

IRIDIUM-CARBONYL CLUSTERS

VI *. MIXED-METAL CLUSTERS VIA METAL-HYDRIDE COUPLING. SYNTHESIS OF $\text{CpMM}'_3(\text{CO})_{11}$ ($M = \text{Mo}, \text{W}; M' = \text{Co}, \text{Ir}$) AND THE CRYSTAL STRUCTURE OF $\text{CpMoIr}_3(\text{CO})_{11}$

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(Received March 19th, 1986)

Summary

The reaction of $\text{CpM}(\text{CO})_3\text{H}$ ($M = \text{Mo}, \text{W}$) with $\text{IrCl}(\text{CO})_2(p\text{-toluidine})$ leads to the species $\text{CpMIr}_3(\text{CO})_{11}$; reaction of $\text{CpM}(\text{CO})_3\text{H}$ with $\text{Co}_4(\text{CO})_{12}$ produces the known species $\text{CpMCo}(\text{CO})_{11}$ in high yield. The newly-reported species $\text{CpMoIr}_3(\text{CO})_{11}$ has been subjected to an X-ray structural analysis. It crystallizes in the centrosymmetric orthorhombic space group *Pbca* (No. 61) with a 12.2830(15), b 13.5113(18), c 24.9418(30) Å, V 4139.3(9) Å³ and $Z = 8$. Diffraction data were collected with a Syntex P2₁ automated diffractometer (Mo- K_α radiation, 2θ 4.0–45.0°) and the structure was refined to R 5.4% for all 2421 data (R 4.5% for those 2141 data above $3\sigma(|F_0|)$).

$\text{CpMoIr}_3(\text{CO})_{11}$ is neither isomorphous nor isostructural with the known species $\text{CpWIr}_3(\text{CO})_{11}$ or $\text{CpMoCo}_3(\text{CO})_{11}$. It differs by possessing three bridging carbonyl ligands which encircle one MoIr_2 face of the tetrahedral MoIr_3 cluster. The structure is completed by a Cp ligand on Mo and eight terminal carbonyl ligands (one on the molybdenum atom, three on the unique iridium atom and two each on the iridium atoms associated with the $\text{MoIr}_2(\mu\text{-CO})_3$ moiety). The molecule has approximate C_s symmetry.

Introduction

In previous work we have shown the utility of metal hydride moieties as agents for the systematic synthesis of mixed-metal clusters. New compounds prepared in

* For Part V, see ref. 4c, for Part IV see ref. 4b.

this manner and characterized crystallographically include $(\mu\text{-H})_2\text{Re}_2\text{Os}_3(\text{CO})_{20}$ [1], $\text{CpW}\text{Os}_3(\text{CO})_{12}(\mu\text{-H})$ [2], $(\mu\text{-H})_5\text{ReOs}_3(\text{CO})_{12}$ [3] and $\text{CpWIr}_3(\text{CO})_{11}$ [4]. We have extended the method mentioned briefly in ref. 4a to the preparation of the new compound $\text{CpMoIr}_3(\text{CO})_{11}$. In a related way we have also prepared the previously reported compounds $\text{CpMCo}_3(\text{CO})_{11}$ ($\text{M} = \text{Mo}, \text{W}$) [5]. In addition to full synthetic details we also report the crystal structure of $\text{CpMoIr}_3(\text{CO})_{11}$ and compare the results with the structures previously determined for $\text{CpWIr}_3(\text{CO})_{11}$ [4] and $\text{CpMoCo}_3(\text{CO})_{11}$ [5].

Experimental

Reactions were carried out under a nitrogen atmosphere. Chemicals and solvents were generally reagent grade and were used without further purification. Infrared spectra were recorded on a Perkin-Elmer Model 281B spectrophotometer. The spectra were calibrated in the carbonyl region against a cyclohexane absorption at 2138.5 cm^{-1} and polystyrene absorptions at 1944 and 1601 cm^{-1} . Elemental and mass spectral analyses were performed at the University of Illinois by the micro-analysis and mass spectroscopy laboratories of the School of Chemical Sciences. ^1H NMR spectra (90 MHz) were recorded on a Varian EM-390 spectrometer and ^{13}C NMR spectra (25.2 MHz) were recorded on a Varian XL-100 spectrometer.

CpWIr₃(CO)₁₁. Solid $\text{CpW}(\text{CO})_3\text{H}$ [6] (100 mg, 0.30 mmol) was added to a dichloromethane solution (30 ml) or $\text{IrCl}(\text{CO})_2(p\text{-toluidine})$ [7] (40 mg, 0.10 mmol) in a pressure bottle along with acid-washed granular zinc (0.5 g). The bottle was then charged to 40 psig with carbon monoxide and warmed in an oil bath to 60°C for 6 h. The bottle was cooled and vented. The reaction mixture was evaporated to dryness, and the solid residue was extracted with dichloromethane (1–2 ml) and then applied to preparative TLC plates. Elution with dichloromethane/petroleum ether (2/5) gave bands of pink $[\text{CpW}(\text{CO})_3]_2$, orange $\text{CpWIr}_3(\text{CO})_{11}$, and brown $\text{Cp}_2\text{W}_2\text{Ir}_2(\text{CO})_{10}$ (trace) [4a,c]. The orange band was extracted with dichloromethane, and the solution was evaporated to dryness. The crude product was then dissolved in a minimum of dichloromethane, a layer of methanol was added, and the mixture was placed at -15°C for 24 h to afford orange crystalline $\text{CpWIr}_3(\text{CO})_{11}$ (27 mg, 0.024 mmol, 71%). Anal. Found: C, 17.01; H, 0.45. $\text{C}_{16}\text{H}_5\text{O}_{11}\text{WIr}_3$ calcd.: C, 16.95; H, 0.44%. IR (C_6H_{12}): $\nu(\text{CO})$, 2093m, 2053vs, 2049vs, 2031s, 1996m, 1979m, 1967w cm^{-1} . IR (KBr): $\nu(\text{CO})$, 2091m, 2045vs, 2025vs, 1987s, 1946m, 1890w cm^{-1} . ^1H NMR (CDCl_3) δ 5.35 (s, C_5H_5). ^{13}C NMR (CDCl_3) δ 169.2 (11CO, $J(^{183}\text{W}-^{13}\text{C})$ 14 Hz).

CpMoIr₃(CO)₁₁. The reaction of $\text{CpMo}(\text{CO})_3\text{H}$ [6] (74 mg, 0.40 mmol) and $\text{IrCl}(\text{CO})_2(p\text{-toluidine})$ (40 mg, 0.10 mmol) was conducted in the same manner as described above to yield orange crystalline $\text{CpMoIr}_3(\text{CO})_{11}$ (22 mg, 0.020 mmol, 60%). Anal. Found: C, 18.31; H, 0.51. $\text{C}_{16}\text{H}_5\text{O}_{11}\text{MoIr}_3$ calcd.: C, 18.38; H, 0.48%. IR (C_6H_{12}): $\nu(\text{CO})$, 2094s, 2069m, 2055vs, 2049vs, 2030s, 2014w, 2001s, 1964m, 1926w, 1874m, 1801w, 1778m cm^{-1} . IR (KBr) $\nu(\text{CO})$, 2090s, 2060s, 2040vs, 2028vs, 1995vs, 1907s, 1858s, 1830s, 1800vs cm^{-1} . ^1H NMR (CDCl_3): δ 5.28 (s, C_5H_5).

CpWCo₃(CO)₁₁. A dichloromethane solution (150 ml) of $\text{Co}_4(\text{CO})_{12}$ (30 mg, 0.055 mmol) and $\text{CpW}(\text{CO})_3\text{H}$ (35 mg, 0.11 mmol) was prepared in a three-necked round bottom flask (300 ml). A dichloromethane solution (100 ml) of trimethylamine oxide dihydrate (Aldrich) (8 mg, 0.07 mmol) was added slowly by syringe.

The solution was stirred for 5 min and evaporated to dryness. Preparative TLC provided bands of orange (minor, uncharacterized), red $[\text{CpW}(\text{CO})_3]_2$ and brown $\text{CpWCo}_3(\text{CO})_{11}$; the last was extracted and isolated (32 mg, 0.044 mmol, 80%). The compound was characterized by comparing its IR ($\nu(\text{CO})$) and ^1H NMR spectra with literature values [5] as well as by its electron-impact mass spectrum: m/z 736 (M^+).

$\text{CpMoCo}_3(\text{CO})_{11}$. This compound was prepared in an analogous manner from $\text{Co}_4(\text{CO})_{12}$ and $\text{CpMo}(\text{CO})_3\text{H}$ and was isolated in 72% yield. The IR and ^1H NMR spectra matched literature values [5] and the expected mass spectrum was observed: m/z 648 (M^+).

Collection of X-ray diffraction data for $(\eta^5\text{-C}_5\text{H}_5)\text{MoIr}_3(\text{CO})_{11}$

A deep orange-red crystal of approximate orthogonal dimensions $0.17 \times 0.23 \times 0.24 \text{ mm}^3$ was selected for the X-ray structural analysis. It was glued onto a thin glass fibre which was fixed (with bees' wax) into an aluminum pin on the Syntex P2₁ automated four-circle diffractometer at SUNY-Buffalo. Crystal alignment, determination of crystal class (orthorhombic), the orientation matrix and accurate cell dimensions were carried out as described previously [8]. Details of data collection (using a coupled $\theta(\text{crystal})-2\theta(\text{counter})$ scan) are presented in Table 1.

The observed diffraction symmetry (D_{2h} , mmm) and systematic absences ($0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$ and $hk0$ for $h = 2n + 1$) are consistent only with the centrosymmetric orthorhombic space group $Pbca$, No. 61 [9].

A total of 2730 reflections was collected and corrected for the effects of absorption; these data were merged to 2421 symmetry-independent reflections ($R(I)$ 4.0%, $R_w(I)$ 4.8% for averaging statistics). All data were converted to unscaled $|F_0|$ values following corrections for Lorentz and polarization factors.

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $(\eta^5\text{-C}_5\text{H}_5)\text{MoIr}_3(\text{CO})_{11}$

(A) Crystallographic parameters at 296 K (23°C)

Cryst. system: orthorhombic	Space group: $Pbca$ (D_{2h}^{15} ; No. 61)
a 12.2830(15) Å	Formula: $\text{C}_{16}\text{H}_5\text{O}_{11}\text{Ir}_3\text{Mo}$
b 13.5113(18) Å	Mol. Wt.: 1045.7
c 24.9418(30) Å	$Z = 8$
V 4139.3(9) Å ³	$D(\text{calcd.}) 3.35 \text{ g cm}^{-3}$

(B) Data collection

Diffractometer: Syntex P2₁
Radiation: Mo- K_α (λ 0.710730 Å)
Monochromator: highly oriented graphite, equatorial geometry, $2\theta_m$ 12.2°, assumed 50% perfect
Reflections measd: $+h$, $+k$, $+l$ for $2\theta = 4.0-45.0^\circ$
Scan type: coupled $\theta(\text{crystal})-2\theta(\text{counter})$
Scan width: symmetrical, $[1.6 + \Delta(\alpha_2 - \alpha_1)]^\circ$
Scan speed: 2.0 deg min⁻¹ (in 2θ)
bkgd measd. stationary-crystal, stationary-counter at beginning and end of 2θ scan; each for one-half of total scan time
Standard reflcns: 3 check reflections rmeasured after each 97 reflections; no significant decay
Reflections collected: 2730 total; merged to 2421 unique data [filename IRFJ-188]
 $\mu(\text{Mo-}K_\alpha)$: 208 cm⁻¹; empirical correction applied

Any datum with $I(\text{net}) < 0$ was assigned the value $|F_0| = 0$; no datum was eliminated. Data were placed on an approximately absolute scale by means of a Wilson plot.

Solution and refinement of the structure of $(\eta^5\text{-C}_5\text{H}_5)\text{MoIr}_3(\text{CO})_{11}$

All calculations were carried out under the SUNY-Buffalo version of the Syntex XTL crystallographic program package [10]. Structure factors were calculated from the analytical functions defining the scattering curves of the appropriate neutral atoms [11a]; both the real ($\Delta f'$) and the imaginary ($i\Delta f''$) components of anomalous dispersion were included for all non-hydrogen atoms [11b]). The function minimized during least-squares refinement was $\sum w(|F_0| - |F_c|)^2$, where $w = [\{\sigma(|F_0|)\}^2 + \{0.02|F_0|\}^2]^{-1}$. Discrepancy indices used below are defined as follows.

$$R_F(\%) = 100 \sum ||F_0| - |F_c|| / \sum |F_0|$$

$$R_{wF}(\%) = 100 \left[\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2 \right]^{1/2}$$

$$GOF = \left[\sum w(|F_0| - |F_c|)^2 / (NO - NV) \right]^{1/2}.$$

In this last equation, NO is the number of observations and NV is the number of variables.

The structure was solved by direct methods with the use of the program MULTAN [12]; the positions of the four heavy atoms (one Mo, three Ir) were determined from an "E-map". All remaining non-hydrogen atoms were located from a difference-Fourier map. Hydrogen atoms of the $\eta^5\text{-C}_5\text{H}_5$ ring were included in idealized positions with $d(\text{C-H})$ 0.95 Å [13], B 6.0 Å² and externally-bisecting (sp^2) geometry about the appropriate carbon atoms. Full-matrix least-squares refinement of positional parameters for all non-hydrogen atoms, anisotropic thermal parameters for Ir, Mo and O atoms, and isotropic thermal parameters for the C atoms led quickly to convergence with R_F 5.4, R_{wF} 4.6% and GOF 1.26 for all 2421 data; and R_F 4.5%, R_{wF} 4.5% and GOF 1.30 for those 2141 data with $|F_0| > 3\sigma(|F_0|)$.

Data were also corrected for the effects of secondary extinction using the simplified Zachariasen formula $|F_{0,\text{cor}}| = |F_{0,\text{uncor}}| (1.0 + gI_0)$. The value determined for g was 0.461×10^{-6} .

A final difference-Fourier map was devoid of significant features; the structure is thus both correct and complete. Positional and thermal parameters are collected in Tables 2 and 3.

Description of the structure of $(\eta^5\text{-C}_5\text{H}_5)\text{MoIr}_3(\text{CO})_{11}$

The crystal consists of discrete molecular units which are separated by normal Van der Waals' distances. There are no abnormally short intermolecular contacts. The overall molecular connectivity, the atomic vibration ellipsoids and the atomic labeling scheme are depicted in Fig. 1. A stereoscopic view of the molecule appears as Fig. 2. Interatomic distances and angles are collected in Tables 4 and 5.

The molecule has a tetrahedral MoIr_3 core in which the iridium-iridium distances are essentially equivalent (Ir(1)-Ir(2) 2.698(1), Ir(1)-Ir(3) 2.700(1) and Ir(2)-Ir(3) 2.703(1) Å, average 2.700 ± 0.002 Å, even though the Ir(2)-Ir(3) bond is

TABLE 2
 ATOMIC COORDINATES FOR $(\eta^5\text{-C}_5\text{H}_5)\text{MoIr}_3(\text{CO})_{11}$

Atom	x	y	z	B_{iso}
Ir(1)	-0.11427(6)	0.20144(5)	-0.08505(3)	
Ir(2)	0.09834(6)	0.18624(5)	-0.11092(3)	
Ir(3)	-0.05239(6)	0.21027(5)	-0.18880(3)	
Mo	0.00039(13)	0.37525(10)	-0.12356(6)	
O(11)	-0.3542(12)	0.2589(12)	-0.09633(56)	
O(12)	-0.0935(15)	0.2159(14)	0.03758(59)	
O(13)	-0.1410(14)	-0.0197(10)	-0.09819(62)	
O(21)	0.1417(15)	0.0260(13)	-0.02794(66)	
O(22)	0.3226(12)	0.2290(11)	-0.15696(62)	
O(31)	-0.2548(12)	0.1194(11)	-0.23495(55)	
O(32)	0.0536(14)	0.2738(11)	-0.29281(53)	
O(M)	-0.1522(13)	0.4374(11)	-0.03052(63)	
O(B1)	0.0630(13)	0.0081(10)	-0.18770(57)	
O(B2)	0.1353(12)	0.3285(10)	-0.01644(51)	
O(B3)	-0.2106(11)	0.38952(90)	-0.19588(51)	
C(11)	-0.2635(16)	0.2381(14)	-0.09302(70)	2.60(35)
C(12)	-0.1003(16)	0.2098(13)	-0.00739(80)	2.95(38)
C(13)	-0.1281(17)	0.0639(15)	-0.09240(76)	3.19(40)
C(21)	0.1299(18)	0.0900(15)	-0.05925(87)	3.87(44)
C(22)	0.2409(18)	0.2105(13)	-0.14065(71)	2.85(37)
C(31)	-0.1786(15)	0.1504(11)	-0.21936(64)	1.65(30)
C(32)	0.0148(16)	0.2508(13)	-0.25405(82)	2.77(35)
C(M)	-0.0980(17)	0.4060(14)	-0.06579(82)	3.29(40)
C(B1)	0.0469(16)	0.0885(14)	-0.17297(75)	2.96(37)
C(B2)	0.0959(16)	0.3134(12)	-0.05845(75)	2.49(34)
C(B3)	-0.1350(16)	0.3535(13)	-0.17575(70)	2.44(35)
C(1)	0.0911(21)	0.5161(17)	-0.1026(10)	5.03(53)
C(2)	0.1641(22)	0.4615(18)	-0.1341(10)	5.66(58)
C(3)	0.1296(24)	0.4511(19)	-0.1823(11)	6.13(62)
C(4)	0.0267(20)	0.4978(17)	-0.18500(93)	4.74(51)
C(5)	-0.0038(23)	0.5429(20)	-0.1389(11)	6.49(67)
H(1)	0.0994	0.5329	-0.0658	6.0
H(2)	0.2309	0.4353	-0.1212	6.0
H(3)	0.1662	0.4183	-0.2108	6.0
H(4)	-0.0172	0.4975	-0.2163	6.0
H(5)	-0.0670	0.5808	-0.1313	6.0

accompanied by a bridging carbonyl ligand, while the others are not. These iridium-iridium distances may be compared with average non-bridged distances of $2.699 \pm 0.003 \text{ \AA}$ in $(\eta^5\text{-C}_5\text{H}_5)\text{WIr}_3(\text{CO})_{11}$ [4b] and 2.693 \AA in the parent homonuclear carbonyl, $\text{Ir}_4(\text{CO})_{12}$ [14].

The iridium-molybdenum distances show more variation. Thus, the non-bridged Ir(1)-Mo distance of $2.902(2) \text{ \AA}$ is slightly, but significantly, longer than the carbonyl-bridged Ir-Mo bonds (Ir(2)-Mo $2.841(2)$, Ir(3)-Mo $2.835(2) \text{ \AA}$, average $2.838 \pm 0.004 \text{ \AA}$).

The molecule contains a MoIr_3 core with 3 terminal carbonyl ligands on Ir(1), 2 terminal carbonyl ligands each on Ir(2) and Ir(3) and one terminal carbonyl and an $\eta^5\text{-C}_5\text{H}_5$ ligand on the Mo atom; the structure is completed by three bridging carbonyl groups around the edges of the Ir(2)-Mo-Ir(3) face of the tetrahedron. As

TABLE 3

ANISOTROPIC THERMAL PARAMETERS ^a FOR (η^5 -C₅H₅)MoIr₃(CO)₁₁

Atom	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Ir(1)	2.016(33)	2.355(32)	1.598(31)	-0.285(28)	0.231(25)	0.161(22)
Ir(2)	1.907(32)	2.326(32)	1.919(32)	0.241(28)	-0.107(25)	0.224(23)
Ir(3)	2.120(33)	2.357(31)	1.393(29)	-0.320(27)	-0.060(26)	-0.174(22)
Mo	2.407(72)	1.623(63)	1.951(65)	-0.328(58)	-0.160(58)	0.109(48)
O(11)	3.89(75)	5.80(81)	4.04(75)	0.25(72)	0.65(65)	1.12(60)
O(12)	6.9(11)	10.8(13)	2.16(71)	-0.6(10)	-0.07(71)	0.15(70)
O(13)	7.5(11)	2.46(64)	6.43(91)	-1.19(68)	3.33(82)	-0.24(56)
O(21)	6.5(11)	7.3(10)	6.03(94)	1.76(87)	-0.67(84)	4.07(77)
O(22)	2.78(68)	5.49(84)	5.93(87)	-1.05(65)	0.64(66)	0.03(63)
O(31)	2.52(66)	6.38(86)	4.94(75)	-1.42(66)	-0.70(66)	-1.25(63)
O(32)	6.8(10)	6.28(87)	2.60(67)	0.07(80)	0.80(71)	-0.01(58)
O(M)	4.66(86)	5.91(87)	5.58(87)	1.45(73)	0.71(74)	-2.00(68)
O(B1)	6.3(10)	2.70(63)	4.90(77)	1.31(65)	-0.39(73)	-0.47(53)
O(B2)	4.85(80)	4.48(69)	2.69(64)	0.66(63)	-2.17(60)	0.06(49)
O(B3)	2.55(61)	3.22(61)	4.46(68)	0.90(55)	-0.73(55)	-0.66(51)

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

such, the molecule may be represented by structure 1 in contrast to structures 2 and 3 for the isoelectronic species CpWIr₃(CO)₁₁ [4b] and CpMoCo₃(CO)₁₁ [5], respectively (see Scheme 1).

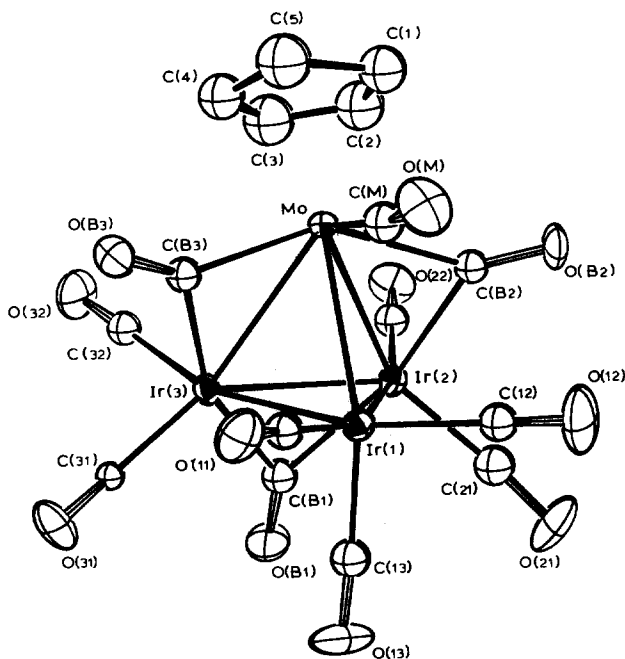
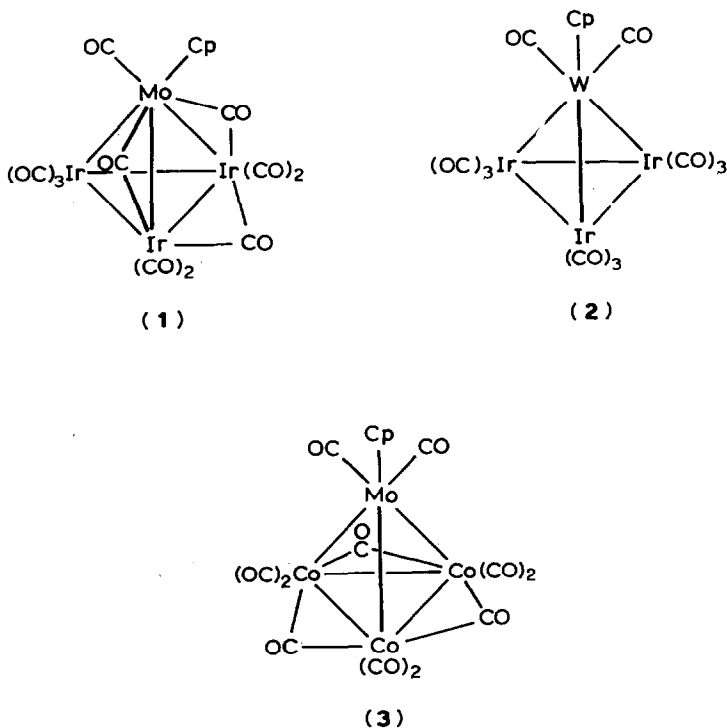


Fig. 1. Molecular stereochemistry, labeling of atoms and atomic vibration ellipsoids for CpMoIr₃(CO)₁₁ (ORTEP-II diagram; 30% probability envelopes).



SCHEME 1. Representation of the solid state structures of three complexes of the type $\text{CpMM}'_3(\text{CO})_{11}$. For 1, $\text{M} = \text{Mo}$, $\text{M}' = \text{Ir}$; for 2, $\text{M} = \text{W}$, $\text{M}' = \text{Ir}$; for 3, $\text{M} = \text{Mo}$, $\text{M}' = \text{Co}$.

The three bridging carbonyl ligands in $(\eta^5\text{-C}_5\text{H}_5)\text{MoIr}_3(\text{CO})_{11}$ are close to symmetric with $\text{Ir}(2)\text{-C}(\text{B}1)$ 2.130(19) vs. $\text{Ir}(3)\text{-C}(\text{B}1)$ 2.085(19), $\text{Ir}(2)\text{-C}(\text{B}2)$ 2.160(17) vs. $\text{Mo-C}(\text{B}2)$ 2.171(19) Å, and $\text{Ir}(3)\text{-C}(\text{B}3)$ 2.209(18) vs. $\text{Mo-C}(\text{B}3)$

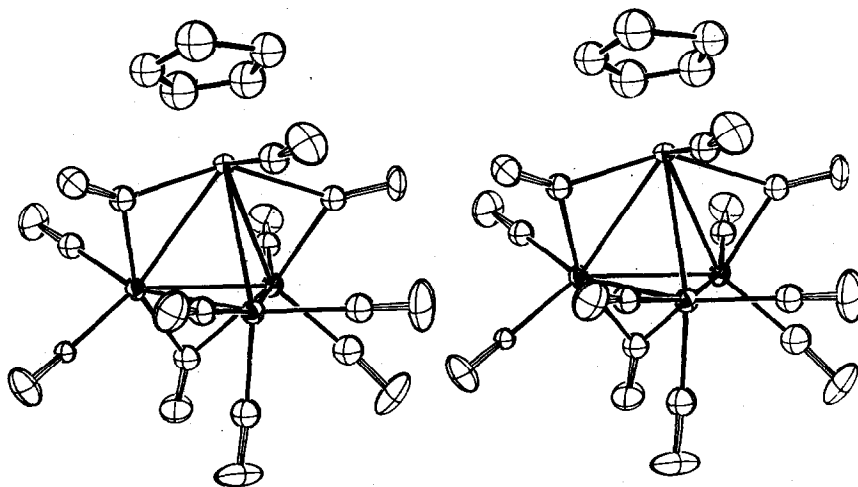


Fig. 2. Stereoscopic view of the $\text{CpMoIr}_3(\text{CO})_{11}$ molecule.

TABLE 4
 INTERATOMIC DISTANCES (Å) FOR $(\eta^5\text{-C}_5\text{H}_5)\text{MoIr}_3(\text{CO})_{11}$

<i>Metal–metal distances</i>			
Ir(1)–Ir(2)	2.698(1)	Ir(2)–Ir(3)	2.703(1)
Ir(1)–Ir(3)	2.700(1)	Ir(2)–Mo	2.841(2)
Ir(1)–Mo	2.902(2)	Ir(3)–Mo	2.835(2)
<i>Metal–carbonyl distances</i>			
Ir(1)–C(11)	1.909(20)	Ir(2)–C(21)	1.871(21)
Ir(1)–C(12)	1.948(20)	Ir(2)–C(22)	1.930(21)
Ir(1)–C(13)	1.875(20)	Ir(3)–C(31)	1.907(17)
Mo–C(M)	1.926(21)	Ir(3)–C(32)	1.905(20)
<i>Metal–(bridging carbonyl) distances</i>			
Ir(2)–C(B1)	2.130(19)	Mo–C(B2)	2.171(19)
Ir(3)–C(B1)	2.085(19)	Ir(3)–C(B3)	2.209(18)
Ir(2)–C(B2)	2.160(17)	Mo–C(B3)	2.132(19)
<i>Carbon–oxygen distances</i>			
C(11)–O(11)	1.152(25)	C(31)–O(31)	1.097(22)
C(12)–O(12)	1.128(25)	C(32)–O(32)	1.122(25)
C(13)–O(13)	1.149(24)	C(B1)–O(B1)	1.164(23)
C(21)–O(21)	1.175(27)	C(B2)–O(B2)	1.172(23)
C(22)–O(22)	1.111(26)	C(B3)–O(B3)	1.162(23)
C(M)–O(M)	1.181(26)		
<i>Mo–C and C–C distances for $(\eta^5\text{-C}_5\text{H}_5)$ ring</i>			
Mo–C(1)	2.266(24)	C(1)–C(2)	1.400(36)
Mo–C(2)	2.338(27)	C(2)–C(3)	1.284(38)
Mo–C(3)	2.391(28)	C(3)–C(4)	1.415(37)
Mo–C(4)	2.279(23)	C(4)–C(5)	1.353(36)
Mo–C(5)	2.298(27)	C(5)–C(1)	1.521(37)

2.132(19) Å. Relative to the Ir(2)–Ir(3)–Mo plane, displacements of the bridging carbonyl groups are +0.197 Å for C(B1), –0.417 Å for C(B2) and –0.437 Å for C(B3) (a minus sign here indicates displacement towards Ir(1), a plus sign indicates displacement away from Ir(1)); these values correspond to “hinge” angles (relative to the Ir(2)–Ir(3)–Mo plane) of +6.99, –14.77 and –15.42° respectively (cf. Fig. 2).

The molecule has approximate $C_s(m)$ symmetry with the pseudo-mirror plane passing through Ir(1), Mo, the centre of the Ir(2)–Ir(3) bond, the carbonyl ligands C(M)–O(M), C(13)–O(13) and C(B1)–O(B1), C(3), and the centre of the C(1)–C(5) bond of the $\eta^5\text{-C}_5\text{H}_5$ ligand.

Other bond lengths and angles within the molecule lie within the expected ranges, viz., Ir–CO 1.871(21)–1.948(20) Å (average 1.906 ± 0.027 Å), Mo–CO 1.926(21) Å, C–O (terminal) 1.097(22)–1.181(26) Å (average 1.139 ± 0.030 Å, C–O (bridging) 1.162(23)–1.172(23) Å (average 1.166 ± 0.005 Å).

The $\eta^5\text{-C}_5\text{H}_5$ ligand is not parallel with the Ir(1)–Ir(2)–Ir(3) face of the metallatetrahedron, but is inclined at 30.33° to this face. Mo–C($\eta^5\text{-C}_5\text{H}_5$) distances range from 2.266(24) through 2.391(28) Å and the molybdenum atom lies 1.983 Å from this plane (cf. Mo–C 2.262(6)–2.353(7) and Mo \cdots centroid 1.992 Å in the simple mononuclear species $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_5\text{Cl}$ [15]).

TABLE 5. INTERATOMIC ANGLES (°) FOR (η^5 -C₅H₅)MoIr₃(CO)₁₁

<i>Angles within the metal cluster</i>			
Ir(1)–Ir(2)–Ir(3)	59.98(2)	Ir(1)–Ir(3)–Ir(2)	59.91(2)
Ir(1)–Ir(2)–Mo	63.14(4)	Ir(1)–Ir(3)–Mo	63.19(4)
Ir(3)–Ir(2)–Mo	61.45(4)	Ir(2)–Ir(3)–Mo	61.66(4)
Ir(2)–Ir(1)–Ir(3)	60.11(3)	Ir(1)–Mo–Ir(2)	56.03(3)
Ir(2)–Ir(1)–Mo	60.84(4)	Ir(2)–Mo–Ir(3)	56.88(4)
Ir(3)–Ir(1)–Mo	60.68(4)	Ir(3)–Mo–Ir(1)	56.13(3)
<i>Angles involving bridging carbonyl groups</i>			
Ir(2)–C(B1)–Ir(3)	79.76(67)	Ir(1)–Ir(2)–C(B2)	77.36(48)
Ir(2)–Ir(3)–C(B1)	50.85(53)	Ir(3)–Ir(2)–C(B2)	109.29(48)
Ir(3)–Ir(2)–C(B1)	49.39(52)	Ir(1)–Mo–C(B2)	72.72(48)
Ir(1)–Ir(2)–C(B1)	86.20(52)	Ir(3)–Mo–C(B2)	104.49(48)
Mo–Ir(2)–C(B1)	110.54(52)	Ir(3)–C(B3)–Mo	81.52(63)
Ir(1)–Ir(3)–C(B1)	87.03(53)	Ir(3)–Mo–C(B3)	50.43(49)
Mo–Ir(3)–C(B1)	112.20(53)	Mo–Ir(3)–C(B3)	48.06(47)
Ir(2)–C(B2)–Mo	81.98(63)	Ir(1)–Ir(3)–C(B3)	76.60(47)
Mo–Ir(2)–C(B2)	49.18(48)	Ir(2)–Ir(3)–C(B3)	108.29(47)
Ir(2)–Mo–C(B2)	48.84(48)	Ir(1)–Mo–C(B3)	73.27(49)
		Ir(2)–Mo–C(B3)	105.92(49)
<i>OC–metal–CO angles</i>			
C(11)–Ir(1)–C(12)	99.97(80)	C(31)–Ir(3)–C(32)	97.62(76)
C(11)–Ir(1)–C(13)	99.21(83)	C(31)–Ir(3)–C(B1)	102.49(73)
C(12)–Ir(1)–C(13)	99.35(83)	C(31)–Ir(3)–C(B3)	93.29(68)
C(21)–Ir(2)–C(22)	101.24(87)	C(32)–Ir(3)–C(B1)	97.75(79)
C(21)–Ir(2)–C(B1)	97.54(84)	C(32)–Ir(3)–C(B3)	94.20(75)
C(21)–Ir(2)–C(B2)	97.94(82)	C(B1)–Ir(3)–C(B3)	158.69(71)
C(22)–Ir(2)–C(B1)	95.47(77)	C(M)–Mo–C(B2)	82.12(77)
C(22)–Ir(2)–C(B2)	96.34(75)	C(M)–Mo–C(B3)	89.81(78)
C(B1)–Ir(2)–C(B2)	158.29(71)	C(B2)–Mo–C(B3)	145.61(69)
<i>Metal–C–O angles</i>			
Ir(1)–C(11)–O(11)	177.9(17)	Mo–C(M)–O(M)	171.0(18)
Ir(1)–C(12)–O(12)	178.8(18)	Ir(2)–C(B1)–O(B1)	139.2(16)
Ir(1)–C(13)–O(13)	176.8(18)	Ir(3)–C(B1)–O(B1)	140.9(16)
Ir(2)–C(21)–O(21)	174.5(19)	Ir(2)–C(B2)–O(B2)	132.4(14)
Ir(2)–C(22)–O(22)	176.7(17)	Mo–C(B2)–O(B2)	145.6(15)
Ir(3)–C(31)–O(31)	175.8(15)	Ir(3)–C(B3)–O(B3)	132.0(14)
Ir(3)–C(32)–O(32)	179.1(18)	Mo–C(B3)–O(B3)	146.0(15)
<i>Other angles about the metal cluster</i>			
Ir(2)–Ir(1)–C(11)	157.56(56)	Ir(3)–Ir(2)–C(22)	108.96(57)
Ir(2)–Ir(1)–C(12)	99.03(56)	Mo–Ir(2)–C(21)	142.07(66)
Ir(2)–Ir(1)–C(13)	89.36(60)	Mo–Ir(2)–C(22)	100.89(57)
Ir(3)–Ir(1)–C(11)	99.15(56)	Ir(1)–Ir(3)–C(31)	97.79(50)
Ir(3)–Ir(1)–C(12)	157.80(56)	Ir(1)–Ir(3)–C(32)	162.46(58)
Ir(3)–Ir(1)–C(13)	88.60(60)	Ir(2)–Ir(3)–C(31)	142.45(50)
Mo–Ir(1)–C(11)	102.80(56)	Ir(2)–Ir(3)–C(32)	110.58(58)
Mo–Ir(1)–C(12)	103.86(56)	Mo–Ir(3)–C(31)	138.48(50)
Mo–Ir(1)–C(13)	144.45(61)	Mo–Ir(3)–C(32)	99.52(58)
Ir(1)–Ir(2)–C(21)	95.08(66)	Ir(1)–Mo–C(M)	67.82(61)
Ir(1)–Ir(2)–C(22)	163.21(57)	Ir(2)–Mo–C(M)	112.14(61)
Ir(3)–Ir(2)–C(21)	136.07(66)	Ir(3)–Mo–C(M)	117.09(61)
<i>Angles about the η^5-C₅H₅ ring</i>			
C(2)–C(1)–C(5)	106.4(21)	C(3)–C(4)–C(5)	114.1(23)
C(1)–C(2)–C(3)	111.8(24)	C(4)–C(5)–C(1)	100.8(22)
C(2)–C(3)–C(4)	106.9(24)		

Results and discussion

Syntheses

The combination of excess $\text{CpM}(\text{CO})_3\text{H}$ ($\text{M} = \text{Mo}, \text{W}$) with $\text{Ir}(\text{CO})_2\text{Cl}$ (*p*-toluidine) in the presence of zinc provides the mixed-metal clusters $\text{CpM}\text{Ir}_3(\text{CO})_{11}$ in good yields. Co-products are the dimers $\text{Cp}_2\text{M}_2(\text{CO})_6$ and small amounts of $\text{Cp}_2\text{M}_2\text{Ir}_2(\text{CO})_{10}$. A better synthesis of $\text{Cp}_2\text{W}_2\text{Ir}_2(\text{CO})_{10}$ has been reported [4a] and its crystal structure has been described [4c]; similar information for $\text{Cp}_2\text{Mo}_2\text{Ir}_2(\text{CO})_{10}$ will be described separately. The conditions used for synthesizing $\text{CpM}\text{Ir}_3(\text{CO})_{11}$ are quite similar to those used for synthesizing $\text{Ir}_4(\text{CO})_{12}$ [16] in the absence of $\text{CpM}(\text{CO})_3\text{H}$. The formation of $\text{Ir}_2(\text{CO})_6$ and thence $\text{Ir}_4(\text{CO})_{12}$ has been proposed. In the present case the tetranuclear compounds could result from coupling of $\text{Ir}_2(\text{CO})_6$ with $\text{CpM}(\text{CO})_2\text{Ir}(\text{CO})_3$. None of these species has been observed, however.

In previous work we have shown that "lightly stabilized" species, e.g., $\text{Os}_3(\text{CO})_{12-x}\text{L}_x$ ($\text{L} = \text{NCMe}, \text{C}_8\text{H}_{14}$), are useful reactants in coupling reactions with metal hydrides [1,3]. Furthermore, the oxidative decarbonylation reagent trimethylamine oxide/acetonitrile can effect replacement of CO by NCMe. Our first attempt at synthesizing an iridium-tungsten cluster involved treating $\text{Ir}_4(\text{CO})_{12}$ first with $\text{Me}_3\text{NO}/\text{NCMe}$ (ca. 1 equiv.) and then with $\text{CpW}(\text{CO})_3\text{H}$. This provided $\text{CpW}\text{Ir}_3(\text{CO})_{11}$, but only in 7% yield; the remainder was an uncharacterized mixture. However, this procedure works well with the combination of $\text{Co}_4(\text{CO})_{12}$ (+ $\text{Me}_3\text{NO}/\text{MeCN}$) and $\text{CpMo}(\text{CO})_3\text{H}$ to give the previously known compounds $\text{CpMCo}_3(\text{CO})_{11}$. This reaction is obviously complex, but the weaker Co-Co bonds (compared with the stronger Ir-Ir bonds) may allow this vertex substitution reaction to proceed further with the cobalt compounds.

Structure and dynamics

The IR ($\nu(\text{CO})$) spectrum of solid $\text{CpMo}\text{Ir}_3(\text{CO})_{11}$ in KBr shows very strong absorptions in the region expected for bridging carbonyls, consistent with the solid state structure. Bands in this region are relatively much weaker in the solution spectrum, suggesting the possibility that isomers with fewer or even no bridging carbonyls are accessible in solution. The solution IR spectrum of $\text{CpW}\text{Ir}_3(\text{CO})_{11}$ shows no evidence for even semi-bridging carbonyls; however, the ^{13}C NMR spectrum shows that the carbonyls exchange rapidly over all positions in the molecule ($J_{\text{avg}}(\text{W}-\text{C})$ 14 Hz) which implies that bridged forms, possibly analogous to those displayed by $\text{CpMo}\text{Ir}_3(\text{CO})_{11}$ and $\text{CpMoCo}_3(\text{CO})_{11}$ in the solid state (cf. 1 and 3), are readily accessible.

Acknowledgements

This work was supported at the University of Illinois by grants from the National Science Foundation to the Materials Research Laboratory (NSF DMR 80-20250 and 83-16981).

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