dihedral angles in $Rh_2(OAc)_4py$, β-$Cu_2(OAc)_4(py)_2$, α-$Cu_2(OAc)_4(py)_2$, $Cr(O_2CH)_4(py)_2$, and $Mo_2(O_2CCF_3)_4(py)_2$ are +33 and −26°, +33 and −26°, 30°, 30°, and 0°. However, if a pyridine ligand does have π interactions with the metal d_{az} or d_{bz} orbitals, the symmetry is immediately reduced from C_4 to C_2 and the d_{az} and d_{bz} orbitals are no longer degenerate, and this is communicated through the metal–metal bonding region to the opposite side. As the second pyridine π^* orbital will interact most effectively with the metal d_{az} or d_{bz} orbital nearest to it in energy, it should assume an orientation orthogonal to that of the first pyridine ring—one py will utilize the d_{az} of metal atom 1 and the other the d_{bz} of metal atom 2.

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Preparation and Characterization of Organoiridium Cluster Compounds from the Reaction of Dodecacarbonyltetrairidium with 1,5-Cyclooctadiene. Crystal Structure of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$

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The reaction of $Ir_4(CO)_{12}$ with 1,5-cyclooctadiene in refluxing chlorobenzene provides $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ as the major product together with $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ in trace amounts. Single-crystal X-ray diffraction has shown $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ to have a *closo*-Ir_4C_2 pseudooctahedral framework analogous to that of $Co_4(CO)_{10}(C_2Et_2)$. The use of $Me_3NO{\cdot}2H_2O$ as an oxidative decarbonylation reagent allows formation of the derivatives $Ir_4(CO)_{12-2x}(C_8H_{12})_x$ (x = 1–3) under relatively mild conditions. The ^{13}C NMR spectra of these complexes completely define the solution structures. Thermal decomposition of both $Ir_4(CO)_8(C_8H_{12})_2$ and $Ir_4(CO)_6(C_8H_{12})_3$ affords $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$, which reacts further with 1,5-cyclooctadiene to give $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$. The ^{13}C NMR spectra at several temperatures for $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ show two distinct carbonyl scrambling processes, which can be explained by a carbonyl scrambling mechanism related to that previously proposed for $Co_4(CO)_{10}(C_2Et_2)$. The structure inferred for $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ from ^{13}C NMR and that determined separately for $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ by X-ray diffraction suggest a pathway for the transformation of tetrahedral $Ir_4(CO)_{12}$ into pseudooctahedral $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$.

Reactions of iron triad metal carbonyl cluster compounds $M_3(CO)_{12}$ (M = Fe, Ru, Os) and $H_4M_4(CO)_{12}$ (M = Ru, Os) with unsaturated organic substrates have received considerable attention; activation of C–H bonds has proved to be a characteristic feature.[1] Less attention has been devoted to examination of analogous reactions for carbonyl clusters in the cobalt triad. The reactions of $YCCo_3(CO)_9$ (Y = alkyl, aryl, or F) with norbornadiene and 1,3-cyclohexadiene give products characterized as $YCCo_3(CO)_7$(diene); with cyclopentadiene, however, $YCCo_3(CO)_4(C_5H_5)_2$ is isolated.[2a–c] Simple substitution products from the reaction of $YCCo_3(CO)_9$ with trienes,[2c] arenes,[2d] and cyclooctatetraene[3] also have been reported. The reactions of $Rh_4(CO)_{12}$ with 1,5-cyclooctadiene, norbornadiene, 1,4-cyclohexadiene, and 2,3-dimethyl-1,3-butadiene afford hexanuclear products formulated as $Rh_6(CO)_{14}$(diene).[4] Additionally, the compounds $Rh_6(CO)_{12}$(norbornadiene)$_2$ and $Rh_6(CO)_{10}$(norbornadiene)$_3$ have been mentioned.[5] However, treatment of $Co_4(CO)_{12}$ with the above dienes gives dinuclear $Co_2(CO)_4$(diene)$_2$.[4] Compounds formulated as $Co_4(CO)_9(C_7H_8)$, $Co_4(CO)_6(C_7H_8)_2$, and $Rh_4(CO)_8(C_8H_8)$ also have been reported,[4] along with a number of compounds of the general formulation $Co_4(CO)_9$(arene).[6–8] Finally, the reaction of substituted acetylenes with $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ gives $M_4(CO)_{10}(C_2R_2)$.[9–12]

In the course of a general survey of the chemistry of $Ir_4(CO)_{12}$, we have isolated a number of cluster compounds from the reaction of $Ir_4(CO)_{12}$ with 1,5-cyclooctadiene. Some of these compounds are simply substitution products, but others are formed as the result of C–H bond scission in the organic ligand. We report here the preparation, characterization, and some interconversions of these new cluster compounds together with the crystal structure of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$.

Experimental Section

$Ir_4(CO)_{12}$ was prepared by a published method.[13] $Me_3NO{\cdot}2H_2O$ (Aldrich) was used as received. Solvents were obtained commercially and generally used without further purification. 1,5-Cyclooctadiene (Aldrich) was passed over alumina prior to use. Preparative-scale TLC plates were prepared with Merck silica gel G.

Infrared spectra were recorded on a Perkin-Elmer 467 spectrophotometer. ^{13}C NMR spectra were recorded on a JEOL FX-60 spectrometer (15 MHz) with Cr(acac)$_3$ (ca. 0.03 M) added as a relaxation agent. ^1H NMR spectra were recorded on Varian HR-220 (200 MHz), Varian HA-100 (100 MHz), and JEOL FX-60 (60 MHz) spectrometers. Electron impact mass spectra were obtained by Mr. Joe Wrona on a Varian-MAT CH-5 mass spectrometer using an ionizing voltage of 70 eV. Field-desorption mass spectra were determined by Mr. Carter Cook on a Varian 731 mass spectrometer. Microanalyses were performed by the University of Illinois analytical laboratory under the direction of Mr. Joseph Nemeth.

$Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ and $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$. To a refluxing solution of chlorobenzene (50 mL) and 1,5-cyclooctadiene (2 mL) was added solid $Ir_4(CO)_{12}$ (250 mg). The resulting solution was heated at reflux under nitrogen for 18 h. The solvent was then removed at reduced pressure to give a brown oil, and the oil chromatographed on a Florisil column. Elution with pentane generated a small green fraction. Further purification of this fraction by preparative-scale TLC (pentane) led to green $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ (16 mg, 3.5%) as well as yellow $Ir_4(CO)_8(C_8H_{12})_2$ (2 mg, 0.7%) which was identified on the basis of its mass spectrum. Further elution from the column with pentane–dichloromethane (1:1) gave a dark brown-orange band. This fraction was collected and purified further by preparative-scale TLC (pentane–dichloromethane, 3:1) to give a pink solid (1.5 mg, 0.5%), formulated as $Ir_4(CO)_6(C_8H_{12})_2(C_8H_{10})$ on the basis of mass spectrometry, and brown $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ (121 mg, 43%). Elution from the column with dichloromethane gave a brown-black band. Purification of this fraction by preparative-scale TLC (pentane–dichloromethane, 1:2)

0020-1669/78/1317-2596$01.00/0

gave a black solid (18 mg) which remains unidentified. Spectroscopic data for $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$: IR (cyclohexane) ν_{CO} 2062 (m), 2029 (vs), 2013 (m), 1999 (m), 1988 (w), 1967 (w), 1821 (m) cm^{-1}; mass spectrum (^{193}Ir, field-desorption mode) *m/e* 2008 (M^+); ^1H NMR ($CDCl_3$) τ 5.00 (m, 1 H), 5.51 (m, 1 H), 5.74 (m, 1 H), 5.99 (m, 1 H), 6.42 (m, 1 H), 6.76 (m, 4 H), 7.50 (m, 2 H), 7.86 (m, 2 H), 7.98 (m, 4 H), 8.16 (m, 4 H), 8.36 (m, 12 H). Anal. Calcd for $C_{29}H_{34}O_5Ir_4$: C, 28.28; H, 2.78. Found: C, 28.03; H, 2.86. Spectroscopic data for $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$: IR (cyclohexane) ν_{CO} 2032 (s), 1983 (s), 1980 (s), 1861 (s), 1825 (s) cm^{-1}; mass spectrum (^{193}Ir) *m/e* 1234 (M^+), 1206 ($M^+ - CO$), 1178 ($M^+ - 2CO$), 1148 ($M^+ - 3CO - H_2$), 1118 ($M^+ - 4CO - 2H_2$), extensive fragmentation at lower *m/e* values; ^1H NMR ($CDCl_3$) τ 5.65 (m, 10 H), 7.35 (m, 24 H). Unidentified black solid: IR (cyclohexane) ν_{CO} 2060 (m), 2029 (s), 2025 (s), 2019 (s), 2005 (m), 1995 (m), 1858 (m) cm^{-1}.

Shorter reaction times led to significantly different product distributions. A solution of chlorobenzene (150 mL) and 1,5-cyclooctadiene (3 mL) was heated to reflux under N_2. To this stirred solution was added $Ir_4(CO)_{12}$ (300 mg). This solution was heated at reflux under N_2 for 1.5 h. The solvent was then removed at reduced pressure and the brown oil extracted with 10 mL dichloromethane. This left unreacted $Ir_4(CO)_{12}$ (124 mg). The dichloromethane extract was concentrated and purified by preparative-scale TLC (pentane (3 elutions) and then pentane–dichloromethane, 5:1). This provided green $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ (6.5 mg, 1%), yellow $Ir_4(CO)_{10}(C_8H_{12})$ (9 mg, 5%, identified by mass spectrometry), pink $Ir_4(CO)_6(C_8H_{12})_2(C_8H_{10})$ (7 mg, 3.5%), brown $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ (13 mg, 7%, identified by mass spectrometry), $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ (57 mg, 29%), and a trace amount of an unidentified black solid which had an infrared spectrum identical with the spectrum of the black solid obtained from the 18-h reaction. Additionally, several other products were observed in very low yield which were not identified. Spectroscopic data for $Ir_4(CO)_6(C_8H_{12})_2(C_8H_{10})$: IR (cyclohexane) ν_{CO} 2061 (s), 2032 (s, br), 2005 (m), 1993 (m), 1843 (w), 1837 (w) cm^{-1}; mass spectrum (^{193}Ir) *m/e* 1262 (M^+), 1234 ($M^+ - CO$), 1206 ($M^+ - 2CO$), 1178 ($M^+ - 3CO$), 1148 ($M^+ - 4CO - H_2$), 1116 ($M^+ - 5CO - 3H_2$), extensive fragmentation at lower *m/e* values.

$Ir_4(CO)_{10}(C_8H_{12})$ and $Ir_4(CO)_8(C_8H_{12})_2$. A solution of THF (200 mL) and 1,5-cyclooctadiene (1 mL) was heated to reflux under nitrogen. Solid $Ir_4(CO)_{12}$ (100 mg) was added and the mixture stirred vigorously until all of the $Ir_4(CO)_{12}$ had dissolved. Then $Me_3NO{\cdot}2H_2O$ (10.0 mg) was added, and heating was continued for 10 min. The solvent was removed at reduced pressure to give a yellow oil. Extraction with dichloromethane (2 mL) left unreacted $Ir_4(CO)_{12}$ (35 mg). The recovered $Ir_4(CO)_{12}$ was treated as before (THF (200 mL), 1,5-cyclooctadiene (1 mL), $Me_3NO{\cdot}2H_2O$ (3.5 mg)) and the dichloromethane-soluble extract was combined with the extract from the first reaction. The products were then separated by preparative-scale TLC (pentane), affording yellow $Ir_4(CO)_{10}(C_8H_{12})$ (38 mg, 36%) and orange $Ir_4(CO)_8(C_8H_{12})_2$ (30 mg, 32%). Since the R_f values were 0.25 and 0.20, respectively, several consecutive elutions were necessary to achieve complete separation. Anal. Calcd for $C_{18}H_{12}O_{10}Ir_4$: C, 18.68; H, 1.05. Found: C, 19.22; H, 1.22. Calcd for $C_{24}H_{24}O_8Ir_4$: C, 23.84; H, 2.00. Found: C, 23.75; H, 2.12. Spectroscopic data for $Ir_4(CO)_{10}(C_8H_{12})$: IR (cyclohexane) ν_{CO} 2090 (m), 2074 (w), 2060 (s), 2025 (m), 2019 (s), 1884 (w), 1836 (s), 1820 (s) cm^{-1}; mass spectrum (^{193}Ir) *m/e* 1160 (M^+), 1132 ($M^+ - CO$), 1104 ($M^+ - 2CO$), 1076 ($M^+ - 3CO$), 1046 ($M^+ - 4CO - H_2$), 1018 ($M^+ - 5CO - H_2$), 988 ($M^+ - 6CO - 2H_2$), 960 ($M^+ - 7CO - 2H_2$), 930 ($M^+ - 8CO - 3H_2$), 902 ($M^+ - 9CO - 3H_2$), 874 ($M^+ - 10CO - 3H_2$); ^1H NMR ($CDCl_3$) τ 5.94 (m, 4 H), 7.13 (m, 4 H), 7.94 (m, 4 H). Spectroscopic data for $Ir_4(CO)_8(C_8H_{12})_2$: IR (cyclohexane) ν_{CO} 2067 (s), 2044 (s), 2037 (sh), 2006 (m), 1999 (m), 1990 (m), 1980 (m), 1821 (s), 1797 (s) cm; mass spectrum (^{193}Ir) *m/e* 1212 (M^+), 1184 ($M^+ - CO$), 1154 ($M^+ - 2CO - H_2$), 1126 ($M^+ - 3CO - H_2$), 1096 ($M^+ - 4CO - 2H_2$), 1068 ($M^+ - 5CO - 2H_2$), extensive fragmentation at lower *m/e* values; ^1H NMR ($CDCl_3$) τ 5.44 (m, 4 H), 6.51 (m, 4 H), 7.14 (m, 8 H), 8.06 (m, 8 H).

$Ir_4(CO)_6(C_8H_{12})_3$. To a solution of $Ir_4(CO)_{10}(C_8H_{12})$ (25 mg) in 1,5-cyclooctadiene (3 mL) was added $Me_3NO{\cdot}2H_2O$ (20 mg). The solution was heated under nitrogen with stirring at 100 °C for 5 min. The 1,5-cyclooctadiene was removed at reduced pressure and the residue extracted with dichloromethane (1 mL). The orange crystals remaining were dissolved in dichloromethane (15 mL), and the solution was filtered. Removal of the solvent gave orange $Ir_4(CO)_6(C_8H_{12})_3$ (8 mg, 29%). Anal. Calcd for $C_{30}H_{36}O_6Ir_4$: C, 28.56; H, 2.88. Found: C, 28.71; H, 2.99. Spectroscopic data: IR (chloroform) ν_{CO} 2038 (w), 1976 (m), 1780 (m) cm^{-1}; mass spectrum (^{193}Ir) *m/e* 1264 (M^+), 1236 ($M^+ - CO$), 1206 ($M^+ - 2CO - H_2$), 1178 ($M^+ - 3CO - H_2$), 1148 ($M^+ - 4CO - 2H_2$), 1118 ($M^+ - 5CO - 3H_2$), extensive fragmentation at lower *m/e* values; ^1H NMR ($CDCl_3$) τ 5.62 (m, 6 H), 6.59 (m, 6 H), 7.20 (m, 12 H), 7.76 (m, 12 H).

Pyrolysis of $Ir_4(CO)_{10}(C_8H_{12})$. A solution of $Ir_4(CO)_{10}(C_8H_{12})$ (20 mg) in cyclohexane (30 mL) was refluxed under nitrogen for 24 h. Only an insoluble black precipitate was formed and no carbonyl-containing products were isolated.

Pyrolysis of $Ir_4(CO)_8(C_8H_{12})_2$. A solution of $Ir_4(CO)_8(C_8H_{12})_2$ (20 mg) in cyclohexane after refluxing under nitrogen for 24 h was brown. The solvent was removed at reduced pressure and the brown oil purified by preparative-scale TLC. Elution with petroleum ether (bp 60–68 °C)–dichloromethane (1:1) provided $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ (6 mg, 30%) as a brown solid and also unidentified black solid. Anal. Calcd for $C_{23}H_{22}O_7Ir_4$: C, 23.43; H, 1.88. Found: C, 23.56; H, 1.98. Spectroscopic data: IR (cyclohexane) ν_{CO} 2059 (m), 2031 (s), 1995 (m, br), 1872 (m), 1854 (m) cm^{-1}; mass spectrum (^{193}Ir) *m/e* 1182 (M^+), 1154 ($M^+ - CO$), 1126 ($M^+ - 2CO$), 1098 ($M^+ - 3CO$), 1068 ($M^+ - 4CO - H_2$), 1036 ($M^+ - 5CO - 3H_2$), 1006 ($M^+ - 6CO - 4H_2$), extensive fragmentation at lower *m/e* values; ^1H NMR ($CDCl_3$) τ 5.51 (m, 2 H), 5.77 (m, 4 H), 7.10 (m, 8 H), 7.74 (m, 8 H).

Pyrolysis of $Ir_4(CO)_6(C_8H_{12})_3$. A solution of $Ir_4(CO)_6(C_8H_{12})_3$ (14 mg) in cyclohexane was refluxed under nitrogen for 3 h. The solvent was removed from the resulting brown solution and the brown oil purified by preparative-scale TLC. Elution with petroleum ether (bp 60–68 °C)–dichloromethane (1:1) gave $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ (4 mg, 31%) and an unidentified black solid.

Reaction of $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ with 1,5-Cyclooctadiene. Treatment of $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ (8 mg) with 1,5-cyclooctadiene (1 mL) in refluxing cyclohexane (25 mL) for 5 h gave a brown solution. The solvent was removed at reduced pressure and the brown oil purified by TLC (pentane–dichloromethane, 1:1) providing unreacted $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ (3 mg) and $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ (4 mg, 50%).

Pyrolysis of $Ir_4(CO)_6(C_8H_{12})_2(C_8H_{10})$. $Ir_4(CO)_6(C_8H_{12})_2(C_8H_{10})$ (7.0 mg) was heated in chlorobenzene at reflux under N_2 for 15 min. The solution rapidly turned light brown. The solvent was removed and the brown oil was applied to a preparative-scale TLC plate. Elution with first pentane and then dichloromethane gave no isolable products.

Structure Determination. A crystal of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ with dimensions 0.13 × 0.26 × 0.39 mm was chosen for crystallographic analysis. Preliminary photographs indicated monoclinic symmetry with systematic absences of $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, consistent with space group $P2_1/n$. The crystal was mounted and aligned on a Syntex $P\bar{1}$ automated diffractometer. The refined settings of 15 reflections with 2θ values greater than 20° were used to calculate cell and other crystal parameters: $a = 12.097$ (2) Å, $b = 18.602$ (5) Å, $c = 12.422$ (2) Å, $\beta = 96.07$ (1)°, $V = 2779.5$ (6) $Å^3$, $Z = 4$, mol wt 1231.4, ρ(calcd) = 2.942 g cm^{-3}, ρ(exptl) = 2.9 (2) g cm^{-3}. A complete set of intensity data was collected using Mo Kα radiation within the angular range $3° \leq 2\theta \leq 50°$. The θ–2θ scan technique was used with a fixed scan rate of 4°/min. Scans ranged from 0.6° below the Kα_1 2θ setting to 0.7° above Kα_2. Four check reflections were monitored after every 96 reflections measured. Their variation in intensity over the time required to collect data was less than 2.5%. A total of 5326 reflections was measured. Data were processed by procedures described previously[14] and corrected for absorption effects. The linear absorption coefficient was calculated to be 203.01 cm^{-1}; transmission coefficients ranged from 0.019 to 0.105.

Crude positional parameters of the four iridium atoms were determined from a Patterson map. Positions of all other nonhydrogen atoms of the structure were determined from a difference Fourier map calculated with phases of the four metal atoms. Three cycles of isotropic refinement on the complete structure converged with $R_F = 0.068$ and $R_{wF} = 0.079$, where $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The function minimized during refinement was $\sum w(|F_o| - |F_c|)$[15] with weights calculated by the equation $w = 4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors used for nonhydrogen atoms were those of Cromer and Waber;[15] hydrogen scattering factors were taken from Stewart et al.[16] Corrections for anomalous dispersion of the Ir atoms were made with values of $\Delta f'$

Table I. Positional and Thermal Parameters for the Atoms of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$

atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir(1)	0.60560 (5)	0.25935 (3)	0.17670 (5)	39.9 (4)	20.10 (21)	33.1 (4)	5.44 (24)	12.3 (3)	2.23 (23)
Ir(2)	0.48197 (5)	0.27842 (3)	0.34258 (5)	46.6 (4)	19.07 (21)	29.7 (4)	1.43 (24)	13.4 (3)	3.95 (23)
Ir(3)	0.57516 (5)	0.39629 (3)	0.24712 (5)	33.1 (4)	17.93 (20)	28.4 (4)	−2.37 (22)	5.5 (3)	1.24 (22)
Ir(4)	0.35147 (4)	0.37930 (3)	0.22960 (5)	31.5 (4)	18.97 (21)	33.5 (4)	0.73 (22)	8.2 (3)	−2.19 (23)
C(1)	0.5310 (13)	0.3140 (10)	0.4856 (13)	61.2 (13)	27.6 (6)	31.4 (12)	9.4 (7)	14.7 (10)	11.3 (7)
O(1)	0.5578 (13)	0.3405 (8)	0.5649 (10)	153.0 (15)	38.8 (6)	29.6 (9)	−5.3 (8)	3.8 (10)	−2.5 (6)
C(2)	0.3782 (14)	0.2123 (10)	0.3876 (13)	73.1 (15)	29.9 (6)	43.4 (12)	−12.8 (8)	36.0 (11)	−2.9 (7)
O(2)	0.3159 (13)	0.1735 (8)	0.4204 (12)	140.6 (15)	38.2 (6)	103.2 (13)	−34.9 (8)	76.9 (12)	0.4 (7)
C(3)	0.7555 (13)	0.2505 (11)	0.1692 (16)	39.5 (11)	36.9 (7)	77.8 (16)	6.4 (7)	32.2 (11)	−12.0 (8)
O(3)	0.8487 (10)	0.2398 (10)	0.1589 (14)	50.3 (10)	59.1 (8)	141.2 (17)	8.7 (7)	21.5 (10)	−16.0 (9)
C(4)	0.6108 (17)	0.2061 (12)	0.3187 (13)	108.2 (17)	41.3 (8)	37.8 (11)	9.4 (10)	24.0 (11)	4.6 (7)
O(4)	0.6638 (15)	0.1607 (10)	0.3672 (12)	195.8 (19)	59.3 (7)	72.3 (13)	68.0 (10)	63.2 (13)	35.2 (8)
C(5)	0.4505 (11)	0.4466 (8)	0.3222 (13)	30.6 (10)	14.6 (5)	58.4 (13)	3.9 (5)	5.0 (9)	3.1 (6)
O(5)	0.4402 (10)	0.4914 (7)	0.3896 (10)	72.9 (10)	35.1 (5)	72.8 (11)	3.2 (6)	15.2 (8)	−32.1 (6)
C(6)	0.4222 (11)	0.2772 (8)	0.1757 (12)	29.5 (9)	20.0 (5)	37.8 (11)	−2.7 (6)	17.1 (8)	−5.1 (6)
C(7)	0.4792 (12)	0.3380 (8)	0.1265 (11)	47.6 (10)	12.5 (4)	19.3 (10)	10.1 (6)	−0.1 (8)	0.3 (5)
C(8)	0.4660 (13)	0.3471 (10)	−0.0017 (12)	54.6 (12)	34.3 (7)	15.7 (10)	9.7 (7)	2.7 (8)	−0.5 (6)
C(9)	0.4992 (15)	0.2784 (11)	−0.0572 (13)	91.5 (16)	38.2 (7)	17.3 (11)	26.0 (8)	−3.8 (10)	−2.4 (7)
C(10)	0.5769 (14)	0.2277 (10)	0.0084 (13)	65.7 (13)	29.3 (7)	27.6 (11)	1.0 (8)	3.2 (10)	−5.3 (7)
C(11)	0.5476 (14)	0.1685 (9)	0.0757 (13)	68.1 (13)	25.0 (6)	39.3 (12)	14.5 (7)	13.8 (11)	−3.7 (7)
C(12)	0.4244 (15)	0.1519 (10)	0.0983 (15)	73.6 (14)	23.2 (6)	55.1 (15)	−12.3 (7)	3.0 (11)	−5.5 (7)
C(13)	0.3548 (14)	0.2190 (10)	0.1130 (15)	53.7 (12)	25.9 (6)	57.3 (15)	−3.7 (7)	−9.8 (11)	−6.2 (8)
C(14)	0.2297 (15)	0.3987 (10)	0.3373 (16)	70.3 (14)	25.7 (6)	76.4 (15)	−1.2 (8)	42.5 (12)	−10.9 (8)
C(15)	0.1972 (13)	0.3373 (10)	0.2704 (16)	30.1 (11)	26.3 (6)	98.6 (18)	−3.4 (6)	25.7 (11)	−1.2 (8)
C(16)	0.1060 (15)	0.3395 (14)	0.1681 (20)	42.6 (13)	56.1 (10)	125.4 (23)	−4.6 (9)	8.8 (14)	−32.7 (13)
C(17)	0.1175 (16)	0.4070 (15)	0.1002 (19)	57.5 (14)	64.4 (11)	87.7 (19)	13.9 (10)	−11.4 (13)	−22.2 (12)
C(18)	0.2356 (14)	0.4277 (14)	0.0996 (15)	39.6 (12)	66.5 (10)	48.2 (14)	16.4 (9)	−12.0 (10)	10.3 (10)
C(19)	0.2815 (13)	0.4798 (11)	0.1629 (14)	51 (12)	37 (7)	44 (13)	13 (8)	−17 (10)	16 (8)
C(20)	0.2254 (16)	0.5245 (11)	0.2484 (17)	83.1 (17)	33.3 (7)	79.0 (17)	13.6 (9)	27.5 (14)	−13.0 (9)
C(21)	0.1708 (16)	0.4721 (10)	0.3299 (13)	74.6 (16)	26.8 (7)	64.2 (15)	18.7 (8)	21.2 (13)	−4.4 (8)
C(22)	0.6802 (12)	0.4440 (9)	0.1363 (13)	46.4 (11)	24.3 (6)	48.9 (12)	−15.4 (7)	22.2 (10)	−0.6 (7)
C(23)	0.6023 (15)	0.4956 (9)	0.1628 (13)	84.4 (15)	21.4 (6)	40.9 (13)	−17.4 (8)	8.0 (11)	6.5 (7)
C(24)	0.6276 (16)	0.5584 (10)	0.2379 (15)	97.7 (17)	23.8 (6)	60.0 (15)	−19.1 (8)	12.1 (13)	−4.7 (7)
C(25)	0.6928 (15)	0.5338 (10)	0.3530 (17)	62.5 (14)	21.9 (6)	87.3 (17)	−8.1 (7)	−19.8 (12)	4.7 (8)
C(26)	0.6696 (13)	0.4580 (10)	0.3799 (14)	43.5 (11)	27.8 (6)	47.3 (13)	−11.9 (7)	3.2 (10)	−4.6 (7)
C(27)	0.7355 (12)	0.3969 (11)	0.3491 (15)	31.3 (11)	39.4 (7)	59.9 (14)	0.7 (7)	−13.7 (9)	−0.6 (8)
C(28)	0.8369 (14)	0.4078 (12)	0.2870 (17)	42.9 (12)	46.1 (9)	92.2 (19)	−10.6 (8)	8.9 (12)	7.6 (10)
C(29)	0.8071 (15)	0.4492 (11)	0.1793 (17)	60.1 (14)	33.1 (7)	88.8 (18)	−12.3 (8)	9.1 (13)	16.5 (9)

[a] Estimated standard deviations in the least significant figures are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The quantities given in the table are the thermal coefficients $\times 10^4$.

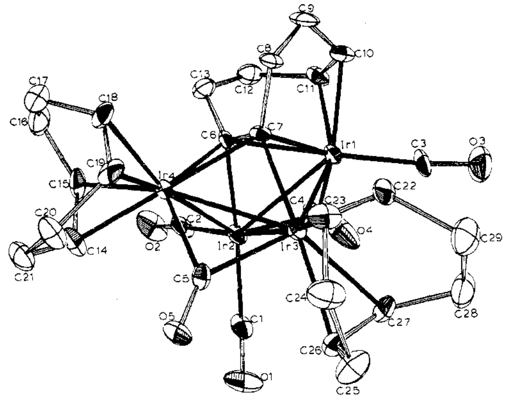


Figure 1. Structure of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$.

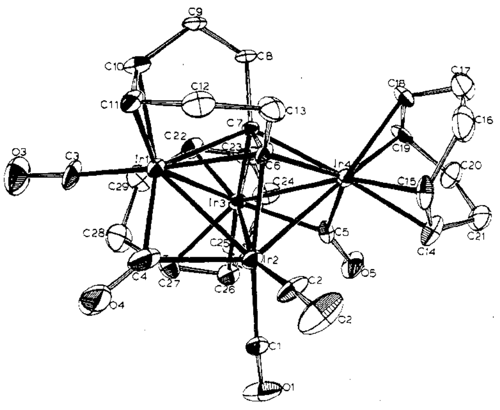


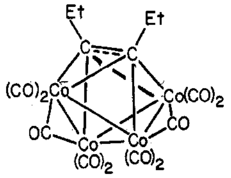
Figure 2. Structure of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ viewed from a different perspective.

and $\Delta f''$ taken from Cromer and Liberman.[17] Four cycles of refinement with anisotropic thermal parameters assigned to all atoms converged with $R_F = 0.034$ and $R_{wF} = 0.044$. In all calculations only the 3163 reflection with $F_o^2 > 3\sigma(F_o^2)$ were included. The final value for the standard deviation of an observation of unit weight was 1.37. Final positional and thermal parameters are listed in Table I. A table of observed and calculated structure factor amplitudes is available as supplementary material.

Results and Discussion

Structural Aspects of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$. The crystal structure of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ consists of molecular units with no unusually short intermolecular contacts. Drawings of the molecule are presented in Figures 1 and 2.

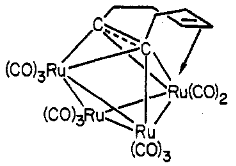
Atomic coordinates and thermal parameters are contained in Table I; intramolecular bond lengths and angles are contained in Tables II and III. The four metal atoms are in the "butterfly" geometry associated with alkyne adducts of tetrametallic clusters. This structural unit was first characterized by Dahl in $Co_4(CO)_{10}(C_2Et_2)$ (I),[18] the product of diethylacetylene insertion into one Co–Co bond of $Co_4(CO)_{12}$.[10] Formally, the acetylenic moiety can be viewed as contributing one electron to each metal center.[19] In this formalism both $Co_4(CO)_{10}(C_2Et_2)$ and $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ are two electrons short of saturation. Alternatively, the four metal atoms and the two bridging carbon atoms can be viewed as



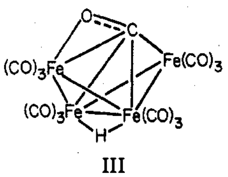
I

a hexanuclear cluster framework. Thus, according to Wade's formalism,[20] seven electron pairs are available for skeletal bonding and the *closo*-octahedral arrangement of the M_4C_2 framework is rationalized. Both $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ and $Co_4(CO)_{10}(C_2Et_2)$ have unsymmetrical carbonyl ligands bridging opposite edges of the M_4 unit, despite the lower tendency for bridged carbonyl structures among clusters of third-row metals. In both cases, the unsymmetrical bridging carbonyls have shorter bonds to the metal atoms at the apex of each M_3 plane. The average bond length between Ir(1)–C(4) and Ir(4)–C(5) is 2.02 Å. The average bond length to the iridium atoms at the fold between the Ir_3 planes (Ir(2) and Ir(3)) is slightly longer (2.09 Å). The corresponding average cobalt–carbon lengths in $Co_4(CO)_{10}(C_2Et_2)$ are 1.84 and 1.97 Å, respectively.[18]

The C_8H_{10} cycloocta-1-ene-5-yne ligand found in $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ also is found in $Ru_4(CO)_{11}(C_8H_{10})$ (II),[21] which was obtained as one product of the reaction between 1,5-cyclooctadiene and $H_4Ru_4(CO)_{12}$.[22] In both structures the acetylenic carbon atoms are bound to all four metal atoms, whereas the "ene" moiety bonds normally with one metal center. Bond lengths between iridium atoms along outer edges of the Ir_4 unit in $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ range from 2.695 (1) to 2.741 (1) Å with the two carbonyl-bridged bonds slightly shorter (2.695 (1), 2.710 (1) Å) than the nonbridged bonds (2.731 (1), 2.741 (1) Å). These values are within the range of single-bond lengths found in $Ir_4(CO)_{12}$ (2.68 Å),[23] $Ir_4(CO)_{10}(PPh_3)_2$ and $Ir_4(CO)_9(PPh_3)_3$ (both 2.73 Å),[24] and $[Ir(NO)_2(PPh_3)]_2$ (2.717 (1) Å).[25] The Ir(2)–Ir(3) bond between iridium atoms at the fold between the Ir_3 planes (2.787 (1) Å) is longer than the others, and this seems to be a pattern present in the two related M_4C_2 clusters. In $Ru_4(CO)_{11}(C_8H_{10})$ this value is 2.823 Å, whereas edge bond lengths range from 2.73 to 2.75 Å. Edge Co–Co lengths in $Co_4(CO)_{10}(Et_2C_2)$ vary from 2.416 (5) to 2.450 (5) Å, but the distance between the fold cobalt atoms is 2.552 (5) Å. Within this series it appears that alkyne insertion into one edge of the M_4 tetrahedron weakens the opposite M–M bond. This may be related chemically to the facility with which $Co_4(CO)_{10}(C_2RR')$ clusters dissociate to form Co_2 species.[10] The origin of bond lengthening at this position appears not to be steric. All carbon–carbon lengths in bicyclobutane are equal[26] and Fe–Fe lengths in the electronically saturated butterfly cluster $Fe_4(CO)_{13}H^-$ (III) are reportedly equivalent.[27] The absence of an unusually long length between the iron atoms at the fold is particularly surprising in view of the presumed hydride bridge associated with this bond. Bridging hydride ligands generally serve to lengthen metal–metal bonds.[28]



II



III

Table II. Intramolecular Bond Distances (Å) in $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$

Metal-Metal Separations			
Ir(1)–Ir(2)	2.695 (1)	Ir(2)–Ir(4)	2.741 (1)
Ir(1)–Ir(3)	2.731 (1)	Ir(3)–Ir(4)	2.710 (1)
Ir(2)–Ir(3)	2.787 (1)	Ir(1)–Ir(4)	3.910 (1)
Carbonyl Ligands			
Ir(1)–C(3)	1.83 (1)	Ir(4)–C(5)	2.01 (1)
Ir(2)–C(1)	1.93 (1)	C(1)–O(1)	1.12 (2)
Ir(2)–C(2)	1.88 (1)	C(2)–O(2)	1.15 (2)
Ir(1)–C(4)	2.02 (1)	C(3)–O(3)	1.16 (2)
Ir(2)–C(4)	2.10 (1)	C(4)–O(4)	1.19 (2)
Ir(3)–C(5)	2.08 (1)	C(5)–O(5)	1.19 (2)
Diene Ligands			
Ir(1)–C(6)	2.24 (1)	C(10)–C(11)	1.45 (2)
Ir(1)–C(7)	2.16 (1)	C(11)–C(12)	1.57 (2)
Ir(4)–C(6)	2.21 (1)	C(12)–C(13)	1.53 (2)
Ir(4)–C(7)	2.24 (1)	C(13)–C(6)	1.52 (2)
Ir(2)–C(6)	2.12 (1)	C(14)–C(15)	1.44 (2)
Ir(3)–C(7)	2.10 (1)	C(15)–C(16)	1.59 (3)
Ir(1)–C(10)	2.16 (1)	C(16)–C(17)	1.53 (3)
Ir(1)–C(11)	2.18 (1)	C(17)–C(18)	1.48 (2)
Ir(3)–C(22)	2.16 (1)	C(18)–C(19)	1.33 (3)
Ir(3)–C(23)	2.17 (1)	C(19)–C(20)	1.55 (2)
Ir(3)–C(26)	2.22 (1)	C(20)–C(21)	1.59 (3)
Ir(3)–C(27)	2.20 (1)	C(21)–C(14)	1.54 (2)
Ir(4)–C(14)	2.12 (1)	C(22)–C(23)	1.41 (2)
Ir(4)–C(15)	2.13 (1)	C(23)–C(24)	1.51 (2)
Ir(4)–C(18)	2.21 (1)	C(24)–C(25)	1.62 (3)
Ir(4)–C(19)	2.18 (1)	C(25)–C(26)	1.48 (2)
C(6)–C(7)	1.49 (2)	C(26)–C(27)	1.46 (2)
C(7)–C(8)	1.59 (2)	C(27)–C(29)	1.53 (2)
C(8)–C(9)	1.53 (2)	C(28)–C(29)	1.55 (2)
C(9)–C(10)	1.51 (2)	C(29)–C(22)	1.57 (2)

The coordination plane at Ir(4) formed by the centers of the cycloocta-1,5-diene olefin groups is at right angles to the related plane at Ir(1) formed by the olefin bond C(10)–C(11) and the terminal carbonyl ligand. Carbonyl carbon C(3) is located approximately trans to C(6)–C(7) at Ir(1), whereas the site trans to C(6)–C(7) at Ir(4) is vacant. Nevertheless, these is no significant structural difference between the bonds of the C(6)–C(7) moiety to Ir(1) and Ir(4). The diene coordination at Ir(4) is somewhat unsymmetrical; distances to C(18) and C(19) of 2.20 (1) Å are slightly longer than the C(14) and C(15) values of 2.13 (1) Å. The origin of this structural feature is unclear, although, it may be related to the presence of the bridging carbonyl ligand along the Ir(3)–Ir(4) bond or an interaction between hydrogen atoms on carbons C(8) and C(18). The separation between C(8) and C(18) is 3.32 Å. Similar inequalities exist for the diene groups at Ir(3) and terminal carbonyl ligands at Ir(2). We have previously noted lengthening of carbonyl bonds under similar bonding conditions in $Os_3(CO)_{10}(C_2Ph_2)$.[14] At both metal centers containing Os–C alkyne σ bonds, lengths to trans carbonyl ligands are 0.05 to 0.09 Å longer than lengths at sites opposite Os–Os bonds. The same pattern is found for Ir(2)–C(1) and Ir(2)–C(2) bonds in the present structure with lengths of 1.93 (1) and 1.88 (1) Å, respectively. Olefin coordination at Ir(3) reflects a similar trans influence in that lengths of C(27) and C(26) of 2.20 (1) and 2.22 (1) Å are longer than the values of 2.16 (1) and 2.17 (1) to C(22) and C(23).

Direct Reaction of 1,5-Cyclooctadiene with $Ir_4(CO)_{12}$. The direct reaction of $Ir_4(CO)_{12}$ with 1,5-cyclooctadiene requires elevated temperatures. In refluxing chlorobenzene, after 18 h, this reaction provides a complex mixture of organoiridium clusters. Most of these products are isolated in very low yields (<10%); however, the major product can be isolated in

Table III. Selected Intramolecular Bond Angles (deg) for $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$

Angles about the Ir_4 Cluster[a]			
Ir(1)-Ir(2)-Ir(3)	59.73 (2)	Ir(1)-Ir(2)-Ir(4)	91.99 (2)
Ir(2)-Ir(3)-Ir(4)	59.81 (2)	Ir(1)-Ir(3)-Ir(4)	91.88 (2)
Ir(3)-Ir(4)-Ir(1)	61.49 (2)	Ir(1)-Ir(3)-Ir(2)	58.45 (2)
Ir(3)-Ir(1)-Ir(2)	61.82 (2)	Ir(4)-Ir(2)-Ir(3)	58.70 (2)
Angles about Ir(1)			
C(3)-Ir(1)-C(4)	93.5 (8)	C(7)-Ir(1)-C(11)	100.6 (6)
C(3)-Ir(1)-C(7)	136.0 (8)	C(7)-Ir(1)-C(6)	39.5 (5)
C(3)-Ir(1)-C(10)	89.1 (7)	C(7)-Ir(1)-Ir(2)	72.5 (3)
C(3)-Ir(1)-C(11)	99.3 (7)	C(7)-Ir(1)-Ir(3)	49.1 (4)
C(3)-Ir(1)-C(6)	175.3 (7)	C(10)-Ir(1)-C(11)	39.0 (6)
C(3)-Ir(1)-Ir(2)	133.1 (6)	C(10)-Ir(1)-C(6)	88.7 (6)
C(3)-Ir(1)-Ir(3)	105.5 (6)	C(10)-Ir(1)-Ir(2)	136.8 (4)
C(4)-Ir(1)-C(7)	122.7 (6)	C(10)-Ir(1)-Ir(3)	123.4 (5)
C(4)-Ir(1)-C(10)	134.2 (8)	C(11)-Ir(1)-C(6)	81.6 (6)
C(4)-Ir(1)-C(11)	95.8 (7)	C(11)-Ir(1)-Ir(2)	111.8 (4)
C(4)-Ir(1)-C(6)	91.0 (7)	C(11)-Ir(1)-Ir(3)	149.6 (4)
C(4)-Ir(1)-Ir(2)	50.6 (5)	C(6)-Ir(1)-Ir(2)	49.9 (4)
C(4)-Ir(1)-Ir(3)	99.9 (6)	C(6)-Ir(1)-Ir(3)	72.3 (4)
C(7)-Ir(1)-C(10)	82.5 (6)		
Angles about Ir(2)			
C(2)-Ir(2)-C(1)	95.8 (7)	C(1)-Ir(2)-Ir(4)	109.9 (5)
C(2)-Ir(2)-C(4)	98.7 (8)	C(1)-Ir(2)-Ir(3)	91.3 (5)
C(2)-Ir(2)-C(6)	96.5 (6)	C(4)-Ir(2)-C(6)	92.1 (6)
C(2)-Ir(2)-Ir(1)	125.6 (5)	C(4)-Ir(2)-Ir(1)	47.8 (4)
C(2)-Ir(2)-Ir(4)	103.5 (6)	C(4)-Ir(2)-Ir(4)	139.5 (4)
C(2)-Ir(2)-Ir(3)	162.2 (6)	C(4)-Ir(2)-Ir(3)	96.0 (5)
C(1)-Ir(2)-C(4)	100.9 (7)	C(6)-Ir(2)-Ir(1)	53.9 (3)
C(1)-Ir(2)-C(6)	160.5 (7)	C(6)-Ir(2)-Ir(4)	52.3 (4)
C(1)-Ir(2)-Ir(1)	127.4 (4)	C(6)-Ir(2)-Ir(3)	72.8 (4)
Angles about Ir(3)			
C(5)-Ir(3)-C(7)	100.4 (6)	C(7)-Ir(3)-Ir(4)	53.9 (3)
C(5)-Ir(3)-C(22)	127.2 (6)	C(7)-Ir(3)-Ir(1)	51.1 (4)
C(5)-Ir(3)-C(23)	89.3 (6)	C(7)-Ir(3)-Ir(2)	71.3 (4)
C(5)-Ir(3)-C(27)	112.1 (6)	C(22)-Ir(3)-C(23)	38.0 (6)
C(5)-Ir(3)-C(26)	77.0 (6)	C(22)-Ir(3)-C(27)	79.8 (6)
C(5)-Ir(3)-Ir(4)	47.4 (4)	C(22)-Ir(3)-C(26)	88.3 (6)
C(5)-Ir(3)-Ir(1)	133.8 (4)	C(22)-Ir(3)-Ir(4)	130.3 (4)
C(5)-Ir(3)-Ir(2)	79.5 (4)	C(22)-Ir(3)-Ir(1)	94.0 (4)
C(7)-Ir(3)-C(22)	94.3 (6)	C(22)-Ir(3)-Ir(2)	152.4 (4)
C(7)-Ir(3)-C(23)	101.3 (6)	C(23)-Ir(3)-C(27)	96.0 (7)
C(7)-Ir(3)-C(27)	143.2 (6)	C(23)-Ir(3)-C(26)	80.0 (6)
C(7)-Ir(3)-C(26)	177.1 (5)	C(23)-Ir(3)-Ir(4)	105.2 (5)
Angles about Ir(3) (*Continued*)			
C(23)-Ir(3)-Ir(1)	127.5 (5)	C(27)-Ir(3)-Ir(2)	97.5 (5)
C(23)-Ir(3)-Ir(2)	164.9 (5)	C(26)-Ir(3)-Ir(4)	123.4 (4)
C(27)-Ir(3)-C(26)	38.6 (6)	C(26)-Ir(3)-Ir(1)	130.0 (5)
C(27)-Ir(3)-Ir(4)	149.1 (5)	C(26)-Ir(3)-Ir(2)	106.8 (4)
C(27)-Ir(3)-Ir(1)	92.8 (5)		
Angles about Ir(4)			
C(5)-Ir(4)-C(14)	86.8 (7)	C(15)-Ir(4)-C(7)	133.1 (6)
C(5)-Ir(4)-C(15)	125.2 (7)	C(15)-Ir(4)-Ir(3)	156.2 (5)
C(5)-Ir(4)-C(19)	82.3 (7)	C(15)-Ir(4)-Ir(2)	95.6 (5)
C(5)-Ir(4)-C(6)	118.8 (5)	C(19)-Ir(4)-C(6)	140.1 (6)
C(5)-Ir(4)-C(18)	117.2 (8)	C(19)-Ir(4)-C(18)	35.3 (8)
C(5)-Ir(4)-C(7)	97.7 (6)	C(19)-Ir(4)-C(7)	109.9 (6)
C(5)-Ir(4)-Ir(3)	49.6 (4)	C(19)-Ir(4)-Ir(3)	106.0 (5)
C(5)-Ir(4)-Ir(2)	81.8 (4)	C(19)-Ir(4)-Ir(2)	164.0 (5)
C(14)-Ir(4)-C(15)	39.6 (7)	C(6)-Ir(4)-C(18)	111.3 (7)
C(14)-Ir(4)-C(19)	80.0 (7)	C(6)-Ir(4)-C(7)	39.0 (5)
C(14)-Ir(4)-C(6)	130.7 (6)	C(6)-Ir(4)-Ir(3)	73.1 (3)
C(14)-Ir(4)-C(18)	87.8 (7)	C(6)-Ir(4)-Ir(2)	49.3 (4)
C(14)-Ir(4)-C(7)	169.5 (6)	C(18)-Ir(4)-C(7)	98.3 (6)
C(14)-Ir(4)-Ir(3)	133.1 (6)	C(18)-Ir(4)-Ir(3)	124.1 (5)
C(14)-Ir(4)-Ir(2)	101.2 (6)	C(18)-Ir(4)-Ir(2)	159.6 (6)
C(15)-Ir(4)-C(19)	95.2 (7)	C(7)-Ir(4)-Ir(3)	49.0 (4)
C(15)-Ir(4)-C(6)	97.7 (6)	C(7)-Ir(4)-Ir(2)	70.4 (3)
C(15)-Ir(4)-C(18)	79.6 (7)		
Angles about C(6)			
C(7)-C(6)-C(13)	125.2 (13)	C(13)-C(6)-Ir(4)	124.2 (10)
C(7)-C(6)-Ir(2)	105.6 (9)	C(13)-C(6)-Ir(1)	111.9 (10)
C(7)-C(6)-Ir(4)	71.6 (8)	Ir(2)-C(6)-Ir(4)	78.4 (5)
C(7)-C(6)-Ir(1)	67.3 (7)	Ir(2)-C(6)-Ir(1)	76.2 (5)
C(13)-C(6)-Ir(2)	128.1 (11)	Ir(4)-C(6)-Ir(1)	122.6 (7)
Angles about C(7)			
C(6)-C(7)-C(8)	119.3 (13)	C(8)-C(7)-Ir(1)	110.7 (9)
C(6)-C(7)-Ir(3)	110.1 (10)	C(8)-C(7)-Ir(4)	122.1 (9)
C(6)-C(7)-Ir(1)	73.2 (8)	Ir(3)-C(7)-Ir(1)	79.8 (5)
C(6)-C(7)-Ir(4)	69.4 (7)	Ir(3)-C(7)-Ir(4)	77.2 (4)
C(8)-C(7)-Ir(3)	130.5 (11)	Ir(1)-C(7)-Ir(4)	125.1 (6)
Carbonyl Bond Angles			
Ir(2)-C(1)-O(1)	174 (1)	Ir(2)-C(4)-O(4)	139 (1)
Ir(2)-C(2)-O(2)	176 (1)	Ir(3)-C(5)-O(5)	139 (1)
Ir(1)-C(3)-O(3)	174 (1)	Ir(4)-C(5)-O(5)	137 (1)
Ir(1)-C(4)-O(4)	139 (1)		

[a] Dihedral angles between planes: Ir(1), Ir(2), Ir(3) and Ir(2), Ir(3), Ir(4) 113.69 (3); Ir(1), C(6), C(7) and Ir(4), C(6), C(7) 139.1 (5).

moderate yield (43%) as an orange-brown solid. Microanalytical, ^1H NMR, and mass spectral data lead to the formulation of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$. Spectroscopic data for a trace green product agree with the formula $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ (3.5%). Other minor products are formulated on the basis of mass spectra alone as $Ir_4(CO)_8(C_8H_{12})_2$ and $Ir_4(CO)_6(C_8H_{12})_2(C_8H_{10})$. Additionally, a small amount of an unidentified black solid (ca. 7%) is obtained. These products contrast with those reported from the interaction of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ with 1,5-cyclooctadiene, namely, $Co_2(CO)_4(C_8H_{12})_2$ in the former case and $Rh_6(CO)_{14}(C_8H_{12})$ in the latter.[4] The formulas of $Ir_4(CO)_8(C_8H_{12})_2$ and $Ir_4(CO)_6(C_8H_{12})_2(C_8H_{10})$ suggested that they might be intermediates in the conversion of $Ir_4(CO)_{12}$ to $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$. In an attempt to prepare these compounds in better yield, 1,5-cyclooctadiene was reacted with $Ir_4(CO)_{12}$ in refluxing chlorobenzene for only 1.5 h. Under these conditions, 41% of the $Ir_4(CO)_{12}$ is recovered unreacted. Additionally, the yields (based on $Ir_4(CO)_{12}$ consumed) of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ (29%), $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ (1%), and $Ir_4(CO)_8(C_8H_{12})_2$ (0%) are significantly reduced. However, the yield of $Ir_4(CO)_6(C_8H_{12})_2(C_8H_{10})$ is improved (3.5%). Also, two new products $Ir_4(CO)_{10}(C_8H_{12})$ (5%), and $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ (7%) are obtained in low yield. These compounds also represent possible intermediates in the formation of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$. However, the severity of the reaction conditions used prevents isolation of these compounds in reasonable amounts.

Trimethylamine Oxide Promoted Reaction of $Ir_4(CO)_{12}$ with 1,5-Cyclooctadiene. Several recent reports have indicated that trimethylamine oxide is a useful reagent for facilitating substitution of metal carbonyls, and we found it useful to facilitate phosphorus ligand substitution of $Ir_4(CO)_{12}$.[29-32] We hoped that the reagent might promote the formation of 1,5-cyclooctadiene derivatives of $Ir_4(CO)_{12}$ under mild conditions. The low solubility of $Ir_4(CO)_{12}$ in most solvents at temperatures <100 °C is a severe restriction, but THF at reflux was found to be a suitable solvent as well as providing moderate reaction conditions. In refluxing THF the reaction of $Ir_4(CO)_{12}$ with $Me_3NO{\cdot}2H_2O$ in the presence of 1,5-cyclooctadiene gives $Ir_4(CO)_{10}(C_8H_{12})$ and $Ir_4(CO)_8(C_8H_{12})_2$ in good total yield. Unfortunately, at 65 °C it is not possible to control the stoichiometry of the reaction so that only $Ir_4(CO)_{10}(C_8H_{12})$ is produced in reasonable quantities. Further reaction of either $Ir_4(CO)_{10}(C_8H_{12})$ or $Ir_4(CO)_8(C_8H_{12})_2$ with $Me_3NO{\cdot}2H_2O$ in neat 1,5-cyclooctadiene at 100 °C gives $Ir_4(CO)_6(C_8H_{12})_3$.

Solution Structures of $Ir_4(CO)_{12-2x}(C_8H_{12})_x$ (x = 1–3). The infrared spectra of $Ir_4(CO)_{12-2x}(C_8H_{12})_x$ (x = 1–3) show the presence of both terminal and bridging carbonyl ligands. In order to gain further structural information, ^{13}C NMR spectra of ^{13}CO-enriched samples (prepared from enriched $Ir_4(CO)_{12}$) were recorded. The resulting data are shown in Table IV.

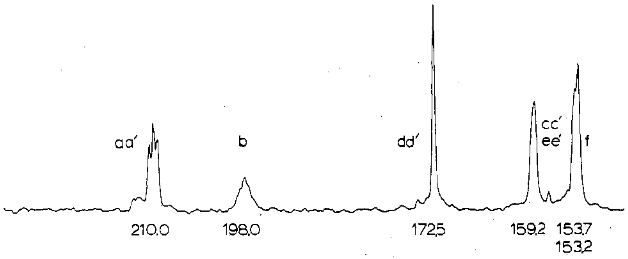
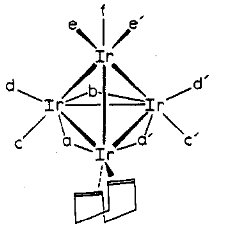
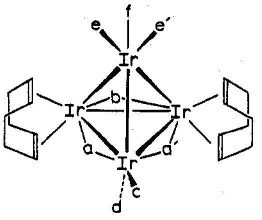


Figure 3. Carbonyl ^{13}C NMR spectrum of $Ir_4(CO)_{10}(C_8H_{12})$ at −75 °C.

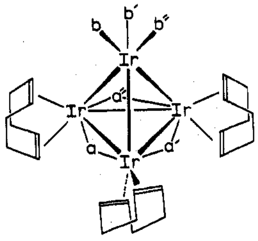
The spectrum of $Ir_4(CO)_{10}(C_8H_{12})$ (Figure 3) displays two resonances at 210.0 (2 C) and 198.0 (1 C) ppm, which can be assigned to bridging carbonyls. A signal of relative intensity 2 C at 172.5 ppm is shifted downfield significantly from the other terminal carbonyl resonances. We have shown previously that this downfield shift is characteristic of terminal carbonyl ligands in radial positions with respect to the basal plane defined by the three bridging carbonyl ligands.[32] Thus, structure IV, with the diene occupying a radial site and an axial site at a basal iridium atom, is consistent with the ^{13}C NMR data. The spectrum of $Ir_4(CO)_8(C_8H_{12})_2$ shows two bridging carbonyl signals at 220.7 (1 C) and 212.1 (2 C) ppm and a signal of relative intensity 1 C at 176.8 ppm in the basal radial terminal carbonyl region. Therefore, structure V can be assigned. For both $Ir_4(CO)_{10}(C_8H_{12})$ and $Ir_4(CO)_8(C_8H_{12})_2$ coupling is observed between the bridging carbonyls (a, b) and between the carbonyl ligands positioned pseudotrans to each other through an Ir–Ir bond (c, e or d, f). Finally, the ^{13}C NMR spectrum of $Ir_4(CO)_6(C_8H_{12})_3$ shows just two signals of equal intensity. One of these is in the downfield region (221.7 ppm) associated with bridging carbonyls, the other in the terminal region (160.0 ppm). Thus, structure VI with C_{3v} symmetry is assigned. $Ir_4(CO)_6(C_8H_{12})_3$ is stereochemically rigid over the temperature range −90 to +28 °C. $Ir_4(CO)_{10}(C_8H_{12})$ and $Ir_4(CO)_8(C_8H_{12})_2$ are both fluxional; however, no mechanistically discriminatory differential line broadening was observed.



IV



V



VI

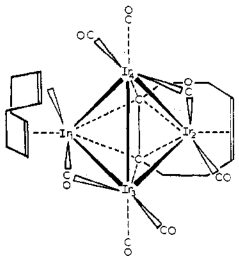
Pyrolysis of $Ir_4(CO)_{12-2x}(C_8H_{12})_x$ (x = 1–3). Since only trace amounts of the 1,5-cyclooctadiene derivatives were obtained in the direct reaction of $Ir_4(CO)_{12}$ with 1,5-cyclooctadiene at 132 °C, but could be isolated in reasonable quantities when prepared at lower temperatures, we have investigated their thermal stability. Heating $Ir_4(CO)_{10}(C_8H_{12})$ in refluxing cyclohexane for 24 h gave only an insoluble black precipitate. However, heating $Ir_4(CO)_8(C_8H_{12})_2$ under the same conditions gave a brown compound characterized by mass spectrometry and ^1H NMR as $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$. Surprisingly, heating $Ir_4(CO)_6(C_8H_{12})_3$ in refluxing cyclohexane for 3 h also provided $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$, with no evidence for $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$. Thus, it appears that dehydrogenation and opening of the Ir_4 framework occurs most readily at the stage where two 1,5-cyclooctadiene ligands are coordinated.

Table IV. ^{13}C NMR Data for $Ir_4(CO)_{12-x}(C_8H_{12})_x$ (x = 1–3)

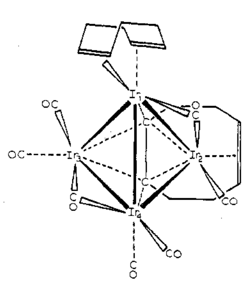
shift, ppm	mult (rel int)	assign
	$Ir_4(CO)_{10}(C_8H_{12})$[a]	
210.0	m (2)	a,a′
198.0	m (1)	b
172.5	s (2)	d,d′
159.2	s, br (2)[d]	c,c′ or e,e′
153.7	s, br (2)[d]	c,c′ or e,e′
153.2	s (1)	f
	$Ir_4(CO)_8(C_8H_{12})_2$[a]	
220.7	m (1)[c]	b
212.1	m (2)[c]	a,a′
176.8	s (1)	c
162.5	s, br (1)[e]	d or f
157.1	s (2)	e,e′
155.0	s, br (1)[e]	d or f
	$Ir_4(CO)_6(C_8H_{12})_3$[b]	
221.7	s (1)	a,a′,a″
160.0	s (1)	b,b′,b″

[a] At −75 °C in CD_2Cl_2. [b] At 28 °C in CD_2Cl_2. [c] J_{ab} = 16 Hz. [d] J_{ce} ≈ 10 Hz. [e] J_{df} ≈ 10 Hz.

Structure of $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$. The color and IR($\nu_{CO}$) spectrum of $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ are quite similar to the same features of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$. This suggests that the two compounds are closely related to structure, but with a chelating diene ligand in the latter replacing two carbonyl ligands in the former. In fact, treatment of $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ with 1,5-cyclooctadiene in refluxing cyclohexane cleanly produced $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$. Working backward from the structure of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ (Figure 1), it is apparent that two structures are possible for $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ (VII or VIII) depending on whether the added cyclooctadiene replaces carbonyls attached to an iridium atom at the fold or at an apex of the "butterfly" framework.



VII



VIII

In order to distinguish between these possibilities, $^{13}C\{^1H\}$ NMR spectra at several temperatures were recorded for $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ (Figure 4). The spectrum at −75 °C displays seven resonances of equal intensity. Two of these resonances (187.6 and 186.3 ppm) are downfield of the other resonances and can be attributed to bridging carbonyls. These resonances are slightly upfield of the resonances arising from the bridging carbonyls in $Ir_4(CO)_{12-2x}(C_8H_{12})_x$ (x = 1–3), suggesting that these bridging carbonyls are unsymmetrical as in the case of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$. As the temperature is raised to −67 °C, the signal at 186.3 ppm remains

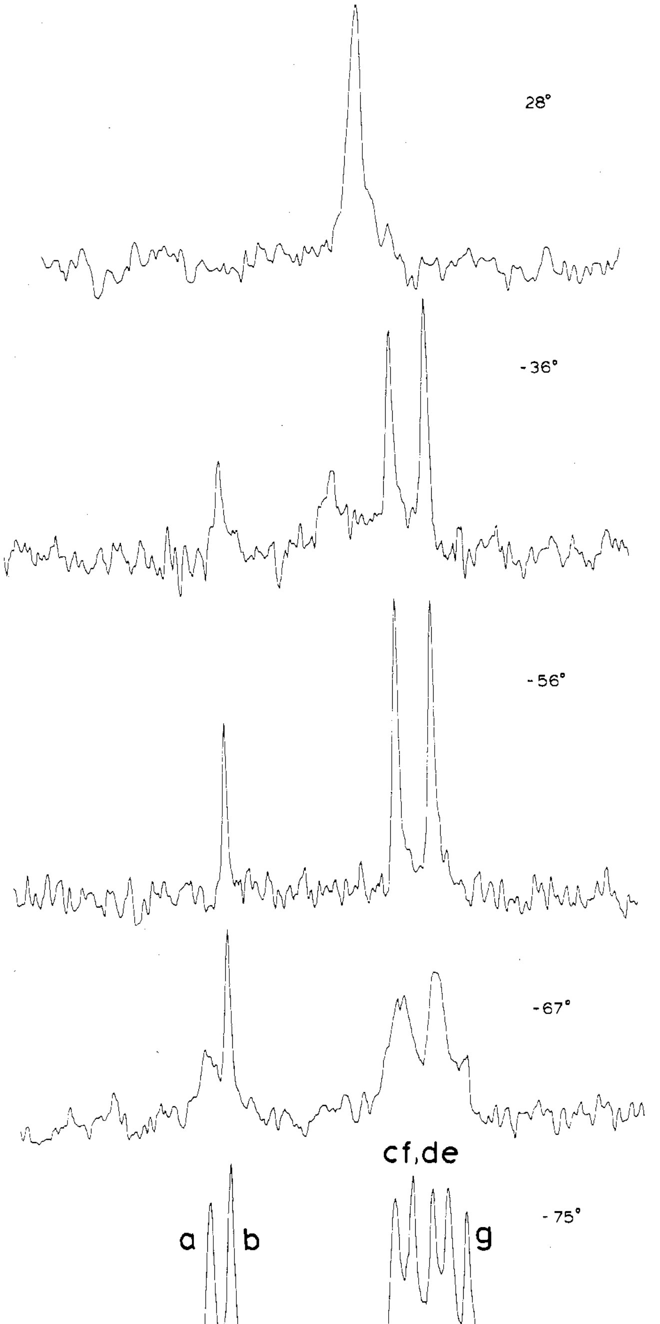


Figure 4. Carbonyl ^{13}C NMR spectra obtained for $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ at several temperatures.

sharp while the other six resonances broaden significantly. At −56 °C the spectrum displays three signals of relative intensity 1:2:2. The signals of relative intensity 2 C are in the proper position and of correct intensity to be the result of averaging the resonances at 175.4 and 174.2 ppm and at 172.9 and 171.9 ppm, respectively. At −36 °C a broad signal at 178.4 ppm is observed, which can be attributed to the average of the resonances at 187.6 and 170.6 ppm. At higher temperatures further averaging occurs, leading ultimately to complete equilibration of all signals.

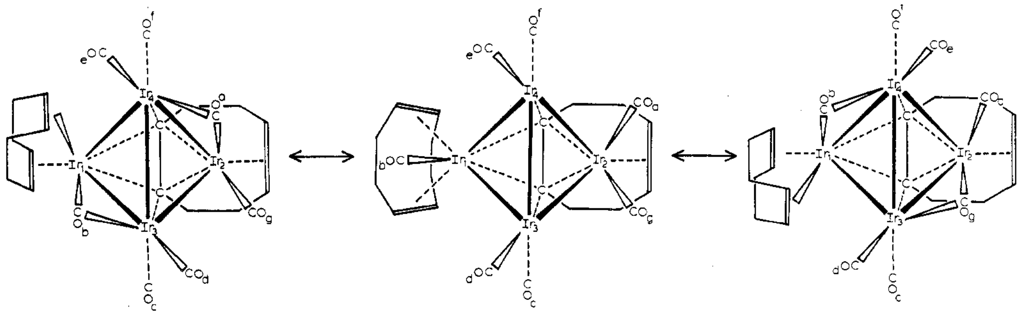
The observed dynamic behavior is more compatible with structure VII than with structure VIII and can be interpreted in terms of the mechanism proposed for carbonyl site exchange in $Co_4(CO)_{10}(C_2Et_2)$ (Scheme I).[33] Thus, formation from VII of intermediate IX, with all terminal carbonyl ligands, followed by re-formation of the bridging carbonyls on opposite edges leads to averaging of three pairs of carbonyl ligands: a and g, c and f, and d and e. One of the bridging carbonyls (b) remains unique throughout the process in accord with spectra between −75 and −36 °C. If VIII is assumed to be the structure adopted by $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$, no mechanistic interpretation of the dynamic behavior is apparent.

The ^{13}C NMR spectrum of $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ is similar to the spectrum of $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$. At −77 °C five resonances of equal intensity are observed at 197.8, 194.7, 175.9, 175.6, and 173.6 ppm. The resonances at 197.8 and 194.7 ppm can be assigned to the unsymmetrical bridging carbonyls. Thus, the solid-state structure is maintained in solution. In contrast to $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$, $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ is not fluxional over the temperature range −77 to +28 °C.

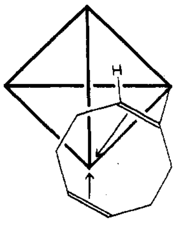
Although, $Ir_4(CO)_6(C_8H_{12})_2C_8H_{10})$ would appear to be closely related to $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$, pyrolysis of $Ir_4(CO)_6(C_8H_{12})_2(C_8H_{10})$ in refluxing chlorobenzene gave only brown decomposition products which would not elute on silica (TLC). Thus, $Ir_4(CO)_6(C_8H_{12})_2(C_8H_{10})$ may have a structure unrelated to $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$. Additionally, an alternative formulation for this compound would be $Ir_4(CO)_6(C_8H_{12})(C_8H_{11})_2$.

Formation of the *closo*-Ir_4C_2 Framework. Assignment of structure VII to $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ indicates that the bond between the substituted iridium atoms in $Ir_4(CO)_8(C_8H_{12})_2$ (see V) is broken in the transformation to $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$. Cleaving either of the other two Ir–Ir bonds adjacent to one of the substituted centers would lead to structure VIII for $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$. The overall transformation presumably requires several steps, which might be sketched as follows. Dissociation of carbon monoxide or one end of a diene in $Ir_4(CO)_8(C_8H_{12})_2$ (V) provides an unsaturated metal center. This allows oxidative addition of a vinylic C–H bond and produces a coordinated C_8H_{11} moiety as in A. After an additional ligand dissociation step, oxidative addition of the vinylic C–H bond leads to a C_8H_{10} group associated in a $2\sigma + \pi$ fashion as in B. Insertion of the

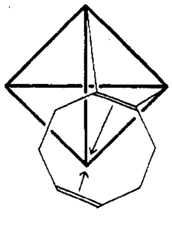
Scheme I



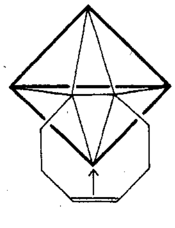
VII IX VII



A



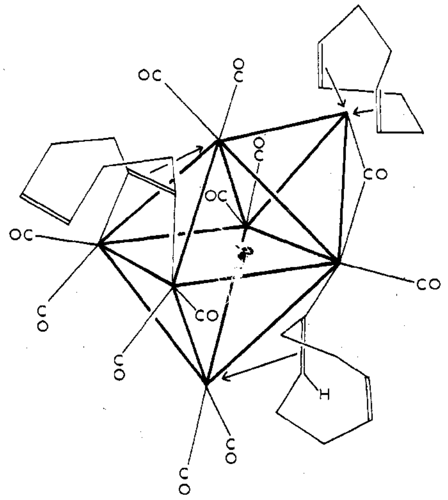
B



C

face-bridging acetylenic unit into an Ir–Ir bond then forms the *closo*-Ir_4C_2 pseudooctahedral framework as in C. The fate of the two removed hydrogenation atoms, whether they are released as molecular hydrogen or transferred to an olefin, is unknown.

General support for the stepwise dehydrogenation is provided by the structure determined for $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$[34] (see X). This molecule has both a C_8H_{11} and a C_8H_{10} moiety bound to the Ir_7 framework, the vinylic group at one edge in a $\sigma + \pi$ manner and the acetylenic group at one face in a $2\sigma + \pi$ fashion. It is notable that these localized coordination modes occur even with the larger number of potential coordination centers.



X

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Registry No. $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$, 66921-69-5; $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$, 65762-17-6; $Ir_4(CO)_6(C_8H_{12})_2(C_8H_{10})$, 66921-67-3; $Ir_4(CO)_{10}(C_8H_{12})$, 66809-80-1; $Ir_4(CO)_8(C_8H_{12})_2$, 66809-81-2; $Ir_4(CO)_6(C_8H_{12})_3$, 66809-79-8; $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$, 66921-68-4; $Ir_4(CO)_{12}$, 11065-24-0; ^{13}C, 14762-74-4.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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