can be attributed to the low solubility of CO in hydrocarbon solvents (for example, 5.8×10^{-3} M in bicyclohexyl at 127 °C)[14] and the low nucleophilic strength of CO vs. $P(C_6H_5)_3$.[15]

Product distributions are sensitive to the added carbon monoxide. Under an atmosphere of N_2, both mono- and bissubstituted products form initially. The complex $Re_2(CO)_8[P(C_6H_5)_3]_2$, evident in the initial IR spectra, was the major species present upon completion of the reaction. Under an atmosphere of CO, only the monosubstituted complex forms initially and the bissubstituted complex slowly reaches an equilibrium concentration.

So that the presence of $Re(CO)_5$ radicals could be tested, $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ were added in equal amounts to rigorously dry and deoxygenated decalin and maintained at 130° C under an atmosphere of N_2.

$$Mn_2(CO)_{10} + Re_2(CO)_{10} \nrightarrow 2MnRe(CO)_{10} \tag{1}$$

After 92 h (5.7 substitution half-lives of $Re_2(CO)_{10}$), there was no detectable IR absorption (at 2056 cm^{-1}) corresponding to $MnRe(CO)_{10}$. If the Re–Re and Mn–Mn bonds break at this temperature, the $MnRe(CO)_{10}$ absorption should appear. This contrasts with the photochemical cross-coupling reaction between $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, which produces bond homolysis and generates, $MnRe(CO)_{10}$ in high yield.[16] We cannot comment as to whether the Mn–Mn bond ruptures but assume it would cleave more readily than the Re–Re bond if conditions were severe enough to lead to Re–Re bond breaking. It seems well established that the order of metal–metal bond strengths is Mn–Mn << Mn–Re ≈ Re–Re.[17–21]

The mixed-metal dimer was examined to be sure that the lack of formation of $MnRe(CO)_{10}$ according to eq 1 was not due to an unfavorable equilibrium. Again, the rate of substitution[22] with $P(C_6H_5)_3$ at 130 °C yielded a k_{obsd} (of 6.4×10^{-5} s^{-1}) in excellent agreement with published results.[5,11] At no point during the reaction were homodimetallic species observed, in concord with Sonnenberger and Atwood's[11] report. So that contribution of bond homolysis could be studied, another crossover test was applied.

$$2MnRe(CO)_{10} \rightarrow Mn_2(CO)_{10} + Re_2(CO)_{10} \tag{2}$$

A 2.6×10^{-3} M solution of $MnRe(CO)_{10}$ in decalin was kept at 130 °C under N_2. Absorptions for $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ appeared very slowly. Following the loss of $MnRe(CO)_{10}$ by monitoring the band at 2056 cm^{-1}, we measure an approximate first-order rate constant of 6.8×10^{-7} s^{-1}. These rate data might suggest a minor contribution due to metal–metal bond scission; however, reaction 2 can be completely quenched with added CO. After 146 h (48 half-lives of the substitution reaction), there was no loss of $MnRe(CO)_{10}$ when the CO pressure above the solution was maintained at 1 atm. We do not fully understand this result. It suggests that the slow process that yields products apparently attributable to metal–metal bond homolysis results from a minor pathway that requires CO loss at some point. If simple $Re(CO)_5$ and $Mn(CO)_5$ radicals were the only intermediates, then inhibition by CO would not be expected. In this context we examined reaction 1 at 140 °C in decalin solvent and did find slow conversion ($t_{1/2} \approx 97$ h) to the heterometal product. Once again, 1 atm of carbon monoxide completely inhibited the cross-coupling reaction.

These crossover experiments support initial dissociation of CO in substitution reactions of $MnRe(CO)_{10}$ and $Re_2(CO)_{10}$ at 130 °C and the absence of significant concentrations of metal radical intermediates. Further experiments will be necessary to solve the dilemma for $Mn_2(CO)_{10}$. Because of the weaker metal–metal bond in this species, we do not think it wise to extend our conclusions for $Re_2(CO)_{10}$ and $MnRe(CO)_{10}$ to $Mn_2(CO)_{10}$. It is also possible that metal–metal bond cleavage may become an important mechanistic pathway for reactions of $MnRe(CO)_{10}$ and $Re_2(CO)_{10}$ at temperatures above 140 °C.[9b]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $Re_2(CO)_{10}$, 14285-68-8; $P(C_6H_5)_3$, 603-35-0; $MnRe(CO)_{10}$, 14693-30-2; $Mn_2(CO)_{10}$, 10170-69-1.

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(14) Tremper, K. K.; Prausnitz, J. M. *J. Chem. Eng. Data* **1976**, *21*, 295–299.

(15) Day, J. P.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 6927–6933.

(16) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065–2072. Wrighton, M.; Bredesen, D. *J. Organomet. Chem.* **1973**, *50*, C35–C38. Evans, G. O.; Sheline, R. K. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2862–2863. Hughey, J. L., IV; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49–C52.

(17) Quicksall, C. O.; Spiro, T. G. *Inorg. Chem.* **1969**, *8*, 2363–2367.

(18) Spiro, T. G. *Prog. Inorg. Chem.* **1970**, *11*, 1–51.

(19) Good, W. D.; Fairbrother, D. M.; Waddington, G. *J. Phys. Chem.* **1958**, *62*, 853–857.

(20) Connor, J. A.; Skinner, H. A.; Virmani, Y. *J. Chem. Soc. Faraday Trans. 1* **1972**, *68*, 1754–1763.

(21) Connor, J. A.; Skinner, H. A.; Virmani, Y. *Symp. Faraday Soc.* **1973**, *No. 8*, 18–28. Connor, J. A.; Skinner, H. A. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, D.C., 1981; ACS Symp. Ser. No. 155, pp 197–205.

(22) In these experiments $[P(C_6H_5)_3] = 0.1$ M, $[MnRe(CO)_{10}] = 2.4 \times 10^{-3}$ M, and the decrease in absorbance of the 2056-cm^{-1} peak obeyed a first-order plot for over 3 half-lives.

Demonstration of the Existence of Single Cubane-Type $MoFe_3S_4$ Clusters with $S = {}^3/_2$ Ground States: Preparation, Structure, and Properties

Sir:

In recent reports describing our development of the chemistry of cubane-type $MoFe_3S_4$ clusters[1–4] we have detailed one of our interests in these species, viz., as preliminary structural models of the Mo atom coordination site in FeMo proteins and the FeMo cofactor of nitrogenase. The most readily accessible clusters are those assembled from simple reactants in methanol reaction mixtures. These clusters are invariably isolated as bridged double-cubanes and include the types $[Mo_2Fe_6S_8(\mu\text{-}SR)_3(SR)_6]^{3-}$,[3,5,6] $[Mo_2Fe_6S_8(\mu\text{-}OMe)_3(SR)_6]^{3-}$,[3,6] and $[Mo_2Fe_7S_8(\mu\text{-}SR)_6(SR)_6]^{3-,4-}$.[7,8] Because of coordination saturation by tightly bound bridge ligands, these clusters offer little promise as effective species for testing the reactivity properties of molybdenum, in a Mo–Fe–sulfide environment, toward enzymatic and other potential substrates. However, a route to more promising clusters has recently been found. Treatment of $[Mo_2Fe_7S_8(SR)_{12}]^{3-}$ with certain 3,6-disubstituted catechols ($3,6\text{-}R'_2catH_2$; R′ = *n*-Pr, $CH_2CH{=}CH_2$)

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(1) Palermo, R. E.; Power, P. P.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 173.

(2) Armstrong, W. H.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 6246. Armstrong, W. H.; Mascharak, P. K.; Holm, R. H., submitted for publication in *J. Am. Chem. Soc.*

(3) Christou, G.; Mascharak, P. K.; Armstrong, W. H.; Papaefthymiou, G. C.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.*, in press.

(4) Holm, R. H. *Chem. Soc. Rev.*, in press.

(5) Wolff, T. E.; Berg, J. M.; Hodgson, K. O.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 4140.

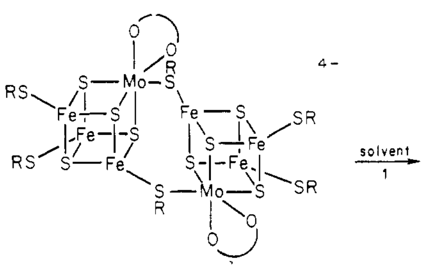
(6) Christou, G.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1980**, 2354.

(7) Wolff, T. E.; Power, P. P.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4694.

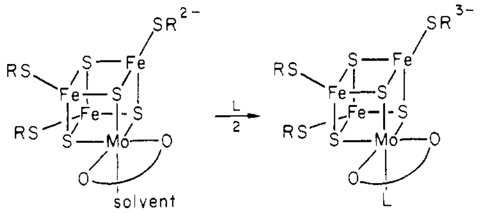
(8) Wolff, T. E.; Berg, J. M.; Power, P. P.; Hodgson, K. O.; Holm, R. H. *Inorg. Chem.* **1980**, *19*, 430.

0020-1669/82/1321-1699$01.25/0

effects bridge disruption and affords the doubly bridged double-cubanes $[Mo_2Fe_6S_8(\mu\text{-}SR)_2(SR)_4(R'_2cat)_2]^{4-}$ (**1**) in



1



2

3a, L = $p\text{-}ClC_6H_4S^-$
b, L = CN^-
c, L = PhO^-
d, L = PEt_3 (2-)

good yield.[2] In coordinating solvents the bridges in **1** are cleaved, resulting in the formation of solvated clusters whose properties are consistent with structure **2**.[2] Unfortunately this structure could not be definitively established by X-ray diffraction because upon crystallization step 1 is reversed and only salts of **1** have been isolated. Here we report structural proof of the existence of single $MoFe_3S_4$ clusters.

In step 2 0.63 mmol of $(Et_4N)_2[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_3((C_3H_5)_2cat)(MeCN)]^{2-}$ in ~200 mL of acetonitrile was treated with an equimolar amount of $(Et_4N)L$ in 20 mL of acetonitrile. After several hours of reaction time, volume reduction to ~20 mL followed by slow addition of ether caused separation of analytically pure, crystalline Et_4N^+ salts of **3a** and **3b** in ≳60% yield. $(Et_4N)_3$ (**3a**) crystallizes in monoclinic space group $C2/c$ with a = 33.918 (8) Å, b = 16.674 (4) Å, c = 27.374 (5) Å, β = 95.98 (2)°, V = 15396 (6) Å^3, and Z = 8.[9] With 5511 unique data ($F_o^2 > 2.5\sigma(F_o^2)$, $4.0° \leq 2\theta \leq 48.5°$), the structure was solved by direct methods and subsequent difference Fourier maps and was refined to R = 6.6% with 752 variables. The structure of **3a**, presented in Figure 1, is that of a single-cubane cluster; the closest intercluster Mo···Mo and Fe···Fe separations are 11.2 and 9.05 Å, respectively. Coordination of the Mo atom, external to the cluster itself, is completed by a terminal thiolate ligand and a catecholate chelate ring, affording a distorted octahedral MoS_4O_2 unit. The ring C–O bond distances (mean, 1.33 Å) are indicative of the $(C_3H_5)_2cat^{2-}$ oxidation level.[10] No symmetry is imposed on the cluster, as is evident from the orientation of the Mo–S-p-C_6H_4Cl ligand and appreciable inequalities (0.02–0.04 Å) of certain interatomic distances that would be equivalent under actual C_s symmetry. Metrical features are comparable to those of the subclusters in centrosymmetric $[Mo_2Fe_6S_8(SEt)_6(Pr_2cat)_2]^{4-2}$ (**1**). An analogous structure is highly probable for **3b** in the solid state where ν_{CN} = 2104 cm^{-1} is indicative of coordination (ν_{CN} = 2050 cm^{-1} for $(Et_4N)CN$).

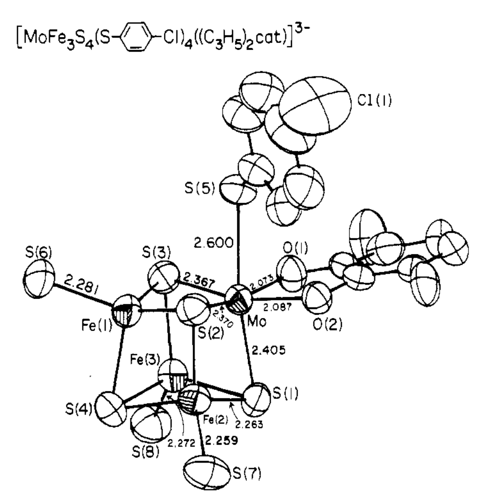


Figure 1. Structure of $[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_4((C_3H_5)_2cat)]^{3-}$ (**3a**) showing 50% probability ellipsoids and certain bond distances (esd values: Mo–S, 0.003; Mo–O, 0.006, 0.007; Fe–S, 0.003, 0.004 Å). The $p\text{-}C_6H_4Cl$ groups of the terminal ligands and the $CH{=}CH_2$ portions of the catecholate ligand are omitted. Fe–(μ_3-S) distances are 2.250 (3)–2.276 (3) Å, except for Fe(3)–S(4) (2.297 (3) Å) and Fe(1)–S(4) (2.320 (4) Å). Mean values of Mo···Fe and Fe···Fe separations are 2.760 (27) and 2.688 (26) Å, with esd's of all individual separations being 0.002 Å.

For **3a** in CD_3CN solution at ~299 K isotropically shifted ^1H NMR signals downfield (negative) and upfield (positive) of the Me_4Si reference were observed at −17.6 (2, m-H(Fe)), −10.7 (2, cat-H, verified by deuteration), −10.5 (4, m-H(Fe)), −7.3 (sh, o-H(Mo)), −7.12 (m-H(Mo), o- + m-H(Mo) ~4), and +9.7 ppm (br, o-H(Fe)).[11] The spectrum of **3b** (−17.8, −10.8, −10.6, +9.4 (br) ppm) is similar but lacks the signals near −7 ppm, which therefore arise from the molybdenum-thiolate ligand in the spectrum of **3a**. Formation of **3c** and **3d** by step 2 in CD_3CN was also demonstrated by ^1H NMR spectroscopy. Cluster **3d** (−19.3 (2), −10.5 (2), −10.3 (4), +9.3 (br) ppm) was quantitatively formed with 1.0 equiv/cluster of PEt_3, whose CH_2 (−8.2, br) and CH_3 (−2.5 ppm) signals were also located.[11] The appearance of two iron-thiolate m-H resonances in a 1:2 intensity ratio in all cases is consistent with effective C_s cluster symmetry and retention in solution of structure **3**. In contrast the solvate clusters **2** show a single set of Fe–SR resonances.[2] This result now can be interpreted in terms of rapid exchange of bound and bulk solvent molecules and attendant reorientation of the R'_2cat chelate ring prior to solvent rebinding, producing average trigonal symmetry at the Mo site on the NMR time scale.

The magnetic moments of **3a** and **3b** (4.09 μ_B, acetonitrile solution, 295 K) indicate a $S = {}^3/_2$ ground state, which is consistent with EPR results. The EPR spectrum of **3a** in Figure 2 is typical and is assigned to transitions within the $m_s = \pm{}^1/_2$ Kramers doublet in rhombic symmetry,[12] i.e., g_x = 4.57, $g_y \approx 3.4$ (unresolved), $g_z \simeq 2.0$, and $|E/D| \approx 0.08$. The weak shoulder at $g \approx 5.9$ may be the g_z feature of the $m_s = \pm{}^3/_2$ doublet.[12] Spectra of the solvate clusters **2** are very similar to that of **3a**. The clusters exhibit two one-electron redox reactions, which for **3b** are chemically reversible (Figure 2; $E_{1/2}$ = −0.24, −1.30 V). Potentials are dependent on L (for **3a** $E_{1/2}$ = −0.36, −1.07 V), indicating that both processes are cluster based (i.e., the initial oxidation does not involve the catecholate ligand).

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(9) Suitable crystals were obtained by diffusion of ether into an acetonitrile solution. The R = $p\text{-}C_6H_4Cl$ substituent was used in this and other cases because it afforded nicely crystalline reaction products. Diffraction data were collected on a Nicolet R3M diffractometer. An empirical absorption correction was applied. All nonhydrogen atoms were refined anisotropically; fixed contributions of hydrogen atoms were included in the final stage of refinement.

(10) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

(11) At lower temperatures the cat-H and m-H(Fe) resonances near −11 ppm are better resolved, permitting determination of the stated relative intensities. A second o-H(Fe) signal is either too broadened by paramagnetic relaxation to be detected or is obscured by cation/solvent resonances.

(12) Münck, E.; Rhodes, H.; Orme-Johnson, W. H.; Davis, L. C.; Brill, W. J.; Shah, V. K. *Biochim. Biophys. Acta* **1975**, *400*, 32.

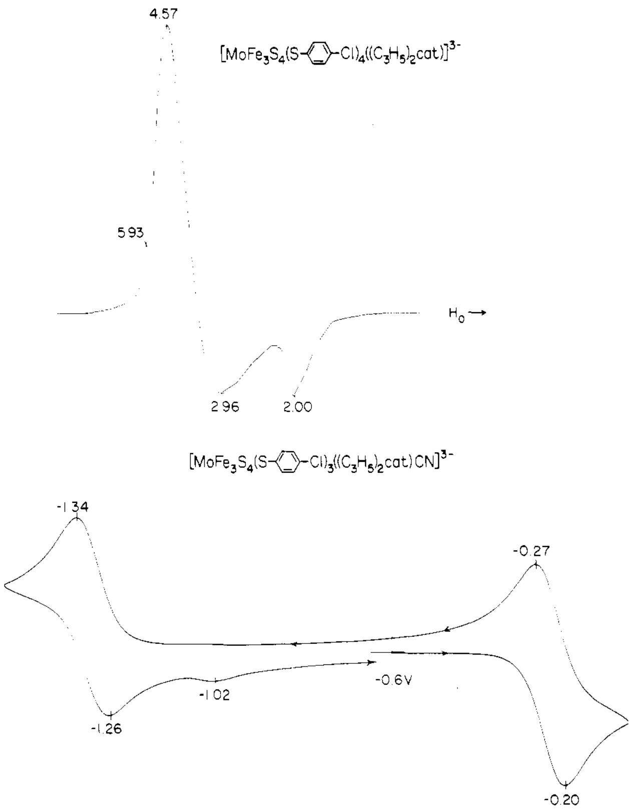

Figure 2. Upper: X-band EPR spectrum of $[\mathrm{MoFe_3S_4(S\text{-}}p\mathrm{\text{-}C_6H_4Cl)_4((C_3H_5)_2cat)}]^{3-}$ (**3a**) in acetonitrile solution at ~6 K; g values at selected fields are indicated. Lower: cyclic voltammogram (100 mV/s) of $[\mathrm{MoFe_3S_4(S\text{-}}p\mathrm{\text{-}C_6H_4Cl)_3((C_3H_5)_2cat)CN}]^{3-}$ (**3b**) in acetonitrile solution; peak potentials vs. SCE are indicated. The reduction at -1.02 V indicates a small amount of solvated cluster **2** formed in the redox cycle.

The foregoing results demonstrate the existence of the single clusters **3** with core oxidation levels $[\mathrm{MoFe_3S_4}]^{2+,3+,4+}$, one of which (3+) has a spin-quartet ground state,[13] and further substantiate formulation **2** for solvated clusters. Similarities with the native Mo–Fe–S cluster of nitrogenase now include Mo EXAFS[5] and $S = {}^3/_2$ spin systems[12,14] but not Mo:Fe:S atom ratios.[2] Current research is directed toward isolation of other cluster oxidation levels and an investigation of the reactions of reducible substrates with the reduced ($[\mathrm{MoFe_3S_4}]^{2+}$) forms of **2** and **3**.

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Supplementary Material Available: A table of positional parameters (3 pages). Ordering information is given on any current masthead page.

Registry No. **2**, solvent = MeCN, 80764-36-9; **3a**, 80789-40-8; **3b**, 80764-35-8; **3c**, 80764-37-0; **3d**, 80764-38-1.

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[13] The "single cluster" $[\mathrm{MoFe_3S_4(SEt)_3Fe(cat)_3}]^{3-}$ has been previously isolated (Wolff, T. E.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1981**, *20*, 174), but it is unsuitable for examination of single cluster electronic properties because of perturbation by the paramagnetic $\mathrm{Fe(cat)_3}^{3-}$ subunit.

[14] Rawlings, J.; Shah, V. K.; Chisnell, J. R.; Brill, W. J.; Zimmermann, R.; Münck, E.; Orme-Johnson, W. H. *J. Biol. Chem.* **1978**, *253*, 1001. Huynh, B. H.; Henzl, M. T.; Christner, J. A.; Zimmermann, R.; Orme-Johnson, W. H.; Münck, E. *Biochim. Biophys. Acta* **1980**, *623*, 124.

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Thermal Elimination of Dihydrogen from $(\eta^5\text{-}C_5H_5)Ir(CO)H_2$. Formation, Structure, and Reactivity of C_s-$(\eta^5\text{-}C_5H_5)_3Ir_3(CO)_3$

Sir:

Formation of the clusters $Cp_3Co_3(CO)_3$[1] and $Cp_3Rh_3(CO)_3$[2] (Cp = η^5-C_5H_5) appears to proceed via generation and formal trimerization of 16-electron CpM(CO) intermediates. Current interest in the chemistry of such Cp_3M_3 clusters[3] led us to consider means of generating CpIr(CO) as a possible route to $Cp_3Ir_3(CO)_3$. We now report the synthesis of $CpIr(CO)H_2$, its thermal loss of H_2 to form CpIr(CO) and thence $Cp_3Ir_3(CO)_3$, the crystal structure of the trimer, and evidence concerning a parallel pattern of reactivity between $Cp_3Ir_3(CO)_3$ and $CpIr(CO)H_2$.

Treatment of $CpIr(CO)Br_2$[4] with zinc and acetic acid in methanol[5] followed by extraction with pentane and evaporation affords $CpIr(CO)H_2$ in nearly quantitative yield as a colorless oil.[6] $CpIr(CO)H_2$ is stable at room temperature in noncoordinating solvents. However, solutions prepared in acetone or tetrahydrofuran soon begin to turn dark and $CpIr(CO)H_2$ disappears completely within several days. Similar behavior is seen at higher temperatures (reflux) in cyclohexane or benzene. The major product[7] has been isolated as a purple solid after chromatography (neutral alumina) and identified as C_s-$Cp_3Ir_3(CO)_3$.[8]

The molecular structure of $Cp_3Ir_3(CO)_3$ is shown in Figure 1.[9] The compound is a closed trimer of CpIr(CO) moieties, with two terminal carbonyls and a Cp group on one side of the Ir_3 plane and two Cp groups and one terminal carbonyl on the other side of the plane, leading to noncrystallographic C_s molecular symmetry. The two metal–metal distances related by the mirror plane are nearly identical (Ir(1)–Ir(2) = 2.6693 (7) Å, Ir(2)–Ir(3) = 2.6697 (6) Å), whereas the third distance is slightly longer (Ir(1)–Ir(3) = 2.6876 (6) Å). These values compare with 2.693 Å for $Ir_4(CO)_{12}$.[10] The carbonyl ligands are nearly perpendicular to the Ir_3 plane, with the carbonyl on Ir(2) bent slightly toward the midpoint of the triangle (87.9 (3)°) but the carbonyls on Ir(1) and Ir(3) bent slightly away from the center. This latter effect as well as the lengthening of the Ir(1)–Ir(3) bond is presumably due to

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[1] (a) Vollhardt, K. P. C.; Bercaw, J. E.; Bergman, R. G. *J. Organomet. Chem.* **1975**, *97*, 283. (b) Lee, W. S.; Brintzinger, H. H. *Ibid.* **1977**, *127*, 87.

[2] (a) Mills, O. S.; Paulus, E. F. *J. Organomet. Chem.* **1967**, *10*, 331. (b) Paulus, E. F.; Fischer, E. O.; Fritz, H. P.; Schuster-Woldan, H. *Ibid.* **1967**, *10*, P3. (c) Paulus, E. F. *Acta Crystallogr., Sect. B* **1969**, *B25*, 2206. (d) Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 7433.

[3] (a) E.g., $[Cp_3Rh_3(CO)_2(\mu_3\text{-}CR)]^+$: Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63. Dimas, P. A.; Duesler, E. N.; Lawson, R. J.; Shapley, J. R. *Ibid.* **1980**, *102*, 7787. (b) E.g., $Cp_3Co_3(\mu_3\text{-}CR)_2$: Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 559. Yamazaki, H.; Wakatsuki, Y.; Aoki, K. *Chem. Lett.* **1979**, 1041.

[4] Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 7870 (prepared by the addition of Br_2 to $CpIr(C_6H_5)H$). We have found that the compound is formed quantitatively by the addition of Br_2 to $CpIr(CO)_2$ in CH_2Cl_2.

[5] Moss, J. R.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 75.

[6] ^1H NMR (C_2D_6CO) δ 5.47 (s, 5 H), -16.47 (s, 2 H); IR (CH_2Cl_2) ν_{M-H} 2156 (w), ν_{CO} 2002 (s) cm^{-1}; mass spectra (electron impact, 70 eV) m/e 288 $(Cp^{193}Ir(CO)H_2)^+$.

[7] The minor products have been identified as $Cp_4Ir_4(CO)_x$ clusters and will be reported elsewhere.

[8] ^1H NMR ($CDCl_3$, -50 °C) δ 5.54 (s, 5 H), 5.50 (s, 10 H); IR(CH_2Cl_2) ν_{CO} 1960, 1918 cm^{-1}; mass spectra m/e 858 (M^+), 830 (M^+ - CO), 802 (M^+ - 2CO), 774 (M^+ - 3CO); ^{13}C NMR (CD_2Cl_2) δ 179.9 (1 C), 178.2 (2 C).

[9] Crystals of $Cp_3Ir_3(CO)_3$ form in space group $P\bar{1}$ with a = 8.9358 (8) Å, b = 8.2461 (8) Å, c = 11.9742 (11) Å, α = 101.73 (1)°, β = 92.98 (1)°, and γ = 98.56 (1)°. The structure was solved and refined with conventional procedures to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.029$, calculated for 2573 observed reflections.

[10] Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528.

0020-1669/82/1321-1701$01.25/0