Table I. Equilibrium Constants (K_3) for Addition of L to $Mo(CO)_2(S_2CNEt_2)_2$ (**1b**)

ligand (L)	Br^- [a]	*trans*-stilbene[a]	Cl^- [a]	tht[a]	py[a]	$P(OPh)_3$ [b]	PPh_3 [b]	CO(g)[b]
K_3, M^{-1}	0.5 (1)[c,d]	0.7 (1)[e]	3.0 (6)[d]	45 (5)[e]	440 (40)[e]	49 (3) × 10^3 [f]	49 (3) × 10^3 [f]	350 (20)[g]

[a] Measurements conducted in CH_2Cl_2 at 22 °C. [b] Measurements conducted in o-$C_6H_4Cl_2$ at 22 °C. [c] The estimated error in the last figure is indicated in parentheses. [d] Determined by quantitative infrared absorption spectroscopy. [e] Determined by quantitative electronic absorption spectroscopy. [f] K_1 was determined by infrared techniques and K_3 was calculated from K_1 and K_2 (see text). [g] The units for L = CO are atm^{-1}; $K_3(CO) \equiv K_2$.

Table II. Selected Bond Distances and Angles for $Mo(CO)_2(SC_4H_8)(S_2CNEt_2)_2$ (**3b**)

Bond Distances, Å			
Mo-S1	2.524 (3)	Mo-C1	1.901 (11)
Mo-S2	2.517 (3)	Mo-C2	1.901 (11)
Mo-S3	2.538 (3)	C1-O1	1.197 (11)
Mo-S4	2.537 (3)	C2-O2	1.160 (10)
Mo-S5	2.701 (3)		
Bond Angles, Deg			
S1-Mo-S2	68.2 (1)	C2-Mo-S5	173.2 (3)
S3-Mo-S4	68.2 (1)	C1-Mo-C2	73.5 (5)
C1-Mo-S5	113.2 (3)		

of **3b** is depicted in Figure 1, and selected bond distances and angles are listed in Table II.[10] The two structural features of **3b** most relevant to the frontier orbital reaction hypothesis are (1) the gross coordination geometry with L capping the quadrilateral S_4 face opposite both carbonyl ligands and (2) the Mo–S(**tht**) length (2.70 Å) which exceeds nominal single-bond expectations.[11] The location of L in the seven-coordinate adducts may reflect the π-acceptor ability of the ligand (CO and PPh_3 cis to both carbonyls and **tht** opposite the carbonyls), but the present data base is insufficient to confirm this hypothesis.

The stepwise substitution mechanism shown in Scheme I incorporates the structural features of "intermediates" **3b** and **1a**. To the extent that **tht** and N_2H_4 are representative of other donor ligands, these results suggest that nucleophiles attack opposite the carbonyls in **1** prior to adopting the final isomeric form, e.g., *cis*-$ML(CO)_2$ for L = CO or PPh_3. It follows from the principle of microscopic reversibility that $M(CO)_2L(S_2CNR_2)_2$ adopts a geometry with L over the S_4 face prior to dissociation of L.

This system illustrates several important mechanistic points. (1) The structure of 16-electron intermediates need not bear a close relationship to saturated reagents or products. (2) Electron-deficient species may adopt geometries which are unprecedented for related 18-electron complexes. (3) Even when ligand substitution occurs with retention of the original coordination geometry, the reaction pathway may be mapped more accurately by a series of reversible structural rearrangements accompanying ligand dissociation and addition than by a principle of least motion reaction scheme. (4) Access to unsaturated intermediates may involve prior rearrangement of the reagent rather than ligand dissociation followed by reorganization of the electron-deficient intermediate. This final point is in accord with Hammond's postulate[12] since the transition state for ligand dissociation would resemble the unsaturated intermediate rather than the reagent.

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

Registry No. **1b**, 74807-43-5; **3b**, 81830-95-7; Br^-, 24959-67-9; *trans*-stilbene, 103-30-0; Cl^-, 16887-00-6; tht, 110-01-0; py, 110-86-1; $P(OPh)_3$, 101-02-0; PPh_3, 603-35-0; CO, 630-08-0.

Supplementary Material Available: A table of positional and thermal parameters for **3b** (2 pages). Ordering information is given on any current masthead page.

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[10] The crystal selected was monoclinic, space group $P2_1/n$, with unit cell dimensions of a = 8.289 (7) Å, b = 17.956 (5) Å, c = 15.913 (6) Å, β = 102.77 (5)°, and Z = 4. Of the 5291 reflections monitored, 1647 independent reflections with $I > 3\sigma(I)$ were used in the structure solution and refinement which converged to 0.061 and 0.044 for R and R_w, respectively. The final difference Fourier map was featureless with the highest residual electron equal to 0.40 e/Å^3.

[11] Compare with the following M–S distances (M = Mo or W). (a) W–S(tht) = 2.57 Å in $[WCl_2(tht)]_2(\mu\text{-}S)(\mu\text{-}SEt)_2$: Boorman, P. M.; Kerr, K. A.; Patel, V. D. *J. Chem. Soc., Dalton Trans.* **1981**, 506. (b) W–S(dithiohexane = dth) = 2.54, 2.58 Å in $(OC)_3W(dth)Cl(SnCl_2Me)$: Elder, M.; Hall, D. *Inorg. Chem.* **1969**, *8*, 1273. (c) Mo-S(S-PPh_3) 2.46 Å in $MoOCl_3(SPPh_3)$: Boorman, P. M.; Garner, C. D.; Mabbs, F. E.; King, T. J. *J. Chem. Soc., Chem. Commun.* **1974**, 663.

[12] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

Heterobimetallic Phosphido-Bridged Complexes Containing Coordinatively Unsaturated Rhodium(I) and Iridium(I) Centers

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Summary: A series of new phosphido-bridged heterometallic dinuclear complexes $FeM(\mu\text{-}PPh_2)(CO)_x(L)_2$ (M = Rh, L = PEt_3, x = 4, 5; M = Ir, L = PPh_3, x = 4–6) have been synthesized by the reaction of $Li[Fe(CO)_4(PPh_2)]$ with the appropriate *trans*-$MCl(CO)L_2$ complex. Each of the new compounds undergoes a series of reversible addition/elimination reactions with CO, and the Fe–Ir compounds react with H_2 to give new H_2 adducts.

Although a very large number of heterobimetallic complexes have been prepared and characterized, nearly all are coordinatively saturated with a high percentage of carbonyls and other ligands that are reluctant to undergo dissociation.[1-3] Thus, most of these complexes have shown relatively low reactivity toward reversible addition and exchange of ligands. The latter are particularly desirable properties if such complexes are to be used as bimetallic catalysts. Ideal complexes would appear to be those which link traditional monomeric homogeneous catalysts of the group 8 metals to another metal center, preferably with a bridging ligand to assist in holding the metals together. Reported herein are the syntheses and preliminary re-

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[1] Roberts, D. A.; Geoffroy, G. L., "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 40.

[2] Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207.

[3] Vyazankin, N. S.; Razuvalo, G. A.; Kruglaya, O. A. *Organomet. Chem. Rev., Sect. A* **1968**, *3*, 823.

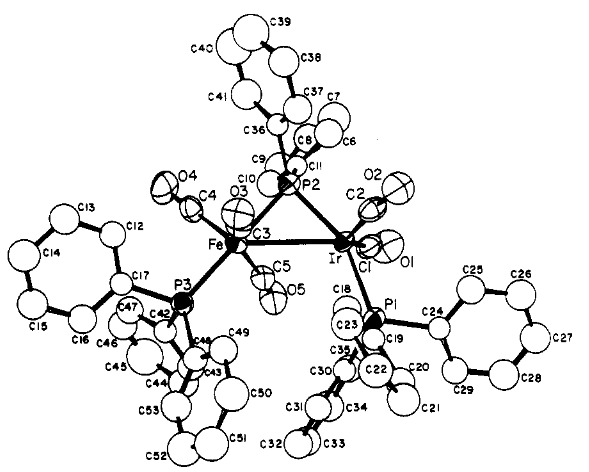


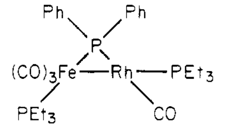
Figure 1. An ORTEP plot of $FeIr(\mu-PPh_2)(CO)_5(PPh_3)_2$. Thermal ellipsoids are drawn at the 25% probability level. Relevant bond distances and angles are as follows: Fe–Ir = 2.960 (1) Å, Ir–P1 = 2.349 (2) Å, Ir–P2 = 2.292 (2) Å, Fe–P2 = 2.239 (2) Å, Fe–P3 = 2.248 (2) Å, P2–Ir–Fe = 48.45 (5)°, Ir–Fe–P2 = 49.99 (5)°, Fe–P2–Ir = 81.62 (7)°, P1–Ir–P2 = 158.07 (6)°, P2–Fe–P3 = 179.52 (8)°, Fe–Ir–P1 = 109.93 (5)°, Ir–Fe–P3 = 129.58 (6)°.

activity studies of a series of such complexes which link Fe to Rh(I) and Ir(I) centers and which undergo rapid and reversible ligand addition and oxidative-addition reactions.

The new complexes were prepared by stirring $Li[Fe(CO)_4(PPh_2)]$[4] with the appropriate *trans*-$MCl(CO)L_2$ (M = Rh, Ir; L = PPh_3, PEt_3)[5] complex in deoxygenated THF for 2–5 h at 25 °C (eq 1).[6] Complexes 1 and 2 were

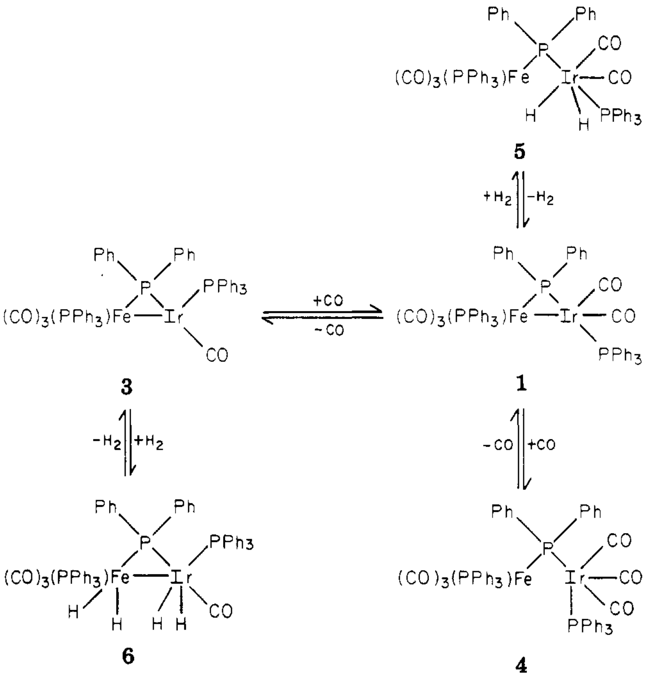
$$\begin{aligned} &Li[Fe(CO)_4(PPh_2)] + trans\text{-}MCl(CO)L_2 \rightarrow \\ &\qquad LiCl + FeM(\mu\text{-}PPh_2)L_2(CO)_x \qquad (1) \\ &\qquad 1,\ M = Ir,\ L = PPh_3,\ x = 5\ (37\%) \\ &\qquad 2,\ M = Rh,\ L = PEt_3,\ x = 4\ (64\%) \end{aligned}$$

characterized by spectroscopy and by satisfactory C and H analyses.[7] The $^{31}P\{^1H\}$ NMR spectrum of 2 implies the structure given below. It shows resonances at $\delta(Rh{-}PEt_3)$ 31.9 (dd, $J_{P_{Rh}-Rh}$ = 182.1 Hz, $J_{P_{Rh}-P_\mu}$ = 23.6 Hz), $\delta(Fe{-}PEt_3)$ 69.8 (d, $J_{P_{Fe}-P_\mu}$ = 22.6 Hz), and $\delta(\mu\text{-}PPh_2)$ 119.7 (ddd, $J_{P_\mu-Rh}$ = 107.3 Hz).[7] The absence of $^{31}P{-}^{103}Rh$ coupling on the δ 69.8 resonance implies this PEt_3 is not attached to Rh, and the downfield position of the μ-PPh_2 resonance argues for the presence of a metal–metal bond.[8] $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$, 1, shows a similar $^{31}P\{^1H\}$ NMR spectrum except for the absence of ^{103}Rh coupling.[7] The ^{13}C NMR spectrum of 2 shows resonances at δ(Fe–CO) 217.3 (dd), δ(Fe–CO) 213.5 (dd), and δ(Rh–CO) 204.1 (ddd, J_{C-Rh} = 84.8 Hz) in relative intensities 1:2:1, implying one CO on Rh and two equivalent and one inequivalent CO groups on Fe, consistent with the structure drawn above.[7]

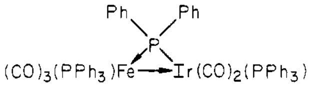


2

Scheme I



Complex 1 was further characterized by a single-crystal X-ray diffraction study, and an ORTEP plot is shown in Figure 1.[9] The structure is similar to that deduced for 2 except that Ir is coordinated by two CO groups in 1. The Fe–Ir bond length of 2.960 (1) Å is significantly longer than expected for a direct single metal–metal bond and may imply a weak donor–acceptor interaction between the two metals as given below.[10] Considering the Fe as a two-electron donor to Ir, both centers are coordinatively-saturated with 18 valence electrons, although a coordination



1

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(4) (a) Treichel, P. M.; Douglas, W. M.; Dean, W. K. *Inorg. Chem.* **1972**, *11*, 1615. (b) Treichel, P. M.; Dean, W. K.; Douglas, W. M. *Ibid.* **1972**, *11*, 1609.

(5) (a) Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *11*, 99. (b) Vrieze, K.; Collman, J. P.; Sears, C. T., Jr.; Kubota, M. *Ibid.* **1968**, *11*, 101.

(6) Preparation of 1: 1 equiv. of *n*-BuLi was added to a dried and deoxygenated tetrahydrofuran (THF) solution of $Fe(CO)_4(PPh_2H)^{4b}$ (0.4607 g, 1.30 mmol) to generate $Li[Fe(CO)_4(PPh_2)]$ in situ. The resultant red solution was slowly added to a THF solution of *trans*-$IrCl(CO)(PPh_3)_2{}^{5b}$ (1.0003 g, 1.28 mmol). After the solution was stirred for 3 h at 25 °C, THF was removed from the resultant green solution and the neutral products were extracted from the residue with toluene. Chromatography on alumina with 20% CH_2Cl_2–80% hexane under N_2 gave 1 as a yellow, air-stable microcrystalline solid in 37% yield (0.520 g, 0.47 mmol).

(7) Characterization data for the new complexes are given in Table A of the supplementary material: elemental analyses for 1 and 2; IR and $^{31}P\{^1H\}$ NMR data for 1 → 7; ^1H NMR data for 5 and 6; ^{13}C NMR data for 2 and 7. $^{31}P\{^1H\}$ NMR spectra for 1 → 4 are also shown in Figure A of the supplementary material.

(8) The μ-PR_2 ligands in compounds with metal bonds generally show downfield (δ 50–300) ^{31}P NMR resonances whereas upfield (δ 50 → δ −200) resonances are observed for compounds in which the μ-PR_2 ligand bridges two metals not joined by a metal–metal bond. Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186. Carty, A. J.; Maclaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, *C27*. Carty, A. J. *Adv. Chem. Ser.*, **1982**, *196*, 163. Garrou, P. *Chem. Rev.* **1981**, *81*, 299. Johannsen, G.; Stelzer, O. *Chem. Ber.* **1977**, *110*, 3438.

(9) Crystals of 1 form in the triclinic space group $P\bar{1}$. Cell constants of a = 11.681 (3) Å, b, = 20.869 (4) Å, c = 10.649 (9) Å, α = 96.74 (3)°, β = 108.86 (3)°, γ = 76.51 (2)°, and V = 2386 (3) Å^3 were obtained from the refined settings of 24 reflections with 2θ settings greater than 20° (Mo Kα radiation). The intensities of 6972 independent reflections were measured using an automated diffractometer. Of these, 6257 had $F_o^2 > 3\sigma(F_o^2)$ and were included in the refinement of the structure. The locations of the Fe and Ir atoms were obtained from a Patterson map. The remaining atoms of the structure were located with phases from these atoms. Least-squares refinement of the complete structure converged with R = 0.053 and R_w = 0.077.

(10) Similar bonding descriptions have been given for other μ-ER_2 (E = As, P) bridged dinuclear complexes: Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379. Keller, E.; Vahrenkamp, H. *Chem. Ber.* **1976**, *109*, 229.

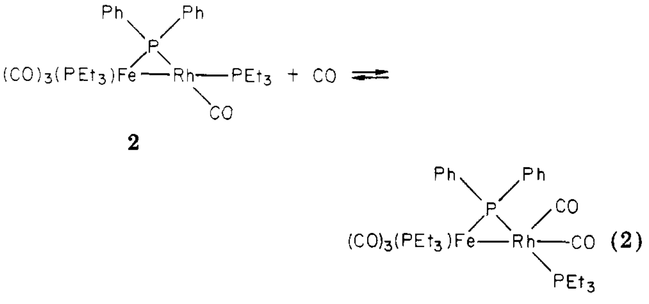
site on Ir can readily open via cleavage of the Fe–Ir bond (vida infra).

The chemistry observed with **1** and its derivatives is summarized in Scheme I. When **1** is heated (110 °C, 0.5 h) or irradiated ($\lambda = 366$ nm) under an N_2 purge, CO loss occurs to generate $FeIr(\mu\text{-}PPh_2)(CO)_4(PPh_3)_2$, **3**, in near quantitative yield.[7] This complex is isoelectronic and presumably isostructural with **2**. Its $^{31}P\{^1H\}$ NMR spectrum shows resonances at $\delta(Ir\text{–}PPh_3)$ 24.7 (d, $J_{P_{Ir}\text{-}P_\mu} = 22.6$ Hz), $\delta(Fe\text{–}PPh_3)$ 78.0 (d, $J_{P_{Fe}\text{-}P_\mu} = 28.5$ Hz), and δ (μ-PPh_2) 104.6 (dd) consistent with such a structure. Even with metal–metal bonds, **2** and **3** are coordinatively unsaturated. The **1** → **3** conversion is readily reversed by exposure to 1 atm of CO at 25 °C, but under these conditions additional CO is added to give $FeIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$, **4**.[7] The **1** → **4** conversion occurs rapidly, and ^{31}P NMR spectra indicate that **4** is quantitatively formed under 1 atm of CO at 25 °C. **1** is easily regenerated simply by removing the CO atmosphere. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows resonances at $\delta(Ir\text{–}PPh_3)$ −1.8 (d, $J_{P_{Ir}\text{-}P_\mu} = 143.7$ Hz), δ-$(Fe\text{–}PPh_3)$ 84.7 (d, $J_{P_{Fe}\text{-}P_\mu} = 29.5$ Hz), and $\delta(\mu\text{-}PPh_2)$ 12.8 (dd). The marked upfield shift in the resonance due to the μ-PPh_2 group in **4** implies the absence of an Fe–Ir bond,[8] as expected since each metal has 18 valence electrons without the necessity of a metal–metal bond.

Both **1** and **3** add H_2 (Scheme I). Addition of H_2 (1 atm, 25 °C) to **1** rapidly gives $FeIrH_2(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$, **5**, in near quantitative yield.[7] Addition to the Ir center is indicated by the ^{31}P NMR resonance attributable to PPh_3 on Ir which appears as a doublet of triplets at δ 1.9 ($J_{^{31}P_{Ir}\text{-}^{31}P_\mu}$ = 187.0 Hz, $J_{^{31}P_{Ir}\text{-}^1H} = 17.6$ Hz).[7] The **1** → **5** conversion necessarily leads to the cleavage of the Fe–Ir bond, as evidenced by the upfield $^{31}P\{^1H\}$ resonance of the μ-PPh_2 group (δ 21.5 (dd, $J_{P_\mu\text{-}P_{Fe}} = 24.6$ Hz)). The tetracarbonyl complex **3** also reacts with H_2. Preliminary spectroscopic evidence indicates that loss of CO occurs and the tetrahydride complex $FeIr(\mu\text{-}PPh_2)H_4(CO)_3(PPh_3)_2$, **6**, forms.[7,11] The −40 °C ^1H NMR spectrum of **6** shows four distinct hydride resonances at δ −9.3 (m), −10.5 (dd), −11.8 (dd), and −16.8 (dd) each of relative intensity 1. Selective decoupling experiments showed that each of the terminal PPh_3 ligands couples to two inequivalent hydrides and thus structure **6** in Scheme I is suggested.[12]

The **3** → **4** and **3** → **5** conversions of Scheme I are particularly interesting in that they illustrate a reactivity feature which is unique to di- and polynuclear complexes. These conversions represent a total of four electron additions without requiring net dissociation of any ligand from the complex. The first CO addition, **3** → **1**, occurs at a coordinatively unsaturated Ir center, but the product **1** has the maximum 18-valence-electron configuration at each metal. The second ligand addition, **1** → **4** or **1** → **5**, occurs at the expense of the Fe–Ir bond. In essence, the $Fe(\mu\text{-}PPh_2)$ unit behaves as a bidentate ligand in which the Fe end is loosely coordinated and can readily, *but reversibly*, dissociate when necessary to open a coordination site for further reactivity.

The FeRh complex **2** has proven less reactive than **3**. It does not add H_2 at ambient to moderate (6 atm) pressures but does reversibly bind CO (25 °C, 1 atm), eq 2. Complex



2

(2)

7

7 has been spectroscopically characterized and appears to be structurally analogous to **1**.[7] Its $^{31}P\{^1H\}$ NMR spectrum shows resonances at $\delta(Rh\text{–}PEt_3)$ 37.5 (dd, $J_{P_{Rh}\text{-}Rh} = 105.9$ Hz, $J_{P_{Rh}\text{-}P_\mu} = 189.7$ Hz), $\delta(Fe\text{–}PEt_3)$ 69.4 (d, $J_{P_{Fe}\text{-}P_\mu} = 19.1$ Hz), and $\delta(\mu\text{-}PPh_2)$ 157.6 (ddd, $J_{P_\mu\text{-}Rh} = 82.7$ Hz). Both ^{31}P and ^{13}C NMR data indicate that the CO addition/elimination reactions of eq 2 are fast at room temperature. At −37 °C, the $^{31}P\{^1H\}$ NMR spectrum of a solution containing approximately equimolar amounts of **2** and **7** show distinct resonances at δ 157.6 (**2**) and 119.7 (**7**) due to the μ-PPh_2 ligands of the two separate compounds. At 27 °C, these have coalesced into a single broad resonance at δ 132, indicating a rapid **2** ⇄ **7** interconversion. The ^{13}C NMR spectrum of ^{13}CO-enriched **7** at −40 °C shows a resonance at δ 196.3 (ddd, $J_{^{13}C\text{-}^{103}Rh} = 78.8$ Hz, $J_{^{13}C\text{-}^{31}P_{Rh}} = 18.7$ Hz, $J_{^{13}C\text{-}^{31}P_\mu} = 7.9$ Hz) due to two exchange-averaged Rh–CO groups. At 25 °C, this resonance has broadened and lost $^{103}Rh\text{–}^{13}C$ coupling, implying rapid exchange of coordinated CO with free CO.

In summary, this work has shown that dinuclear complexes which contain coordinatively unsaturated group 8 metals exhibit the type of ligand addition/elimination reactions that are required in many catalytic transformations, and furthermore, as shown for the **2** ⇄ **7** equilibrium, such reactions can be quite rapid. These complexes provide the opportunity to explore the chemistry that can occur at a metal center that is ligated by a second transition metal and to take advantage of the ease of cleavage of single metal–metal bonds to reversibly open coordination sites.[13] The coordinative unsaturated nature of the Rh and Ir centers in these particular complexes should also allow the preparation and study of derivatives with organic ligands which should result from addition and oxidative-addition reactions.

Acknowledgment. This work was supported by the National Science Foundation and by grants from the Standard Oil Co. (Ohio) and Air Products and Chemicals, Inc. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award for the period 1978–1983.

Registry No. 1, 81987-86-2; 2, 82135-57-7; 3, 82135-53-8; 4, 81987-87-3; 5, 81987-88-4; 6, 81987-89-5; 7, 81987-90-8; $Li[Fe(CO)_4(PPh_2)]$, 82042-06-6; *trans*-$IrCl(CO)(PPh_3)_2$, 15318-31-7; *trans*-$RhCl(CO)(PEt_3)_2$, 15631-52-4.

Supplementary Material Available: Listings of positional and thermal parameters for the X-ray structure of 1 (Tables B–D) and calculated and observed structure factors for 1 (Table G), a figure showing the $^{31}P\{^1H\}$ NMR spectra of 1–4 (Figure A), and tables of analytical and spectroscopic data (Table A) and selected bond distances (Table E) and angles (Table F) for 1 (36 pages). Ordering information is given on any current masthead page.

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(11) $^{31}P\{^1H\}$ for **6**: $\delta(Ir\text{–}PPh_3)$ 10.0 (d, $J_{P_{Ir}\text{-}P_\mu} = 225$ Hz), $\delta(Fe\text{–}PPh_3)$ 67.4 (d, $J_{P_{Fe}\text{-}P_\mu} = 61$ Hz), $\delta(\mu\text{-}PPh_2)$ 117.8 (dd).

(12) Although the structure drawn for **6** in Scheme I with the hydride ligands terminal rather than bridging may seem unusual, other μ-PPh_2 and μ-SR bridged compounds have been prepared and shown to possess terminal rather than bridging hydrides. See: Bonnet, J. J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, J. *J. Am. Chem. Soc.* **1979**, *101*, 5940. Braunstein, P.; Matt, D.; Bars, O.; Louer, M.; Grandjean, D.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1981**, *213*, 79.

(13) a) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379. b) Meyer, T. J. *Prog. Inorg. Chem.* **1975**, *19*, 1.