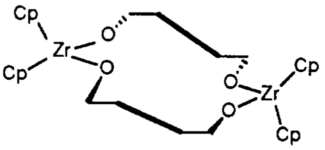
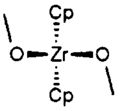
Organometallics **1990,** *9,* 2723-2727 2723

to accompany changes in the ring conformation.

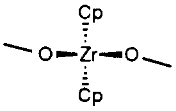
The conformation of the dimetalated macrocycle 2 is best described as a pseudochair (**2a**). The differing conformations of the macrocyclic rings for 1 and 2 result from the differing disposition of the substituents on oxygens. In the pseudocrown conformation of 1, the C-O-Zr-O dihedral angles are 81.69° and thus the orientation of the alkyl substituent on the oxygen atoms is best described as endo (**3**). In 2, the corresponding dihedral angles are 121.84 and -164.78°; thus, the substituents are exo (**4**). Presumably, the pseudocrown conformation for 1 minimizes the steric interactions between endo substituents, whereas for 2 such steric interactions are avoided by the exo disposition of the ligands, and thus a pseudochair conformation is adopted. In a similar manner, the exo substituents in $[Cp_2Ti(C_8N_2O_8)ZrCp_2]_2$ and $[Cp_2Ti(C_8N_2O_8)TiCp_2]_2$ afford pseudochair conformations for the macrocyclic ring within these compounds.[24]



2a



3



4

Molecular orbital and modeling calculations provide some insight into the question of substituent disposition. By extended Hückel methods, the total energy for $Cp_2Zr(OH)_2$ was calculated as a function of the H-O-Zr-O dihedral angles. The minimum total energy corresponded to dihedral angles of 85°. This endo orientation appears to be a compromise between the maximization of the π interaction between the oxygen and the metal and the minimization of lone-pair-lone-pair repulsion. Molecular mechanics calculations also predict the energetic preference for the endo conformer of $Cp_2Zr(OH)_2$. In contrast, MMX calculations for $Cp_2Zr(OCH_3)_2$ predict that the exo conformer is energetically preferred. These results imply that steric demands may override the electronic preference for an endo conformation. Although these calculations may not accurately reflect the threshold for domination of ligand disposition by steric factors, the correlation between orientation and substituent size is consistent with literature data. For example, the methyl groups of $Cp_2M(SMe)_2$ (M = Ti, V)[2b] are endo, while the phenyl rings in $Cp_2Nb(SPh)_2$[2h] are exo in disposition. In addition, the observation of an endo conformation of the substituents in 1 and an exo disposition in 2 is consistent with the predicted size/orientation correlation.

Acknowledgment. Financial support from the NSERC of Canada is gratefully acknowledged.

Supplementary Material Available: Tables of thermal and hydrogen atom parameters and bond distances and angles (3 pages); a listing of values of $10F_o$ and $10F_c$ (8 pages). Ordering information is given on any current masthead page.

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[24] Guthner, T.; Thewalt, U. *J. Organomet. Chem.* **1989**, *371*, 43.

Heterometallic Analogues of $[(\eta^5\text{-}C_5Me_5)M(CO)_2]_2$ (M = Fe, Ru, Os). Synthesis and Structures of $(\eta^5\text{-}C_5Me_5)_2(CO)_4IrRe$, $(\eta^5\text{-}C_5Me_5)_2(CO)_4IrMn$, and $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)(CO)_4IrRe$

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The heterobimetallic, metal-metal bonded complexes $(\eta^5\text{-}C_5Me_5)(CO)Ir(\mu_2\text{-}CO)_2Mn(CO)(\eta^5\text{-}C_5Me_5)$ (1), $(\eta^5\text{-}C_5Me_5)(CO)Ir(\mu_2\text{-}CO)_2Re(CO)(\eta^5\text{-}C_5Me_5)$ (2), and $(\eta^5\text{-}C_5Me_5)(CO)Ir(\mu_2\text{-}CO)_2Re(CO)(\eta^5\text{-}C_5H_5)$ (3) have been synthesized by reaction of $(\eta^5\text{-}C_5R_5)M(CO)_2$ (THF) (M = Mn, R = H; M = Re, R = H, Me) with $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$. The IR, NMR, and mass spectral data for these complexes are reported and are discussed in relation to the molecular structure of 3, which has been established by X-ray diffraction. Crystals of 3 are orthorhombic, space group $Pna2_1$ with a = 16.739 (2) Å, b = 9.591 (2) Å, c = 11.554 (2) Å, V = 1854.9 Å^3, and Z = 4. The structure has been refined to $R(F) = 0.027$ from 1427 independent observed intensities with $I_o \geq 2.5\sigma(I_o)$ in the range $4° \leq 2\theta \leq 52°$. The $\eta^5\text{-}C_5Me_5$ with $\eta^5\text{-}C_5H_5$ groups are oriented trans as are the two terminal CO groups. The remaining two semibridging carbonyl groups are primarily bound to the Re atom. The Ir-Re bond length, not corrected for the thermal motion, is 2.8081 (6) Å.

Introduction

The homometallic complexes $[Cp^*M(CO)_2]_2$ (M = Fe, Ru, Os; $Cp^* = \eta^5\text{-}C_5Me_5$)[1-3] have all been synthesized in recent years and may be compared with the earlier and generally better known cyclopentadienyl analogues $[CpM(CO)_2]_2$ ($Cp = \eta^5\text{-}C_5H_5$). To date, the osmium compound[3] has scarcely been studied; however, the ruthenium compound, like its Cp analogue, appears potentially to be a rich source of novel transformations at the diruthenium center.[4] Currently, there is considerable interest in heterobimetallic complexes,[5-7] stimulated in part by the an-

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[1] King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1971**, *93*, 4950.

[2] King, R. B.; Iqbal, M. Z.; King, A. D., Jr. *J. Organomet. Chem.* **1979**, *171*, 53.

[3] (a) Weber, L.; Bungardt, D. *J. Organomet. Chem.* **1986**, *311*, 269. (b) Hoyano, J. K.: May, C. J.; Graham, W. A. G. *Inorg. Chem.* **1982**, *21*, 3095.

[4] Forrow, N. J.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1984**, 679.

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ticipation that these might provide new chemistry not hitherto observed in homometallic compounds, including possible novel catalysis potential.[7] Here, we report the synthesis and structures of heterobimetallic analogues of [Cp*M(CO)$_2$]$_2$ with iridium–manganese and iridium–rhenium bonds. A related compound with a rhodium–manganese bond is known.[8]

Experimental Section

General Procedures. Reactions and manipulation of products were carried out by using standard Schlenk techniques in an atmosphere of dry nitrogen. Hexane, cyclohexane, benzene, and diethyl ether were dried and distilled under N$_2$ from sodium. Tetrahydrofuran (THF) was distilled under N$_2$ from sodium benzophenone ketyl. Cp*Ir(CO)$_2$,[9] Cp*Re(CO)$_3$,[10] Cp*Mn(CO)$_3$,[11] and Cp*Re(CO)$_2$(N$_2$)[12] were synthesized as described elsewhere. Photolyses were carried out on magnetically stirred solutions in a quartz photolysis tube fitted with a Teflon valve, placed adjacent to a water-cooled 200-W Hanovia Model 654A-0360 high-pressure mercury-vapor lamp. Infrared spectra were run on either a Perkin-Elmer Model 983G spectrophotometer or a Bomem Michelson-120 FTIR instrument. ^{1}H and ^{13}C NMR spectra were obtained by using a Bruker WM-400 instrument at 400 and 100.6 MHz, respectively. Electron-impact (EI) mass spectra were obtained at 70 eV with a Hewlett-Packard 5985 GC–MS instrument. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory at Simon Fraser University.

Synthesis of (η^5-C$_5$Me$_5$)(CO)Mn(μ_2-CO)$_2$Ir(CO)(η^5-C$_5$Me$_5$) (1). A solution of (η^5-C$_5$Me$_5$)Mn(CO)$_3$ (80 mg, 0.292 mmol) in freshly distilled THF (100 mL) was irradiated for ca. 20 min at 0 °C with a nitrogen purge, until the IR absorptions of the tricarbonyl complex (ν(CO): 2003, 1916 cm^{-1}) were almost completely replaced by those of (η^5-C$_5$Me$_5$)Mn(CO)$_2$(THF) (ν(CO): 1906, 1833 cm^{-1}). Then (η^5-C$_5$Me$_5$)Ir(CO)$_2$ (50 mg, 0.130 mmol) was added as a solid, and the solution was stirred in the dark for 36 h at room temperature with no further irradiation. The IR spectrum now showed the almost complete consumption of the THF complex and the presence of new ν(CO) absorptions at 1963, 1905, and 1759 cm^{-1} from the product. THF was removed under vacuum, and the resulting orange–red solid was washed with hexane. It was then extracted with benzene to give an orange–red solution, from which the product was obtained as orange–red microcrystals by removal of the solvent under vacuum: yield 60% (based on iridium); mp 140 °C dec. Anal. Calcd for C$_{24}$H$_{30}$IrMnO$_4$: C, 45.71; H, 4.76. Found: C, 45.60; H, 4.78. IR (C$_6$D$_6$, cm^{-1}): ν(CO) 1962 (m), 1902 (vs), 1756 (s, br). ^{1}H NMR (C$_6$D$_6$): δ 1.768 (s), 1.749 (s). ^{13}C{^{1}H} NMR (C$_6$D$_6$/C$_6$H$_6$ 1:4, 280 K): δ 8.23, 8.47 (C$_5$*Me*$_5$), 96.69, 101.13 (*C*$_5$Me$_5$), 168.2 (Ir*C*O), 247.9 (μ_2-*C*O). MS (EI, 70 eV): *m/z* 630 (M$^+$, ^{193}Ir), 574 (M$^+$ – 2CO), 546 (M$^+$ – 3CO), 516 (M$^+$ – 4CO – 2H).

In a modification of the above method, a THF solution of (η^5-C$_5$Me$_5$)Mn(CO)$_2$(THF), prepared as before, was treated with (η^5-C$_5$Me$_5$)Ir(CO)$_2$ dissolved in cyclohexane (10 mL), and the mixture was heated to ca. 70 °C under N$_2$ for 2 h in the dark (the flask was aluminum foil wrapped). The solvent was removed under vacuum, and the remaining red–brown solid was washed with hexane and then dissolved in benzene and passed through a short column of Celite. Removal of the benzene under vacuum gave the product in 80% yield (based on iridium).

Synthesis of (η^5-C$_5$Me$_5$)(CO)Re(μ_2-CO)$_2$Ir(CO)(η^5-C$_5$Me$_5$) (2). A solution of (η^5-C$_5$Me$_5$)Re(CO)$_3$ (80 mg, 0.197 mmol) in freshly distilled THF (50 mL) was irradiated at 0 °C in a quartz reactor for 1.5 h with a slow nitrogen purge until about 70% of the rhenium complex had converted to (η^5-C$_5$Me$_5$)Re(CO)$_2$(THF) (ν(CO): 1892, 1822 cm^{-1}) as judged by IR spectroscopy. To the light brown solution was then added (η^5-C$_5$Me$_5$)Ir(CO)$_2$ (40 mg, 0.104 mmol) dissolved in cyclohexane (15 mL). The apparatus was wrapped in aluminum foil, and the solution was heated at 60–65 °C for 3.5 h. The solvent was removed under vacuum, and the remaining dark solid was washed three times with large portions of hexane to remove residual (η^5-C$_5$Me$_5$)Re(CO)$_3$ and (η^5-C$_5$Me$_5$)Ir(CO)$_2$. The solid was then dissolved in benzene and twice passed through a short column of Celite to give a bright yellow solution. Removal of the benzene under vacuum gave the product as a yellow powder in 13% yield. A similar reaction, in which solid (η^5-C$_5$Me$_5$)Ir(CO)$_2$ was added directly to the THF solution of the rhenium–THF complex and the solution was stirred at room temperature for 3 days, gave a similar yield of the product after an analogous workup. Anal. Calcd for C$_{24}$H$_{30}$IrO$_4$Re: C, 37.84; H, 3.94. Found: C, 37.69; H, 3.99. IR (C$_6$H$_6$, cm^{-1}): ν(CO) 1954 (s), 1898 (vs), 1739 (m, br). ^{1}H NMR (C$_6$D$_6$): δ 1.814 (s), 1.875 (s). ^{13}C NMR (C$_6$D$_6$/C$_6$H$_6$ 1:4, 293 K): δ 8.45, 8.90 (C$_5$*Me*$_5$), 98.45, 100.43 (*C*$_5$Me$_5$), 170.32 (Ir*C*O), 203.72 (Re*C*O), 224.65 (μ_2-*C*O). MS (EI, 70 eV): *m/z* 762 (M$^+$, ^{193}Ir, ^{187}Re), 734 (M$^+$ – CO), 706 (M$^+$ – 2CO), 678 (M$^+$ – 3CO), 676 (M$^+$ – 3CO – 2H), 674 (M – 3CO – 4H).

An alternative synthesis was conducted by stirring (η^5-C$_5$Me$_5$)Re(CO)$_2$(N$_2$) (20 mg, 0.049 mmol) and (η^5-C$_5$Me$_5$)Ir(CO)$_2$ (20 mg, 0.052 mmol) in hexane (10 mL) at 60–65 °C for 1 h in the dark. A yellow–brown solid precipitated, which was purified as above to give the golden–yellow product (21.7 mg, 58%).

Synthesis of (η^5-C$_5$H$_5$)(CO)Re(μ_2-CO)Ir(CO)(η^5-C$_5$Me$_5$) (3). A solution of (η^5-C$_5$H$_5$)Re(CO)$_3$ (100 mg, 0.298 mmol) in THF (70 mL) was irradiated in a quartz reactor at 0 °C under a purge of N$_2$ for ca. 60 min, when it was almost completely converted to (η^5-C$_5$H$_5$)Re(CO)$_2$(THF) (μ(CO): 1911, 1837 cm^{-1}) as determined by IR. To this solution was added (η^5-C$_5$Me$_5$)Ir(CO)$_2$ (40 mg, 0.104 mmol), and the mixture was stirred at room temperature in the dark for 10 days. The solvent was removed under vacuum, and the resulting brown solid was redissolved in diethyl ether and then chromatographed on a 6-cm column of neutral alumina. Removal of the solvent under vacuum gave the product as a yellow powder (yield: 21 mg, 29.2%). This proceure was preferred over washing with hexane, in which the product is significantly soluble. Anal. Calcd for C$_{19}$H$_{20}$IrO$_4$Re: C, 33.04; H, 2.92. Found: C, 33.08; H, 2.93. IR (C$_6$H$_6$, cm^{-1}): ν(CO) 1962 (m), 1917 (vs), 1739 (m, br). ^{1}H NMR (C$_6$D$_6$): δ 1.83 (C$_5$Me$_5$), 4.78 (C$_5$H$_5$). ^{13}C NMR (C$_6$D$_6$/C$_6$H$_6$ 1:4, 281 K): δ 9.05 (q, *J* = 129 Hz, C$_5$*Me*$_5$) 87.6 (d, *J* = 182 Hz, C$_5$H$_5$), 100.9 (s, *C*$_5$Me$_5$), 170.6 (Ir*C*O), 200.5 (Re*C*O), 219.5 (μ_2-*C*O). MS (EI, 70 eV): *m/z* 692 (M$^+$, ^{193}Ir, ^{187}Re), 664 (M$^+$ – CO), 636 (M$^+$ – 2CO), 606 (M$^+$ – 3CO – 2H), 604 (M$^+$ – 3CO – 4H).

X-ray Structure Determination for Compound 3. A yellow–orange crystal was selected from a sample of **3** recrystallized from benzene–hexane and was mounted in a Lindemann capillary.

Intensity data were collected with an Enraf Nonius CAD-4F diffractometer with graphite monochromated Mo Kα radiation. The unit cell was determined from 25 well-centered reflections (13.9° ≤ θ ≤ 18.1°). Three intensity standards were measured

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[5] Geoffroy, G. L.; Roberts, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, p 763.

[6] (a) Usõn, R.; Forniés, J.; Espinet, P.; Fortuno, C.; Tomas, M.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1988**, 3005. (b) Dey, K.; Werner, H. *Chem. Ber.* **1979**, *112*, 823. (c) Werner, H.; Feser, R.; Büchner, W. *Chem. Ber.* **1979**, *112*, 834. (d) Nowell, I. W.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1972**, 2393. (e) Dey, K.; Werner, H. *J. Organomet. Chem.* **1977**, *137*, C28. (f) Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Gales, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1309. (g) Werner, H.; Juthani, B. *J. Organomet. Chem.* **1981**, *209*, 211. (h) Barr, R. D.; Green, M.; Marsden, K.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 507. (i) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Organometallics* **1985**, *4*, 250. (j) Del Paggio, A. M.; Muetterties, E. L.; Heinekey, D. M.; Day, V. W.; Day, C. S. *Organometallics* **1986**, *5*, 575. (k) Green, M.; Mills, R. M.; Pain, G. N.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1309. (l) Davis, H. B.; Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K.; Rushman, P. *Organometallics* **1989**, *8*, 1030 and references therein.

[7] Recent articles with extensive literature citations are: (a) Zheng, P. Y.; Nadasdi, T. T.; Stephan, D. W. *Organometallics* **1989**, *8*, 1393. (b) Gelmini, L.; Stephan, D. W. *Organometallics* **1988**, *7*, 849. (c) Sartain, W. J.; Selegue, J. P. *Organometallics* **1989**, *8*, 2153. (d) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41.

[8] Aldridge, M. L.; Green, M.; Howard, J. A. K.; Pain, G. N.; Porter, S.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1333.

[9] Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

[10] Klahn, A. H.; Sutton, D. *Organometallics* **1989**, *8*, 198.

[11] Bernal, I.; Korp, J. D.; Herrmann, W. A.; Serrano, R. *Chem. Ber.* **1984**, *117*, 434. The sample used in this work was kindly synthesized by Dr. R. D. Sharma of this department.

[12] Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.

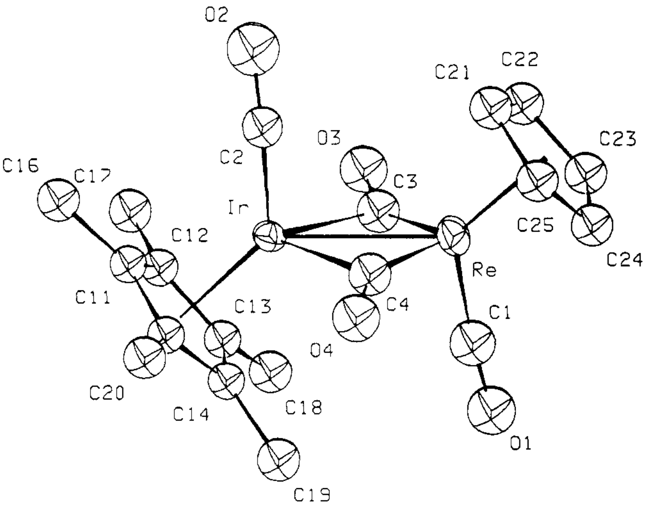

Figure 1. Molecular structure of 3.

every 1.5 h of acquisition time. These showed no significant variations in intensity during the course of data acquisition. The data were corrected empirically for the effects of absorption,[13] scaled, and corrected for Lorentz and polarization effects.

The structure was initially solved in the space group *Pnam*. The molecule is bisected by the crystallographic mirror, the metal atoms and terminal carbonyls (see below) lying in the mirror plane. Poor agreement and high thermal motion, particularly in the *z* direction for the metal atoms, indicated that a better model involved disorder of the entire molecule about the mirror plane with two equal sites for each atom. With such a model, an agreement of $R(F) = 0.027$ could be obtained with anisotropic thermal parameters for Ir and Re and isotropic thermal parameters for the other atoms including hydrogens placed in calculated positions. This model was stabilized by the inclusion of numerous soft distance and angle restraints. Correlations between the coordinates of mirror-related atoms as well as between $U(33)$ and z for the metal atoms and the general complexity of this model led us to attempt an ordered solution in the noncentrosymmetric space group.

A completely ordered model in $Pna2_1$, yielding similar agreement, is presented here because of its relative simplicity; however, another similar model, differing slightly in the relative rotational conformations of the Cp and Cp* ligands, agreed equally well with the data. Not surprisingly, tests to determine the polarity were inconclusive. The Cp and Cp* ligands were refined as rigid groups. A single isotropic temperature factor was refined for each of the following sets of atoms: the Cp ring carbon atoms, the Cp* ring carbon atoms, the methyl carbon atoms, the methyl hydrogen atoms, the Cp hydrogen atoms, the carbon atoms of the bridging carbonyls; and the oxygen atoms of the bridging carbonyls. In order to minimize the correlation, the coordinates and anisotropic thermal parameters for the Ir and Re atoms were refined as their respective sums and differences, as were the coordinates for the pairs C(3) and C(4) and O(3) and O(4). An extinction parameter was also refined.[14] A weighting scheme was applied such that $\langle w(|F_o| - |F_c|)^2\rangle$ was near constant as a function of both $|F_o|$ and $\sin\theta/\lambda$.[15] The maximum |shift/esd| was 0.16 for the final full matrix least-squares refinement of only 67 parameters for 1427 observations ($I_o \geq 2.5\sigma(I_o)$) and 12 restraints. The largest peak in the final difference map (1.4 (2) e Å^{-3}) occurred 0.98 Å from Ir.

Complex scattering factors for neutral atoms[16] were used in the calculation of structure factors. The programs used for data reduction, structure solution, and initial refinement were from the NRCVAX Crystal Structure System.[17] The program CRYSTALS[18] was employed in the refinement involving the use of restraints, rigid groups, and combined parameters. The diagram (Figure 1) was generated with the program SNOOPI.[19] All computations were carried out on a MicroVAX-II computer. Crystallographic data are summarized in Table I. The final positional and isotropic or equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table II. Full experimental details and the coordinates and temperature factors for the hydrogen atoms, as well as the anistropic temperature factors and lists of observed and calculated structure factors, are deposited as supplementary material.

Table I. Crystallographic Data for the Structure Determination of Cp*(CO)Ir(μ_2-CO)$_2$Re(CO)Cp (3)

formula	$IrReO_4C_{19}H_{20}$
crystal system	orthorhombic
space group	$Pna2_1$
a, Å	16.739 (2)
b, Å	9.591 (2)
c, Å	11.554 (2)
V, Å^3	1854.9
Z	4
fw	690.79
ρ_c, g cm^{-3}	2.474
μ(Mo Kα), cm^{-1}	137.7
λ, Å	0.71069
rel transmission	0.48–1.00
min–max 2θ, deg	4–52
$R(F)^a$	0.027
$R_w(F)^b$	0.033

$^a R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$, for observed data. $^b R_w(F) = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o^2)]^{1/2}$, for observed data.

Table II. Atomic Coordinates (×10^4) and Isotropic or Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) for the Non-Hydrogen Atoms of Cp*(CO)Ir(μ_2-CO)$_2$Re(CO)Cp (3)

atom	*x/a*	*y/b*	*z/c*	*U*(iso)
Ir	4172.7 (2)	5374.4 (4)	2533 (4)	279
Re	3273.3 (3)	2903.0 (5)	2531 (5)	374
O(1)	1611 (7)	4135 (12)	2258 (12)	565 (34)
O(2)	5732 (6)	3869 (12)	2401 (29)	668 (37)
O(3)	3747 (11)	4163 (21)	179 (13)	546 (24)
O(4)	3589 (11)	4299 (22)	4855 (13)	546 (24)
C(1)	2276 (9)	3709 (15)	2377 (26)	505 (43)
C(2)	5098 (7)	4416 (12)	2563 (40)	393 (37)
C(3)	3554 (15)	4067 (21)	1190 (12)	439 (26)
C(4)	3660 (16)	3990 (21)	3863 (11)	439 (26)
C(11)	4655 (3)	7504 (5)	2640 (4)	330 (11)
C(12)	4238 (3)	7435 (7)	1555 (3)	330 (11)
C(13)	3403 (3)	7197 (6)	1807 (4)	330 (11)
C(14)	3319 (3)	7166 (6)	3071 (4)	330 (11)
C(15)	4094 (3)	7397 (7)	3559 (3)	330 (11)
C(16)	5547 (3)	7797 (9)	2769 (7)	437 (18)
C(17)	4580 (5)	7651 (14)	343 (4)	437 (18)
C(18)	2724 (4)	7110 (11)	976 (6)	437 (18)
C(19)	2562 (3)	7026 (11)	3699 (7)	437 (18)
C(20)	4287 (5)	7522 (14)	4821 (3)	437 (18)
C(21)	4191 (5)	1096 (11)	2778 (8)	434 (19)
C(22)	3829 (6)	966 (15)	1658 (7)	434 (19)
C(23)	2985 (6)	737 (12)	1788 (9)	434 (19)
C(24)	2795 (5)	781 (13)	3016 (10)	434 (19)
C(25)	3555 (7)	916 (16)	3616 (6)	434 (19)

Results and Discussion

Syntheses. The complexes Cp*Mn(CO)$_2$(THF), Cp*Re(CO)$_2$(THF), and CpRe(CO)$_2$(THF), generated by

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[13] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351. Normalized corrections ranged between 0.48 and 1.00.

[14] $r^* = 0.30$ (3): Larson, A. C. In *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 291, eq 22.

[15] $w = [6.2445t_0(x) + 8.2477t_1(x) + 3.0244t_2(x)]^{-1}$, where $x = |F_o|/F_{max}$ and t_n are the polynomial functions of the Chebyshev series: Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, *A35*, 698.

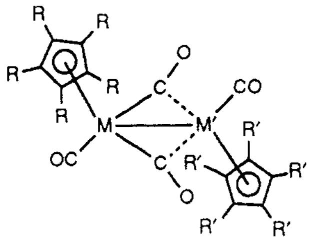
[16] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV. p 99.

[17] Gabe, E. J.; Larson, A. C.; Lee, F. L.; LePage, Y. *NRC VAX Crystal Structure System*; National Research Council: Ottawa, Ontario, Canada 1984.

[18] Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS*; Chemical Crystallography Laboratory: University of Oxford: Oxford, England, 1984.

[19] Davies, E. K. *SNOOPI Plot Program*; Chemical Crystallography Laboratory: University of Oxford; Oxford, England, 1984.

ultraviolet photolysis of the corresponding tricarbonyl complexes in THF, reacted with $Cp^{*}Ir(CO)_2$ with displacement of the labile THF ligand to give moderate yields of the heterobinuclear complexes 1–3. When the syntheses were conducted at room temperature in THF alone, displacement of the THF ligand was inefficient, and reaction times of several hours were required. These reaction times could be shortened considerably at higher temperatures, generally with no decrease in yield (and sometimes a small improvement, particularly where THF was diluted with cyclohexane). The products, particularly 1, are somewhat light sensitive so the reactions were done best in the dark. Complex 1 was alternatively synthesized by displacement of the dinitrogen ligand from $Cp^{*}Re(CO)_2(N_2)$; although an increased yield was observed with this procedure, it offers little advantage when the relatively poor conversion[12] of $Cp^{*}Re(CO)_3$ to $Cp^{*}Re(CO)_2(N_2)$ is taken into account. Several unsuccessful attempts were also made to synthesize the (methylcyclopentadienyl)manganese analogue of 1 $(\eta^5\text{-}MeC_5H_4)(CO)Mn(\mu\text{-}CO)_2Ir(CO)(\eta^5\text{-}C_5Me_5)$ by analogous procedures, starting from the readily available and inexpensive $(\eta^5\text{-}MeC_5H_4)Mn(CO)_3$.



1, M = Mn, M′ = Ir, R = R′ = CH_3
2, M = Re, M′ = Ir, R = R′ = CH_3
3, M = Re, M′ = Ir, R = H, R′ = CH_3

Compounds 1–3 are moderately soluble in THF, diethyl ether, benzene, and toluene and slightly soluble in hexane. They are not stable in polar solvents such as acetone, chloroform, or dichloromethane. The IR spectrum shows rapid loss of the absorption from the complexes and the production of absorptions attributable to $Cp^{*}Mn(CO)_3$, $Cp^{*}Re(CO)_3$, $CpRe(CO)_3$, $Cp^{*}Ir(CO)_2$, or $Cp^{*}Ir(CO)Cl_2$, depending on the complex and solvent. Solutions in benzene and THF slowly deteriorate in the dark at room temperature with the production of the mononuclear carbonyl complexes or do so rapidly when UV irradiated in Pyrex.

Characterization. Compounds 1–3 were formulated on the basis of microanalysis and spectroscopy. The electron-impact mass spectrum (70 eV) in each case gave the parent ion with an isotope abundance pattern in agreement with the calculated pattern. In each case, there is the sequential loss of the four CO groups and the expected loss of H atoms from the Cp* ring, though for 2 and 3 the loss of the final CO group is accompanied by considerable hydrogen loss, resulting in a broad envelope of peaks extending below the predicted position. A feature common to all three compounds is the strong appearance of the fragments $Cp^{*}Ir(CO)$ m/z 356, and $(Cp^{*} - 2H)Ir(CO)$ m/z 354, indicating that fragmentation of the molecular ion by way of the loss of $Cp^{*}Re(CO)_3$, $CpRe(CO)_3$, and $Cp^{*}Mn(CO)_3$ in 2, 3, and 1, respectively, is important. This is in accord with the view adopted later on the basis of the crystallography data that the structures can be rationalized in terms of a donor metal–metal bond from these fragments to an unsaturated $Cp^{*}Ir(CO)$ moiety. By contrast, the loss of $Cp^{*}Ir(CO)_2$ is not observed in the mass spectra. The IR spectra exhibited two ν(CO) absorptions for terminal CO groups above ca. 1900 cm^{-1} and a third, broad, weaker absorption near ca. 1750 cm^{-1} associated with one or more bridging carbonyl groups. The presence of the $\eta^5\text{-}C_5Me_5$ or $\eta^5\text{-}C_5H_5$ groups was clearly revealed in the ^{1}H NMR spectra and confirmed by the ^{13}C NMR spectra. The latter showed, for compound 2, sharp resonances for carbonyl groups at δ 170.32, 203.72, and 224.65 in approximate ratio 1:1:2. The first can be assigned to a CO group terminally bound to the iridium atom by comparison with $Cp^{*}Ir(CO)_2$ for which we have measured δ(CO) 178.0 in C_6D_6 (and with $CpIr(CO)_2$, δ(CO) 173.8),[20] the second to a CO terminally bound to the Re atom by comparison with $Cp^{*}Re(CO)_3$ for which we have measured δ(CO) 198.2 in C_6D_6 (and with $CpRe(CO)_3$, δ(CO) 195),[21] and the third to two equivalent bridging CO groups. For the manganese compound (1), the resonance for the terminal Ir(CO) group was in a similar position (δ 168.2) and the resonance for the bridging CO groups was evident at δ 247.9; however, no resonance could be observed corresponding to the CO group terminally bound to the Mn. This is attributed to quadrupolar broadening of this signal by coupling to the ^{55}Mn nucleus.[22] We were able to observe a CO resonance for $Cp^{*}Mn(CO)_3$ in C_6D_6 at δ 227.2.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Cp^{*}(CO)Ir(\mu_2\text{-}CO)_2Re(CO)Cp$ (3)[a]

	Distances		
Ir–Re	2.8081 (6)		
Ir–Cp*[b]	1.92	Re–Cp[b]	1.95
Ir–C(2)	1.80 (1)	Re–C(1)	1.85 (2)
Ir–C(3)	2.25	Re–C(3)	1.97
Ir–C(4)	2.20	Re–C(4)	1.97
O(2)–C(2)	1.20 (1)	O(1)–C(1)	1.19 (2)
O(3)–C(3)	1.22	O(4)–C(4)	1.19
	Angles		
C(2)–Ir–Re	91.7 (4)	C(1)–Re–Ir	97.5 (5)
C(3)–Ir–Re	44.1	C(3)–Re–Ir	52.6
C(4)–Ir–Re	44.2	C(4)–Re–Ir	51.4
C(3)–Ir–C(2)	97 (2)	C(3)–Re–C(1)	84 (2)
C(4)–Ir–C(2)	91 (2)	C(4)–Re–C(1)	99 (2)
C(4)–Ir–C(3)	88	C(4)–Re–C(3)	104
Cp*–Ir–C(2)	132	Cp–Re–C(1)	125
Cp*–Ir–C(3)	117	Cp–Re–C(3)	122
Cp*–Ir–C(4)	121	Cp–Re–C(4)	117
Cp*–Ir–Re	136	Cp–Re–Ir	138
O(2)–C(2)–Ir	169 (4)	O(1)–C(1)–Re	175 (2)
O(3)–C(3)–Ir	120 (2)	O(3)–C(3)–Re	150 (2)
O(4)–C(4)–Ir	124 (2)	O(4)–C(4)–Re	149 (2)
Re–C(3)–Ir	83.3	Re–C(4)–Ir	84.4

[a] Estimated standard deviations are not given for parameters affected by the soft distance restraints employed during least-squares refinement. [b] Cp* and Cp signify the centers of gravity of the respective C_5 rings.

The structure of 3 determined by X-ray crystallography is illustrated in Figure 1, and selected interatomic distances and angles are given in Table III. The structure consists of discrete molecules of 3 with no significant intermolecular contacts. In the ordered model presented here, the molecule has no crystallographic symmetry elements. Chemically, however, the molecule has pseudo-C_s symmetry, where the mirror plane contains atoms Re and Ir and the terminal carbonyl groups C(1)–O(1) and C(2)–O(2). The possibility of crystallographic mirror symmetry cannot be entirely excluded by our work (see Experimental Section, above).

Only two Ir–Re bond distances have been previously reported, and they are 2.9117 (7) Å for the single covalent bond in $(P(Cy)_2)(CO)_2Re(\mu\text{-}PCy_2)_2Ir(CO)_2(PCy_2)$ (Cy =

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(20) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981; p 180.

(21) Reference 20 p 166.

(22) Reference 20, p 3.

cyclohexyl) and 2.6573 (5) Å for the formally double bond in $(PCy_2)_2Re(\mu\text{-}PCy_2)_2Ir(PMe_3)_2$.[23] These species are rather chemically different from **3**. The Re–Ir distance of 2.8081 (6) Å for **3** (not corrected for thermal motion[24]) is more comparable to the Ir–Ir single covalent bond in $[Cp^*Ir(CO)_2]_2^{2+}$ (2.8349 (12) Å).[25]

The carbonyl groups (C(3)–O(3), C(4)–O(4)) can be described as primarily bound to the Re atom and semibridging to the Ir atom. This is a feature that has been previously observed in the structures of two related molecules of the type (arene)(CO)M(μ_2-CO)$_2$M′(CO)(arene′), but in each previous case, M has been a 3d metal bound to a 4d metal M′. Here we see the same structural feature occuring where both metals are 5d metals. The previous examples are $Cp(CO)Mn(\mu_2\text{-}CO)_2Rh(CO)Cp^*$[8] and $(\eta^6\text{-}C_6H_6)(CO)Cr(\mu_2\text{-}CO)_2Rh(CO)Cp^*$.[6h] While the reaction can be envisaged to proceed by displacement of the weakly bonded THF ligand from $CpRe(CO)_2(THF)$ by the basic $Cp^*Ir(CO)_2$ with the formation of a dative bond from Ir to Re in $Cp(CO)_2Re \leftarrow Ir(CO)_2Cp^*$, clearly CO rearrangement occurs and the structure of **3** that results may be visualized to be built from a dative bond[6l] from an 18-electron $CpRe(CO)_3$ moiety to the 16-electron fragment $Cp^*Ir(CO)$, assisted by return of electron density from Ir via the semibridging CO groups in order to mitigate the charge imbalance, as proposed by Cotton for the similar situation in $Cp_2V_2(CO)_3(\mu_2\text{-}CO)_2$.[26] Since this structural pattern is now so well established for this type of binuclear complex, there is every reason to expect that complexes **1** and **2** also are structurally analogous to **3** and also possess semibridging CO groups as illustrated. In fact, complex **2** was also investigated by single-crystal X-ray diffraction, but the structure solution was abandoned at a point where it was clear that there was severe disorder between the rhenium and iridium atom positions and their associated carbonyl and $\eta^5\text{-}C_5Me_5$ groups, in a molecular structure similar to that of **3**.

Thus, these structures may be compared directly with the structures of the corresponding homometallic analogues $[Cp^*M(CO)_2]_2$ (M = Fe, Ru, Os). Although no crystallographic determinations appear to have been reported for these, the IR spectrum in each case displays a single ν(CO) absorption at 1908–1922 cm^{-1} for terminal carbonyls and a single ν(CO) absorption at 1707–1745 cm^{-1} for bridging carbonyls. Such a simple spectrum is consistent with a trans structure, with both terminal and bridging CO groups, and inversion symmetry.

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Supplementary Material Available: Tables of full crystallographic data (Table SI), hydrogen atom coordinates and isotropic thermal parameters (Table SII), and anisotropic thermal parameters for Ir and Re (Table SIII) (3 pages); a table of observed and calculated structure factors for 3 (7 pages). Ordering information is given on any current masthead page.

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[23] Baker, R. T.; Calabrese, J. C.; Glassman, T. E. *Organometallics* **1988**, *7*, 1889.

[24] The upper and lower limit corrected bond lengths are 2.855 and 2.817 Å; Johnson, C. K. *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 220.

[25] Einstein, F. W. B.; Jones, R. H.; Zhang, X.; Yan, X.; Nagelkerke, R.; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1424.

[26] (a) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1. For a recent discussion of semibridging carbonyl groups, see: (b) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1986**, *25*, 805. (c) Sargent, A. L.; Hall, M. B. *J. Am. Chem. Soc.* **1989**, *111*, 1563.

Formation of Carbon–Hydrogen and Oxygen–Hydrogen Bonds at Iridium Centers: Addition of H_2 and HCl to *trans*-RIr(CO)L_2 (R = Me, OMe; L = PPh_3, P(*p*-tolyl)$_3$)

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Reaction of *trans*-RIr(CO)L_2 with HX (R = Me, L = P(*p*-tolyl)$_3$, X = H, Cl; R = OMe, L = PPh_3, X = H; R = OMe, L = P(*p*-tolyl)$_3$, X = Cl results in RH and $HIr(X)_2(CO)L_2$. Low-temperature NMR spectra (^1H and ^{31}P) show that these reactions occur through oxidative-addition, reductive-elimination sequences. A normal deuterium isotope effect is observed ($k_H/k_D = 1.4$). Formation of the carbon (sp^3)–hydrogen bond occurs more readily than formation of the carbon (sp^2)–hydrogen bond or the oxygen–hydrogen bond. The nature of the hydrogen source (HX; X = H, Cl) does not significantly affect CH_4 formation but is significant for CH_3OH formation. Considering the geometric and product differences, however, the three types of bonds are formed with remarkably similar barriers.

Formation of bonds to hydrogen is central in many catalytic reactions.[1] Although the ready formation of carbon–hydrogen bonds initially limited modeling these reactions, there have now appeared several studies of C–H bond formation.[2] Formation of O–H bonds has received much less attention.[3]

Table I. NMR Data (ppm) for RIr(H)(Cl)(CO)L_2

	^1H			
R	Me(*p*-tolyl)	R	H^-	$^{31}P\{^1H\}$
Me	2.25 (s)	–0.04 (t)	–18.7 (t)	–0.05 (s)
Ph	2.25 (s)		–17.8 (t)	–1.0 (s)
OMe	2.25 (s)	3.2 (s)	–15.7 (t)	–3.0 (s)
Cl	2.25 (s)		–16.2 (t)	–2.7 (s)

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[1] (a) Masters, C. *Homogeneous Transition-Metal Catalysis*; Chapman and Hall: London, 1981. (b) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

0276-7333/90/2309-2727$02.50/0