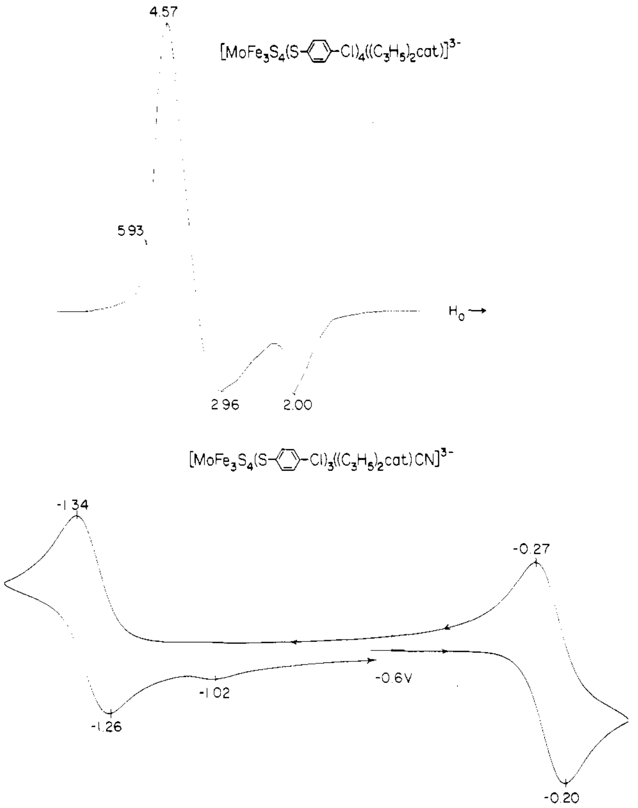

Figure 2. Upper: X-band EPR spectrum of $[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_4((C_3H_5)_2cat)]^{3-}$ (**3a**) in acetonitrile solution at ~6 K; *g* values at selected fields are indicated. Lower: cyclic voltammogram (100 mV/s) of $[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_3((C_3H_5)_2cat)CN]^{3-}$ (**3b**) 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 $[MoFe_3S_4]^{2+,3+,4+}$, 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 ($[MoFe_3S_4]^{2+}$) forms of **2** and **3**.

Acknowledgment. This research was supported by NSF Grant CHE 81-06017. X-ray and NMR equipment used in this research were obtained by NSF Grants CHE 80-00670 and CHE 80-08891.

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" $[MoFe_3S_4(SEt)_3Fe(cat)_3]^{3-}$ 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 $Fe(cat)_3{}^{3-}$ 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 $C_s\text{-}(\eta^5\text{-}C_5H_5)_3Ir_3(CO)_3$

Sir:

Formation of the clusters $Cp_3Co_3(CO)_3$[1] and $Cp_3Rh_3(CO)_3$[2] ($Cp = \eta^5\text{-}C_5H_5$) 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 $C_s\text{-}Cp_3Ir_3(CO)_3$.[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.

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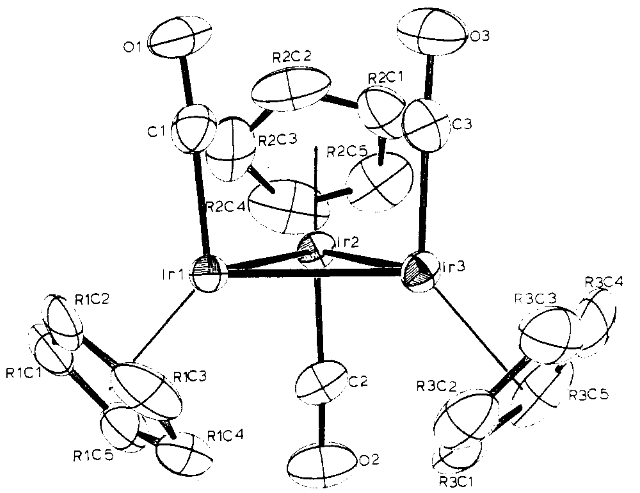


Figure 1. Perspective view of the C_s-$Cp_3Ir_3(CO)_3$ molecule.

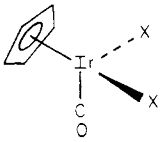
nonbonded repulsions between the two nearly parallel carbonyl ligands. Note that the configuration around Ir(1) (or Ir(3)) is that of a CpIr(CO) complex of a pseudo-ethylene $Cp_2Ir_2(CO)_2$ moiety. This suggests an abvious, though as yet experimentally unexamined, route for the formation and/or decomposition of C_s-$Cp_3Ir_3(CO)_3$.[11]

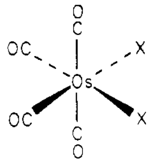
Under conditions in which it would normally decompose, $CpIr(CO)H_2$ is stabilized by a hydrogen atmosphere. Furthermore, $CpIr(CO)D_2$ under an atmosphere of H_2 is transformed into $CpIr(CO)H_2$. These observations support the equilibrium shown in eq 1. The role of the coordinating

$$CpIr(CO)H_2 \rightleftarrows CpIr(CO) + H_2 \tag{1}$$

solvent in the decomposition of $CpIr(CO)H_2$ may be seen as a trapping agent to form a "lightly stabilized" species CpIr(CO)S,[12] which facilitates H_2 loss from solution and ultimate formation of $Cp_3Ir_3(CO)_3$. The reactive intermediate CpIr(CO) or CpIr(CO)S is trapped by stronger donors to produce the stable, isolable compounds CpIr(CO)L (L = PPh_3,[13] $PPhMe_2$,[14] CN-*t*-Bu,[14] CO) in good yields. $CpIr(CO)_2$, which is known to be basic,[15] also works well as a trapping agent and forms $Cp_2Ir_2(CO)_3$.[16] Furthermore, decomposition of $CpIr(CO)H_2$ in the presence of benzaldehyde produces benzene and $CpIr(CO)_2$ (as well as $Cp_3Ir_3(CO)_3$), presumably via CpIr(CO)(C(O)Ph)H and CpIr(CO)(Ph)H.[4]

Upon treatment of $Cp_3Ir_3(CO)_3$ with $PPhMe_2$ at increasingly higher temperatures, no reaction occurs until ca. 140 °C (refluxing xylene). The only product is the mononuclear derivative $CpIr(CO)PPhMe_2$. Similarly, at the same temperature in the presence of excess ^{13}CO, only $CpIr(^{13}CO)_2$ is formed[17] and recovered $Cp_3Ir_3(CO)_3$ is unlabeled. This preference for metal-metal bond scission over carbonyl substitution in $Cp_3Ir_3(CO)_3$ parallels the preference for dihydrogen elimination over carbonyl loss from $CpIr(CO)H_2$ (see I). In





I, X_2 = H_2, $Cp_2Ir_2(CO)_2$ II, X_2 = H_2, $Os_2(CO)_8$

contrast the electronically equivalent pair of molecules $Os_3(CO)_{12}$ and $H_2Os(CO)_4$ (see II) show preferential dissociation of carbon monoxide.[18] The difference in behavior may imply greater relative stability for CpIr(CO) than for $Os(CO)_4$.[19] Nevertheless, despite the thermal stability of $Cp_3Ir_3(CO)_3$, reactions analogous to the extensive chemistry developed by direct substitution of $Os_3(CO)_{12}$[20] will not likely be accessible directly from $Cp_3Ir_3(CO)_3$. Alternative means of developing Cp_3Ir_3 chemistry are being investigated.

Acknowledgment. This research was supported at the University of Illinois by grants from the National Science Foundation (CHE 78-17911, 81-00140, and DMR 77-23999, 80-20250).

Registry No. $Cp_3Ir_3(CO)_3$, 80630-37-1; $CpIr(CO)H_2$, 78829-47-7; $CpIr(CO)_2$, 12192-96-0; $CpIr(CO)(PPh_3)$, 32612-68-3; $CpIr(CO)(PPhMe_2)$, 80630-38-2; CpIr(CO)(*t*-BuNC), 80630-39-3; $Cp_2Ir_2(CO)_3$, 80630-40-6; $CpIr(CO)Br_2$, 64867-78-3.

Supplementary Material Available: A listing of positional and thermal parameters for C_s-$Cp_3Ir_3(CO)_3$ (1 page). Ordering information is given on any current masthead page.

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[11] A similar structural feature is apparent for C_s-$Cp_3Rh_3(CO)_3$, except that the $Cp_2Rh_2(CO)_2$ moiety is doubly carbonyl bridged.[2c] For theoretical analysis of related compounds see: Hofmann, P.; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 554. Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29. For the addition of unsaturated metal fragments to $(\eta^5\text{-}C_5Me_5)_2M_2(CO)_2$ (M = Co, Rh) see: Cirjak, L. M.; Huang, J.-S.; Zhu, Z.-H.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 6673. Boag, N. M.; Green, M.; Mills, R. M.; Pain, G. N.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1980**, 1171.

[12] A similar solvent effect was noted for the elimination of H_2 from $H_2Co[P(OMe)_3]_4^+$: Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978.

[13] Graham, W. A. G.; Oliver, A. J. *Inorg. Chem.* **1970**, *9*, 2653.

[14] $CpIr(CO)(PPhMe_2)$: IR (CH_2Cl_2) ν_{CO} 1915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8–7.5 (m, 5 H), 5.16 (s, 5 H), 1.96 (d, 6 H, J = 10.5 Hz). CpIr(CO)(CN-*t*-Bu): IR (CH_2Cl_2) ν_{CO} 1939 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.33 (s, 5 H), 1.30 (s, 9 H).

[15] Hart-Davis, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 2658.

[16] Treatment of $CpIr(CO)_2$ with $Me_3NO{\cdot}2H_2O$ also appears to generate CpIr(CO); but in this case, $Cp_2Ir_2(CO)_3$ is the major product: ^1H NMR ($CDCl_3$, 30 °C) δ 5.57 (s); ^{13}C NMR (CH_2Cl_2, −50 °C) 206 (s, 1 C), 172 (s, 2 C); IR (C_6H_{12}) ν_{CO} 1966, 1796 cm^{-1}; mass spectra m/e 600 (M^+) 572 (M − CO), 544 (M − 2CO), 516 (M − 3CO). $Cp_2Ir_2(CO)_3$ appears to be isostructural with $Cp_2Rh_2(CO)_3$: Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* **1967**, *10*, 337.

[17] At 140 °C $CpIr(CO)_2$ should undergo relatively rapid exchange with ^{13}CO: Schuster, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657.

[18] Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.

[19] Whether the ease of H_2 loss from $CpIr(CO)H_2$ is due to more electron density at the metal center is not clear. $CpIr(PPh_3)H_2$ reacts with D_2 and CO more rapidly than does $CpIr(CO)H_2$. However, under similar conditions $(\eta^5\text{-}C_5Me_5)Ir(CO)H_2$ is much less reactive (Dimas, P.; Shapley, J. R., unpublished results).

[20] See especially the work of Deeming and co-workers reviewed by: Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145.

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Kinetics of Carbon Monoxide Activation: Reactions of Methoxide and of Hydroxide with Ruthenium and Iron Carbonyls[1]

Sir:

Nucleophilic activation of coordinated CO is a key feature of proposed mechanisms for homogeneously catalyzed processes such as the water-gas shift reaction[2] (WGSR) and the

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[1] Reported in part at the Symposium on Catalytic Activation of Carbon Monoxide, Second Chemical Conference of the North American Continent (180th National Meeting of the American Chemical Society), Las Vegas, NV, Aug 1980.

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