref 3).



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Within the present molecule, the Ir–CO distances range from 1.816 (21) Å through 1.946 (20) Å, averaging 1.893 [41] Å, and the terminal Ir–C–O systems are all close to linear (∠Ir–C–O = 174.7 (19)–179.0 (10)°). The W–CO distances are substantially greater than the Ir–CO distances, with W–WC(1) = 2.003 (22) Å and W–WC(2) = 1.981 (21) Å (average = 1.992 [16] Å). Although the W–C–O systems are bent from linearity by a significant amount (W–WC(1)–WO(1) = 171.1 (18)° and W–WC(2)–WO(2) = 171.2 (17)°), this appears to be a matter of interligand repulsion rather than due to any "semibridging" character is the carbonyl ligands.[11] The closest contacts to these carbon atoms are Ir(3)···WC(2) = 2.990 (18) Å and Ir(3)···WC(1) = 3.078

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(11) For a discussion of semibridging carbonyl ligands, see: Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

Table V. Interatomic Angles (Deg) with Esd's for $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$

		(A) Metal Cluster			
Ir(2)-Ir(1)-Ir(3)	59.92 (2)	Ir(1)-Ir(2)-W	61.66 (3)	Ir(2)-Ir(3)-W	60.18 (2)
Ir(2)-Ir(1)-W	60.80 (3)	Ir(3)-Ir(2)-W	62.90 (3)	Ir(1)-W-Ir(2)	57.54 (2)
Ir(3)-Ir(1)-W	62.53 (2)	Ir(1)-Ir(3)-Ir(2)	59.98 (3)	Ir(1)-W-Ir(3)	56.80 (2)
Ir(1)-Ir(2)-Ir(3)	60.10 (2)	Ir(1)-Ir(3)-W	60.67 (2)	Ir(2)-W-Ir(3)	56.93 (2)
		(B) M-M-(CO)			
Ir(2)-Ir(1)-C(11)	98.5 (6)	Ir(1)-Ir(2)-C(23)	96.4 (6)	Ir(2)-Ir(3)-C(32)	98.2 (6)
Ir(2)-Ir(1)-C(12)	150.5 (5)	Ir(3)-Ir(2)-C(21)	98.8 (6)	Ir(2)-Ir(3)-C(33)	157.9 (5)
Ir(2)-Ir(1)-C(13)	96.2 (6)	Ir(3)-Ir(2)-C(22)	96.8 (5)	W-Ir(3)-C(31)	144.8 (5)
Ir(3)-Ir(1)-C(11)	154.0 (6)	Ir(3)-Ir(2)-C(23)	152.7 (5)	W-Ir(3)-C(32)	104.9 (6)
Ir(3)-Ir(1)-C(12)	95.0 (5)	W-Ir(2)-C(21)	159.5 (6)	W-Ir(3)-C(33)	103.2 (5)
Ir(3)-Ir(1)-C(13)	98.4 (5)	W-Ir(2)-C(22)	91.4 (6)	Ir(1)-W-WC(1)	88.9 (6)
W-Ir(1)-C(11)	95.3 (5)	W-Ir(2)-C(23)	94.6 (5)	Ir(1)-W-WC(2)	129.8 (5)
W-Ir(1)-C(12)	95.0 (5)	Ir(1)-Ir(3)-C(31)	88.7 (5)	Ir(2)-W-WC(1)	131.7 (5)
W-Ir(1)-C(13)	154.9 (6)	Ir(1)-Ir(3)-C(32)	157.4 (6)	Ir(2)-W-WC(2)	90.4 (5)
Ir(1)-Ir(2)-C(21)	102.1 (6)	Ir(1)-Ir(3)-C(33)	100.0 (5)	Ir(3)-W-WC(1)	76.2 (5)
Ir(1)-Ir(2)-C(22)	149.8 (5)	Ir(2)-Ir(3)-C(31)	90.6 (5)	Ir(3)-W-WC(2)	73.7 (5)
		(C) (OC)-M-(CO)			
C(11)-Ir(1)-C(12)	100.5 (8)	C(31)-Ir(3)-C(33)	98.6 (8)	C(22)-Ir(2)-C(23)	99.3 (8)
C(11)-Ir(1)-C(13)	98.1 (8)	C(21)-Ir(2)-C(22)	100.3 (9)	C(32)-Ir(3)-C(33)	100.3 (7)
C(12)-Ir(1)-C(13)	103.2 (8)	C(21)-Ir(2)-C(23)	100.0 (8)	WC(1)-W-WC(2)	86.5 (9)
C(31)-Ir(3)-C(32)	97.8 (8)				
		(D) M-C-O			
Ir(1)-C(11)-O(11)	176.6 (14)	Ir(3)-C(32)-O(32)	176.9 (14)	Ir(2)-C(23)-O(23)	179.0 (10)
Ir(1)-C(12)-O(12)	179.5 (8)	Ir(3)-C(33)-O(33)	176.0 (20)	W-WC(1)-WO(1)	171.1 (18)
Ir(1)-C(13)-O(13)	174.7 (19)	Ir(2)-C(21)-O(21)	176.3 (16)	W-WC(2)-WO(2)	171.2 (17)
Ir(3)-C(31)-O(31)	177.5 (13)	Ir(2)-C(22)-O(22)	179.0 (10)		
		(E) Cyclopentadienyl Ring			
Cp(5)-Cp(1)-Cp(2)	107.8 (17)	Cp(2)-Cp(3)-Cp(4)	107.3 (18)	Cp(4)-Cp(5)-Cp(1)	110.3 (18)
Cp(1)-Cp(2)-Cp(3)	107.5 (16)	Cp(3)-Cp(4)-Cp(5)	107.1 (18)		

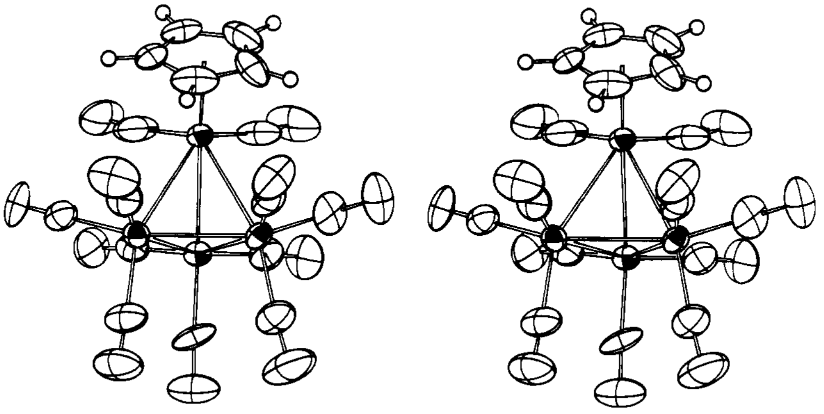

Figure 2. Stereoscopic view of the $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ molecule.

(19) Å. The η^5-cyclopentadienyl ligand is bound symmetrically to the tungsten atom with W–C distances ranging only from 2.327 (15) through 2.364 (17) Å (average = 2.344 [18] Å); rather surprisingly, the $(\eta^5\text{-}C_5H_5)\rightarrow W$ linkage is more symmetrical than those found in such simple species as $(\eta^5\text{-}C_5H_5)W(CO)_3Cl^{12}$ (W–C = 2.260 (10)–2.376 (9) Å or $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2{}^{13}$ (W–C = 2.305 (6)–2.377 (6) Å).

There are two important *general* aspects to the derived structure.

(1) It is one of the few tetrahedral cluster complexes held together only by metal–metal bonds (i.e., with no bridging ligands). The only other examples with which we are conversant are $Ir_4(CO)_{12}{}^1$ and $Ir_4(CO)_{11}[\eta^1\text{-}CN(t\text{-}Bu)]$.[2]

(2) If we use the normal assumption that an η^5-C_5H_5 ligand occupies the same surface area as about $2^1/_2$ carbonyl ligands, the complex may be seen to be about as crowded as would be a hypothetical tetrahedral $M_4(CO)_{13.5}$ cluster. We note that $[Fe_4(CO)_{13}{}^{2-}]$ can be synthesized whereas $Fe_4(CO)_{14}$ cannot[14] and that $[Fe_4(CO)_{13}H^-]$ has an opened "butterfly"-shaped core[15] rather than the tetrahedral core expected for a 60-electron cluster. The stability of the present molecule is probably due to the increased size of its internal WIr_3 tetrahedron vis à vis the Fe_4 tetrahedron in $[Fe_4(CO)_{13}{}^{2-}]$. However, the present molecule is among the most crowded of the extant tetrahedral clusters. A stereoscopic view of the species appears as Figure 2.

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Registry No. $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$, 79201-49-3.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters (Table III), and data processing formulas (19 pages). Ordering information is given on any current masthead page.

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