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Heterobimetallic Phosphido-Bridged Complexes Containing Coordinatively Unsaturated Rhodium(I) and Iridium(I) Centers. Structural Characterization of FeIr(μ-PPh_2)$(CO)_5(PPh_3)_2$

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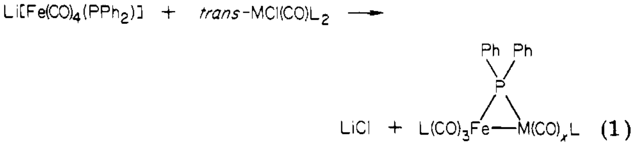
The series of new phosphido-bridged heterometallic binuclear complexes FeM(μ-PPh_2)$(CO)_x(L)_2$ (M = Rh, L = PEt_3, x = 4, 5; M = Ir, L = PPh_3, x = 4–6) have been synthesized by the reaction of Li[Fe$(CO)_4(PPh_2)$] with the appropriate *trans*-MCl(CO)L_2 complex. The new complexes have been characterized spectroscopically, and FeIr(μ-PPh_2)$(CO)_5(PPh_3)_2$ has been characterized by a complete single-crystal X-ray diffraction study. It crystallizes in the space group $P\bar{1}$ with 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)°, V = 2386 (3) Å^3, and Z = 2. Diffraction data ($0° \leq 2\theta \leq 50°$) were collected with an Enraf-Nonius CAD4 automated diffractometer, using graphite-monochromatized Mo Kα radiation, and the structure was refined to R = 0.053 and R_w = 0.077 for 6257 independent reflections with $I \geq 3.0\sigma(I)$. The μ-PPh_2 ligand bridges the Fe and Ir atoms, and each metal is ligated by a PPh_3 ligand. The Fe is further ligated by three CO's and the Ir by two. The relatively long Fe–Ir bond length of 2.960 (1) Å suggests a weak donor–acceptor type interaction between the two metal centers. 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.

Binuclear and polynuclear transition-metal complexes have been widely considered as having the potential to carry out unique catalytic and stoichiometric transformations as a result of cooperative interaction between adjacent metals.[1] Heteronuclear complexes are particularly interesting in view of the unique reactivity features that should accrue as a result of adjacent metals with differing sets of chemical properties.[2] Most of the heterometallic compounds that have been previously prepared and studied are coordinatively saturated and do not possess readily dissociable ligands. They thus show relatively low reactivity toward reversible addition and exchange of ligands. The latter are particularly desirable properties if such complexes are to be used as catalysts,[3] and thus a need exists for the synthesis and characterization of new compounds that are either coordinatively unsaturated or possess easily dissociable ligands. Ideal complexes would appear to be those that link traditional mononuclear homogeneous catalysts of the group 8 metals to another metal center, preferably with a bridging ligand to assist in holding the metals together.

We have thus set out to prepare and study a series of such compounds. Reported herein are the synthesis, characterization, and reactivity studies of a set of binuclear complexes that link Rh(I) and Ir(I) centers to Fe via bridging μ-PPh_2 ligands and that undergo rapid and reversible ligand addition and oxidative-addition reactions. The complexes are easily 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] reagent in deoxygenated tetrahydrofuran (THF) for 2–5 h at 25 °C (eq 1). The new complexes and their derivatives have been characterized spectroscopically and FeIr(μ-PPh_2)$(CO)_5(PPh_3)_2$ by a complete single-crystal x-ray diffraction study, details of which are given herein.[6]



1, M = Ir, L = PPh_3, x = 2 (37%)
2, M = Rh, L = PEt_3, x = 1 (64%)
3, M = Rh, L = PPh_3, x = 1 (51%)

Experimental Section

$Fe(CO)_4PPh_2H$,[4b] Li[$Fe(CO)_4PPh_2$],[4a] and *trans*-MCl(CO)L_2 (M = Rh, Ir; L = PPh_3, PEt_3)[5] were prepared according to literature procedures. n-Butyllithium (Aldrich Chemical Corp.), PPh_3, and PEt_3 (Strem Chemical Co.), dimethylacetamide (DMA), 1-hexene, 2,5-norbornadiene, and MeI (Aldrich Chemical Corp.) were purchased and used as received. Dimethylacetamide hydrochloride (DMA·HCl) was prepared by bubbling HCl gas through a benzene solution of DMA which gave immediate formation of DMA·HCl as a white precipitate. The latter was washed with benzene, dried under vacuum, and stored under N_2 for later use. Solvents were dried by standard methods, and all reactions were conducted under a prepurified N_2 atmosphere using standard Schlenk techniques.[7] IR spectra were recorded on a Perkin-Elmer 580 grating IR spectrophotometer using 0.5-mm NaCl solution IR cells. These were sealed with Luer-lock fittings and purged with N_2 to record spectra of air-sensitive solutions. Electron-impact mass spectra were obtained by using an AEI-MS9 mass spectrometer with a source voltage of 70 eV and probe temperature in the 100–200 °C range. NMR spectra were recorded on JEOL

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[1] (a) Muetterties, E. L. *Bull. Soc. Chem. Belg.* **1976**, *85*, 451. (b) Johnson, B. F. G., Ed. "Transition Metal Clusters"; Wiley: New York, 1980. (c) Chisholm, M. *Prog. Inorg. Chem.* **1982**, *29*, 1. (d) Smith, A. K.; Basset, J. M. *J. Mol. Catal.* **1977**, *2*, 229. (e) Pittman, C. U., Jr.; Ryan, R. C. *Chem. Tech.* **1978**, 170.

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PS-100 FT, Bruker WH 200, and Bruker WM 360 NMR spectrometers. All reported ^{13}C and ^{1}H NMR chemical shifts are relative to Me_4Si. ^{31}P NMR chemical shifts are relative to H_3PO_4 with downfield chemical shifts reported as positive. A Varian 1400 gas chromatograph with a 6-ft Poropak-N column using N_2 carrier gas, and a flame-ionization detector was used for analysis of the hydrogenation catalysis experiments. Elemental analyses were obtained by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY.

Preparation of $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$, 1. *n*-BuLi (0.940 mL, 1.32 mmol) was added to a THF (100 mL) solution of $Fe(CO)_4PPh_2H$ (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 (100 mL) suspension of *trans*-$IrCl(CO)(PPh_3)_2$ (1.0003 g, 1.28 mmol). The solution turned dark green over the course of stirring for 3 h at 23 °C. The THF was removed and the residue extracted with 50-mL portions of toluene until the extracts were colorless. The toluene extracts were combined, filtered, and concentrated. Chromatography on alumina with 20% CH_2Cl_2–80% hexane under N_2 yielded a yellow fraction of 1 followed by a faint green fraction of an uncharacterized compound and a pink fraction containing a trace amount of $FeIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)$, 4. Removal of solvent from the yellow fraction gave 1 as an orange, air-stable microcrystalline solid in 37% yield (0.520 g, 0.474 mmol). Anal. Calcd for $C_{53}H_{40}FeIrO_5P_3$: C, 58.02; H, 3.67. Found: C, 57.84; H, 3.84. IR: 1 (toluene) 2050 (vw), 1995 (m), 1960 (s), 1935 (vs), 1902 (s), 1886 (m) cm^{-1}; 4 (CH_2Cl_2) 2028 (m), 2010 (m), 1977 (s), 1960 (s), 1930 (sh), 1913 (m) cm^{-1}.

Preparation of $FeIr(\mu\text{-}PPh_2)(CO)_4(PPh_3)_2$, 7. Loss of CO occurs when 1 is heated (110 °C) or irradiated (366 nm) in toluene solution under N_2 or reduced pressure for 0.5–1.5 h to give 7 in near quantitative yield, as evidenced by IR and ^{31}P NMR spectral analysis of the resultant solution. Removal of solvent gives 7 as an extremely air-sensitive orange oil. An orange microcrystalline solid can be obtained by repeated washing with hexane, but IR spectra indicate persistent contamination of this solid with 5–10% of unreacted 1. 7: IR (toluene) 2020 (w), 1982 (m), 1950 (s), 1910 (m) cm^{-1}.

Preparation of $FeRh(\mu\text{-}PPh_2)(CO)_4(PEt_3)_2$, 2. *n*-BuLi (1.00 mL, 2.5 mmol) was added to a THF (30 mL) solution of $Fe(CO)_4PPh_2H$ (0.5910 g, 1.66 mmol) to generate $Li[Fe(CO)_4(PPh_2)]$ in situ. The resultant red solution was slowly added to a THF (30 mL) solution of *trans*-$RhCl(CO)(PEt_3)_2$ (0.6370 g, 1.66 mmol). The solution turned dark orange over the course of stirring for 3 h at 23 °C. The THF was removed and the residue extracted with 50-mL portions of toluene until the extract was colorless. The extracts were combined, filtered, and chromatographed on alumina with 20% CH_2Cl_2–80% hexane under N_2 to give a yellow fraction of 2 followed by a faint green fraction of an uncharacterized material. Evaporation of solvent from the first fraction gave 2 as a yellow, air-stable, microcrystalline solid (0.730 g, 1.1 mmol, 64% yield). Anal. Calcd for $C_{28}H_{40}FeRhO_4P_3$: C, 48.55; H, 5.78. Found: C, 48.10; H, 5.81. IR (toluene): 1972 (s), 1943 (vs), 1900 (s), 1863 (m) cm^{-1}. A ^{13}CO-enriched sample of 2 was prepared by stirring 2 under 1 atm ^{13}CO in toluene for 3 days at 25 °C.

Preparation of $FeRh(\mu\text{-}PPh_2)(CO)_4(PPh_3)_2$, 3. 3 was prepared in a manner analogous to 2 except that *trans*-$RhCl(CO)(PPh_3)_2$ was employed. 3 was obtained following chromatography as a yellow microcrystalline solid in 51% yield. Anal. Calcd for $C_{52}H_{40}FeRhO_4P_3$: C, 63.71; H, 4.12. Found: 63.51; H, 4.66. IR (CH_2Cl_2): 1977 (m), 1956 (s), 1898 (s), 1875 (sh) cm^{-1}.

Reaction of 4 with HCl. A toluene solution of 1 (0.0587 g, 0.052 mmol) was refluxed under N_2 for 1 h to yield 4. After being cooled to 25 °C, this solution was added to a 100-mL Schlenk flask containing solid DMA·HCl (0.0098 g, 0.079 mmol). The color of the solution instantly changed from orange to yellow. After being stirred for 1 h, the solution was filtered and the solvent evaporated to yield 11 as an impure yellow powder, containing small amounts of unreacted 1 (5–10% by ^{31}P NMR). The complex is unstable to SiO_2 and Al_2O_3 chromatography, and an analytically pure sample was not obtained.

Reactions of 1, 2, 3, and 7 with H_2 and CO. These reactions were conducted by placing the complex to be studied in the appropriate solvent, usually CH_2Cl_2 (CD_2Cl_2) or toluene-d_8, and then stirring under the appropriate atmosphere. Reactions were conducted in either 100-mL Schlenk flasks or specially constructed NMR tubes equipped with a small stopcock and a 7/25 female glass joint. 7 was generated in situ by the method given above. As described in the text, all four compounds were observed to react rapidly with CO, and 1 and 7 reacted with H_2. No attempts were made to isolate solid samples of the products. In one experiment, 2 was stirred in toluene under 1500 psi H_2 pressure for 24 h at 25 °C in a Parr Model 4753 pressure vessel. No pressure drop was observed and 2 was recovered unchanged. IR data: $FeIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$, 8 (toluene), 1995 (m), 1979 (vs), 1880 (s), 1868 (s) cm^{-1}; $FeIrH_2(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$, 9 (toluene), 2141 (w), 2066 (w), 2052 (w), 2028 (m), 1910 (w), 1872 (s), 1858 (s) cm^{-1}; $FeIrH_4(\mu\text{-}PPh_2)(CO)_3(PPh_3)_2$, 10 (toluene), 2102, 2065 (w), 1998 (s), 1983 (s), 1970, 1950 (vs), 1915 (m) ; cm^{-1}; $FeRh(\mu\text{-}PPh_2)(CO)_5(PEt_3)_2$, 5 (toluene), 1945 (m), 1984 (vs), 1888 (s), 1862 (ms) cm^{-1}; $FeRh(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$, 6 ($CH_2Cl_2$), 2048 (w), 2008 (m), 1957 (vs), 1885 (s).

Table I. Data for the X-ray Diffraction Study of $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$, 1[a]

Crystal Parameters

cryst system: triclinic	$a = 11.681\ (3)$ Å
space group: $P\bar{1}$	$b = 20.869\ (4)$ Å
$V = 2386\ (3)$ Å^3	$c = 10.649\ (9)$ Å
$Z = 2$	$\alpha = 96.74\ (3)°$
calcd density = 1.528 g cm^{-3}	$\beta = 108.86\ (3)°$
temp: 22 °C	$\gamma = 76.51\ (2)°$
cryst dimens: 0.22 mm × 0.30 mm × 0.22 mm	
abs coeff: 34.07, empirically corrected	

Measurement of Intensity Data

diffractometer:	Enraf-Nonius CAD4
radiation:	Mo Kα (λ 0.710 73 Å)
monochromator:	graphite crystal
scan type:	θ-2θ
scan speed:	variable, 7-20°/min
scan range:	variable[a]
takeoff angle:	2.8°
std reflctns:	3 std reflctns measd every 3 h, no significant variation
data limits:	$0° \leqslant 2\theta \leqslant 50°$
reflctns measd.:	$+h, \pm k, \pm l$
unique data:	6972
nonzero data:	6257 ($I \geqslant 3\sigma(I)$)
$p = 0.01$	
$R = 0.053$; $R_w = 0.077$	

[a] See ref 8b for details on computer programs utilized and data collection procedure.

X-ray Structural Analysis of 1. Crystals suitable for an X-ray diffraction study of 1 were grown by slow evaporation of a CH_2Cl_2 solution of 1. A crystal measuring 0.22 × 0.30 × 0.22 mm was mounted on a glass fiber inside a capillary tube, affixed into an aluminum pin and mounted on an eucentric goniometer. Diffraction data were collected on an Enraf-Nonius four-circle CAD4 automated diffractometer controlled by a PDP8a computer coupled to a PDP 11/34 computer. The Enraf-Nonius program SEARCH was employed to obtain 25 accurately centered reflections that were then used in the program INDEX to obtain an orientation matrix for data collection and to provide cell dimensions.[8a] Pertinent crystal and intensity data are listed in Table I. Details of the data collection and reduction procedures have been previously described.[8b]

Of the two possible triclinic space groups $P1$ and $P\bar{1}$, the latter was arbitrarily chosen and led to a successful refinement of the structure. The Fe and Ir atoms were located $P1$ a three-dimensional Patterson map, and the coordinates of the remaining 61 nonhydrogen atoms were located by successive least-squares refinements and difference Fourier maps. The Fe, Ir, phosphorus, and carbonyl carbon and oxygen atoms were refined anisotropically whereas the phenyl carbons were refined by using isotropic thermal parameters. The positions of the phenyl hydrogen atoms

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(8) (a) All programs used in this study are part of Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975, revised 1977. (b) Steinhardt, P. C.; Gladfelter, W. L.; Harley, A. D.; Fox, J. R.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 332.

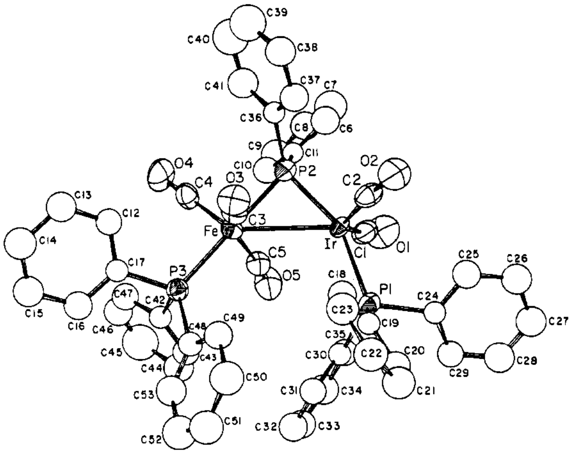

Figure 1. An ORTEP drawing of $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$. Thermal ellipsoids are drawn at the 25% probability level.

Table II. Selected Bond Distances (Å) in $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$

	Metal-Metal		
Fe-Ir	2.960 (1)		
	Metal-Phosphorus		
Ir-P1	2.349 (2)	Fe-P2	2.239 (2)
Ir-P2	2.292 (2)	Fe-P3	2.248 (2)
	Metal-Carbon		
Ir-C1	1.871 (10)	Fe-C4	1.766 (8)
Ir-C2	1.890 (8)	Fe-C5	1.796 (8)
Fe-C3	1.812 (9)		
	Carbon-Oxygen		
C1-O1	1.123 (10)	C4-O4	1.152 (9)
C2-O2	1.155 (9)	C5-O5	1.149 (9)
C3-O3	1.153 (9)		

were calculated by using an assumed C-H bond length of 0.98 Å and were assigned an arbitrary isotropic thermal parameter of 5.0. They were included in the structure factor calculations but were not refined. Several cycles of least-squares refinement reduced R to 0.053 and R_w to 0.077. The residuals are defined as $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

A final difference fourier map revealed the presence of two peaks (approximately 5.2 e Å^{-3}), indicating a disordered methylene chloride molecule at the special position 0, 0, $^1/_2$; site symmetry $\bar{1}$. Partial occupancy was evident from attempts at further refinement, which produced no improvements in the residuals. No significant changes in the positional parameters for $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ were observed from these attempts. The data presented are derived from calculations that do not include the disordered solvent molecule in the model. The final error of an observation of unit weight was 4.567. An ORTEP drawing which shows the atom numbering scheme for $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ is shown in Figure 1. Final positional and anisotropic thermal parameters for the non-phenyl atoms, and the positional and isotropic thermal parameters for the phenyl carbon atoms are respectively listed in Tables A and B of the supplementary material. Table C of the supplementary material lists the calculated hydrogen atom parameters. Relevant bond distances and bond angles are set out in Tables II and III. A listing of the observed and calculated structure factors is given as Table D in the supplementary material.

Results

Synthesis and Spectroscopic Characterization of $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$, 1, $FeRh(\mu\text{-}PPh_2)(CO)_4(PEt_3)_2$, 2, and $FeRh(\mu\text{-}PPh_2)(CO)_4(PPh_3)_2$, 3. These three compounds were prepared by allowing $Li[Fe(CO)_4(PPh_2)]$ to react with the appropriate *trans*-$MCl(CO)(PR_3)_2$ complex (eq 1). The product yields varied from 37% for 1 to 64% for 2. IR spectral data for the new complexes are given in the Experimental Section and $^{31}P\{^1H\}$ NMR data are presented in Table IV.

Table III. Selected Bond Angles (deg) in $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$

	M-P-M		
Fe-P2-Ir	81.62 (7)		
	P-M-P		
P1-Ir-P2	158.07 (6)	P2-Fe-P3	179.52 (8)
	M-M-P		
Ir-Fe-P1	49.99 (5)	Fe-Ir-P1	109.93 (5)
Ir-Fe-P3	129.58 (6)	Fe-Ir-P2	48.45 (5)
	P-M-C		
P1-Ir-C1	92.32 (24)	P2-Fe-C4	89.33 (27)
P1-Ir-C2	92.64 (23)	P2-Fe-C5	89.93 (26)
P2-Ir-C1	92.65 (24)	P3-Fe-C3	91.36 (24)
P2-Ir-C2	100.89 (22)	P3-Fe-C4	91.13 (27)
P2-Fe-C3	88.35 (24)	P3-Fe-C5	90.09 (26)
	C-P-C		
C19-P1-C24	101.57 (34)	C17-P3-C42	103.92 (34)
C19-P1-C30	106.78 (34)	C17-P3-C48	99.26 (35)
C24-P1-C30	102.29 (33)	C42-P3-C48	103.94 (34)
C11-P2-C36	101.12 (34)		
	M-M-C		
Fe-Ir-C1	109.46 (24)	Ir-Fe-C4	138.31 (27)
Fe-Ir-C2	116.72 (24)	Ir-Fe-C5	71.84 (24)
Ir-Fe-C3	81.28 (23)		
	M-C-O		
Ir-C1-O1	173.10 (81)	Fe-C4-O4	177.73 (82)
Ir-C2-O2	170.95 (79)	Fe-C5-O5	180.60 (73)
Fe-C3-O3	175.88 (68)		
	M-P-C		
Ir-P1-C19	116.86 (23)	Fe-P2-C11	119.90 (24)
Ir-P1-C24	113.22 (26)	Fe-P2-C36	114.49 (25)
Ir-P1-C30	114.92 (24)	Fe-P3-C17	114.43 (24)
Ir-P2-C11	116.49 (24)	Fe-P3-C42	111.20 (27)
Ir-P2-C36	124.12 (24)	Fe-P3-C48	121.99 (25)
	C-M-C		
C1-Ir-C2	128.39 (30)	C3-Fe-C5	146.00 (30)
C3-Fe-C4	109.95 (30)	C4-Fe-C5	103.98 (32)

The $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ complex has been fully characterized by a single-crystal X-ray diffraction study (see below) that showed the structure 1 (Figure 1). The $^{31}P\{^1H\}$ NMR spectrum of 1 (Table IV), is fully consistent with the structure determined by X-ray diffraction. The resonance at δ 114.1 (dd) is logically attributed to the bridging μ-PPh_2 group which couples to both terminal PPh_3 ligands. The doublet at δ 74.2 is due to the PPh_3 ligand attached to Fe, and the doublet at δ 14.0 is assigned to PPh_3 on Ir. The assignment of the terminal PPh_3 resonances is made primarily by reference to the spectra of the $FeRh(\mu\text{-}PPh_2)(CO)_x(PR_3)_2$ compounds 2, 3, and 5 discussed below. Clear distinction can be made in those compounds as to which metal a PR_3 ligand is attached by the presence or absence of ^{103}Rh–^{31}P coupling. The resonances assigned to the PR_3 ligands attached to Fe in 2, 3, and 5 fall within the δ 69.4–77.9 chemical shift range, and thus the δ 74.2 resonance of $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ is

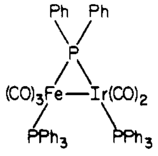

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Table IV. $^{31}P\{^1H\}$ NMR Spectral Data in Benzene-d_6 Solution at 25 °C

complex	$\delta(\mu\text{-PPh}_2)$	$\delta(\text{Fe-PR}_3)$	$\delta(\text{M-PR}_3)^a$	$J_{^{31}P_{Fe}-^{31}P_\mu}{}^b$	$J_{^{31}P_M-^{31}P_\mu}{}^{a,b}$	$J_{^{31}P_{Rh}-^{103}Rh}{}^b$	$J_{^{31}P_\mu-^{103}Rh}{}^b$
$FeIr(\mu\text{-PPh}_2)(CO)_5(PPh_3)_2$, 1	114.1 dd	74.2 d	14.0 d	20.7	192.0		
$FeIr(\mu\text{-PPh}_2)(CO)_4(PPh_3)_2$, 7	104.6 dd	78.0 d	24.7 d	28.5	22.6		
$FeIr(\mu\text{-PPh}_2)(CO)_6(PPh_3)_2$, 8	12.8 dd	84.7 d	−1.8 d	29.5	143.7		
$FeIrH_2(\mu\text{-PPh}_2)(CO)_5(PPh_3)_2$, 9	21.5 dd	84.1 d	1.9 d	24.6	187.0		
$FeIrH_4(\mu\text{-PPh}_2)(CO)_3(PPh_3)_2$, 10	118.0 dd	67.5 d	10.0 d	61.0	224.4		
$FeIrHCl(\mu\text{-PPh}_2)(CO)_4(PPh_3)_2$, 11	101.8 dd	61.2 d	18.7 d	13.8	9.8		
$FeIr(\mu\text{-PPh}_2)(CO)_6(PPh_3)$, 4	110.8 d		11.1 d		200.2		
$FeRh(\mu\text{-PPh}_2)(CO)_4(PEt_3)_2$, 2	119.7 ddd	69.8 d	31.9 dd	22.6	23.6	182.1	107.3
$FeRh(\mu\text{-PPh}_2)(CO)_5(PEt_3)_2$, 5	157.6 ddd	69.4 d	37.5 dd	19.1	189.7	105.9	82.7
$FeRh(\mu\text{-PPh}_2)(CO)_4(PPh_3)_2$, 3	123.3 ddd	77.7 d	36.9 dd	25.1	20.6	194.8	113.1
$FeRh(\mu\text{-PPh}_2)(CO)_5(PPh_3)_2$, 6	147.7 br m	77.9	35.9 br m	24.4	c	c	c

[a] M = Rh or Ir as appropriate. [b] Coupling constants given in hertz units. [c] Not resolved.

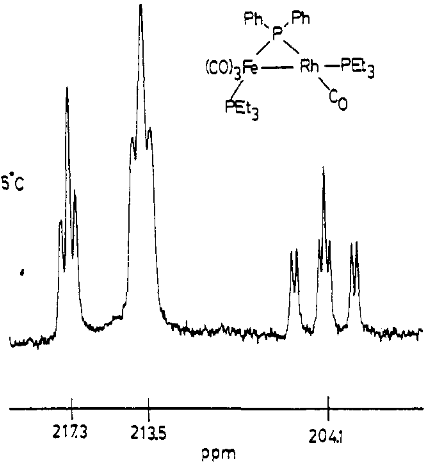
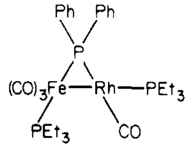


Figure 2. Carbonyl region $^{13}C\{^1H\}$ NMR spectrum of $FeRh(\mu\text{-}PPh_2)(CO)_4(PEt_3)_2$, **2**, at −75 °C in toluene-d_8 solution.

assigned to the PPh_3 bound to Fe.

Both $^{31}P\{^1H\}$ and ^{13}C NMR spectra of $FeRh(\mu\text{-}PPh_2)(CO)_4(PEt_3)_2$, **2**, imply the structure shown. The downfield



2

$^{31}P\{^1H\}$ resonance at δ 119.7 (ddd) is assigned to the μ-PPh_2 bridge. This phosphorus couples to ^{103}Rh ($J_{^{31}P_\mu-^{103}Rh}$ = 107.3 Hz) and to two inequivalent PEt_3 ligands. The doublet of doublets at δ 31.9 is assigned to a PEt_3 on Rh since it shows a large $^{31}P-^{103}Rh$ coupling (182.1 Hz) and also a smaller coupling to the phosphido bridge ($J_{^{31}P_{Rh}-^{31}P_\mu}$ = 23.6 Hz). The doublet at δ 69.8 must be due to PEt_3 bound to Fe since it does not show $^{31}P-^{103}Rh$ coupling. A similar spectrum was obtained with an analogous interpretation for the PPh_3 analogue $FeRh(\mu\text{-}PPh_2)(CO)_4(PPh_3)_2$, **3** (Table IV).

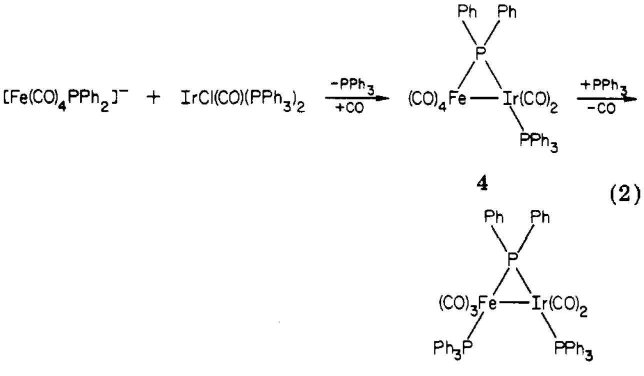
The −75 °C ^{13}C NMR spectrum of **2** is shown in Figure 2. The resonances at δ 217.3 and 213.5 are assigned to the carbonyls on Fe, and the δ 204.1 resonance is assigned to the single CO on Rh. They integrate as approximately 1:2:1, consistent with the structure sketched in **2**, with three CO's attached to Fe and one on Rh. The δ 204.1 resonance shows a large $^{13}C-^{103}Rh$ coupling (84.8 Hz) in addition to $^{13}C-^{31}P$ coupling to the μ-PPh_2 bridge (70.4 Hz) and the terminal PEt_3 ligand (12.5 Hz). The latter coupling was also observed in the $^{31}P\{^1H\}$ NMR spectrum of the enriched sample. The pseudotriplet patterns of the Fe–CO resonances are due to $^{13}C-^{31}P$ coupling of similar magnitude to the μ-PPh_2 bridge and to the terminal Fe–PEt_3 ligand. Although not well resolved, $J_{^{13}C-^{31}P}$ is approximately 18 Hz for the δ 217.3 resonance and 23 Hz for the δ 213.5 resonance.

Two of the Fe–CO's are equivalent on the NMR time scale at −75 °C but clearly inequivalent to the third CO. Upon warmup, the Fe–CO resonances broaden, coalesce, and at 35 °C appear as a single pseudotriplet at δ 214 ($J_{^{31}P-^{13}C} \simeq$ 22 Hz). At this temperature the δ 204 (Rh–CO) resonance is broad with no discernible coupling. These spectra imply that at 35 °C the Fe–CO's rapidly exchange with each other and are equivalent on the NMR time scale. The broadened Rh–CO resonance indicates that at 35 °C an exchange process is occurring at the Rh center, possibly involving the carbonyls on Fe but certainly involving exchange with free CO in solution (see below).

The relatively small coupling (20–24 Hz) of the PR_3 ligand on Rh to the phosphido bridge in both **2** and **3** suggests that this ligand is cis to the μ-PPh_2 ligand rather than trans.[9] Complex **1**, for example, where the trans arrangement of the corresponding ligands is established by X-ray diffraction, shows a 192-Hz coupling on the δ (Ir–PPh_3) resonance. Indeed, the data given in Table IV show that the $^{31}P_M$–$^{31}P_\mu$ coupling constants for all the complexes reported herein fall within two widely separated groups. In accord with established correlations,[9] those compounds with these coupling constants in the 140–225-Hz range would be expected to have a trans arrangement of phosphorus ligands, whereas those with 9–25-Hz coupling constants should have a cis arrangement.

The downfield positions of the ^{31}P NMR resonances for the μ-PPh_2 ligands in complexes **1**–**3** are consistent with this ligand bridging two metals joined by a metal–metal bond in each of the compounds. The μ-PPh_2 ligands in compounds that have short metal–metal distances, implying the presence of metal–metal bonds, and correspondingly compressed M–P_μ–M bond angles have been shown to generally display downfield (δ 50 → δ 200) resonances.[10] In contrast, upfield resonances (δ 50 → δ −200) are usually observed for compounds in which the μ-PR_2 ligands bridge two metals not joined by a metal–metal bond.[10]

A pink compound was also isolated in about 10% yield from the preparation of **1** and is tentatively formulated as $FeIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)$, **4** on the basis of its $^{31}P\{^1H\}$ NMR spectrum. The latter shows two doublets of equal intensity at δ 110.8 ($J_{^{31}P_\mu-^{31}P_{Ir}}$ = 200 Hz) and δ 11.1 ($J_{^{31}P_{Ir}-^{31}P_\mu}$ = 200 Hz) that are respectively attributed to a μ-PPh_2 bridging ligand and a terminal PPh_3 ligand on Ir. Both of the resonances are in the same chemical shift regions as the corresponding resonances of **1**. An important feature of the synthesis of compounds **1** → **3** is the transfer of a PR_3 ligand from the Rh(I) or Ir(I) precursor complex to the Fe center in the final product. Although we have not investigated the mechanisms of the synthetic reactions, a reasonable sequence of events is that shown in eq 2, with compound **4** an intermediate in the synthesis of **1**.

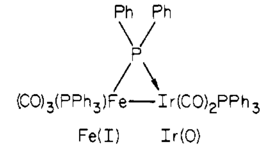


4 (2)

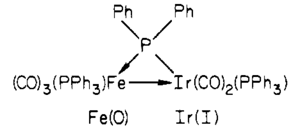
1

Structural Characterization of $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$, 1. The FeIr complex **1** was fully characterized by a complete single-crystal X-ray diffraction study. An ORTEP drawing of the structure is shown in Figure 1. The μ-PPh_2 ligand bridges the Fe and Ir centers, and each metal is also ligated by an additional PPh_3. The Fe is further coordinated by three CO's and the Ir by two. The FeIr bond length of 2.960 (1) Å is significantly longer than expected for a direct single metal–metal bond, although this is the first reported structure with an Fe–Ir bond and there are no literature values for comparison. However, based on values found for Fe–Pt single bonds that range from 2.530 to 2.601 Å[11] and Fe–Rh bonds that vary from 2.568 to 2.615 Å[12], one would expect a value for Fe–Ir in the 2.5–2.7-Å range. The long Fe–Ir bond is relatively weak as it can be readily cleaved by added reagents (see below), but the 2.960 (1) Å distance does imply some degree of metal–metal interaction.

A priori, there are two reasonable descriptions of the molecule. It could be viewed as having a direct covalent metal–metal bond between d^7 Fe(I) and d^9 Ir(0) centers with the μ-PPh_2 ligand strongly bound to Fe, serving as the anion to balance the 1+ charge on this metal.



Alternatively, the complex can be formulated as having a donor–acceptor bond between Ir(I) and Fe(0) centers with the Fe functioning as a two-electron donor to Ir and the phosphido ligand serving as the uninegative ligand to balance the 1+ charge on the Ir center.



Of course these are just two extreme views that simply reflect the polarity of the metal–metal bond, moving from a purely covalent bond in the former description to the extremely polar donor–acceptor bond in the latter. The true structure could be anywhere in between, although the structural data are more consistent with the donor–acceptor view. This conclusion derives from the fact that the Fe–Ir bond is significantly longer than expected for a direct covalent metal–metal bond and also from a comparison of the metal–phosphorus distances. The bridging Ir–P2(μ-PPh_2) distance (2.292 (2) Å) is significantly shorter (0.057 Å) than the terminal Ir–P1(PPh_3) distance (2.349 (2) Å), implying a stronger interaction of Ir with the μ-PPh_2 ligand than with the terminal PPh_3. In contrast, the Fe–P2(μ-PPh_2) and Fe–P3(PPh_3) distances differ by only 0.009 Å (2.239 (2) and 2.248 (2) Å), implying similar two-electron donor bonding to Fe for both of these ligands. Similar donor–acceptor bonding descriptions have been given for other μ-ER_2 (E = As, P) bridged binuclear complexes.[13]

Reactions of 1 and 2 with Carbon Monoxide. $FeRh(\mu\text{-}PPh_2)(CO)_4(PEt_3)_2$, **2**, and $FeRh(\mu\text{-}PPh_2)(CO)_4(PPh_3)_2$, **3**, are coordinatively unsaturated with 16-valence-electron Rh centers. As such they should readily add donor ligands such as CO. Indeed, exposure of **2** to CO

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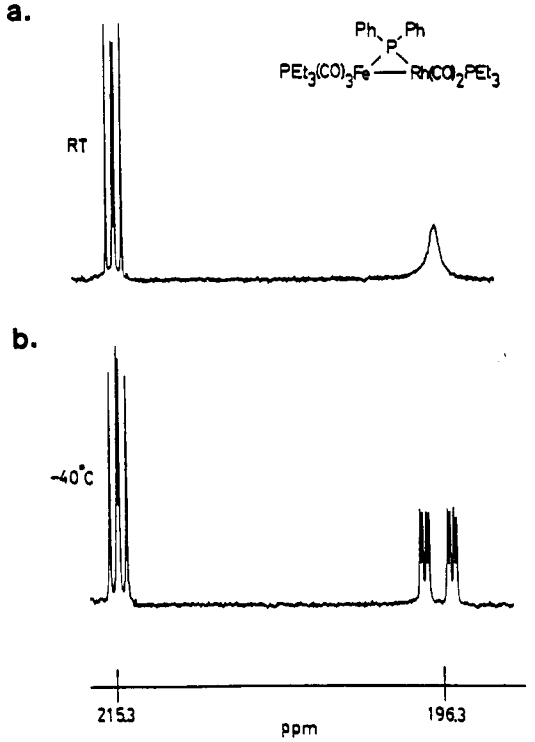
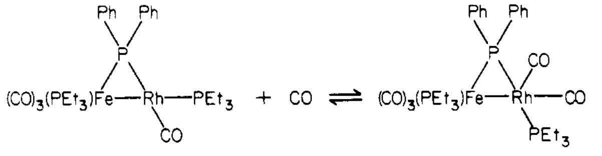


Figure 3. Carbonyl region $^{13}C\{^1H\}$ NMR spectra of $FeRh(\mu\text{-}PPh_2)(CO)_5(PEt_3)_2$, **5**, in toluene-$d_8$ solution at (a) 25 °C and (b) -40 °C.

(25 °C, 1 atm) results in the formation of $FeRh(\mu\text{-}PPh_2)(CO)_5(PEt_3)_2$, **5** (eq 3). This reaction is readily reversed simply by removing the CO atmosphere. Even solid samples of **5**, which can be obtained by evaporation of solvent from solutions of **2** maintained under an atmosphere of CO, rapidly lose CO and convert into **2** when the CO atmosphere is removed. Similar results are obtained upon addition of CO to **3** which gives $FeRh(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$, **6**.



2	5	(3)

The CO adducts **5** and **6** have been spectroscopically characterized, with **5** examined most extensively. The **2** ⇄ **5** conversion is most conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy. When a sample of **2** in an NMR tube is exposed to 1 atm CO, new $^{31}P\{^1H\}$ NMR resonances appear at δ 156.6 (ddd), 69.4 (d), and 37.5 (dd) (Table IV) that are respectively assigned to the bridging μ-PPh_2 ligand, a PEt_3 terminally bound to Fe, and a PEt_3 attached to Rh. The downfield position of the bridging μ-PPh_2 resonance implies the presence of an Fe–Rh bond.[10] These spectral changes can be driven to completion with total disappearance of the resonances assigned to **2**, by maintenance of the sample under a CO atmosphere.

The ^{13}C NMR spectrum of **5** at -40 °C is shown in Figure 3b. It shows resonances at δ 215.3 (dd, $J_{^{13}C-^{31}P_{Fe}}$ = 26.6 Hz; $J_{^{13}C-^{31}P_{\mu}}$ = 20.7 Hz) and 196.3 (ddd, $J_{^{13}C-^{31}P_{Rh}}$ = 18.7 Hz; $J_{^{13}C-^{31}P_{\mu}}$ = 7.9 Hz; $J_{^{13}C-^{103}Rh}$ = 78.8 Hz) that are respectively assigned to the carbonyls on Fe and Rh. The specific assignment of the coupling constants was determined by comparing ^{31}P and ^{13}C NMR data of the enriched sample. For example, the $J_{^{31}P_{Fe}-^{13}C}$ coupling of 26.6 Hz was clearly observable on the δ 69.4 ^{31}P NMR resonance due to the PEt_3 ligand bound to Fe. The ^{13}C NMR resonances integrate in the expected 3:2 intensity ratio, and the δ 196.3 resonance shows a pronounced ^{13}C–^{103}Rh coupling. Thus, the three Fe–CO's are equivalent on the NMR time scale at -40 °C as are the two Rh–CO's. Upon warming to 25 °C, the ^{13}C NMR spectrum of **5** changes to that shown in Figure 4a. The resonance at δ 196.3 has broadened and lost ^{13}C–^{103}Rh coupling, whereas the δ 215.3 resonance pattern is virtually unchanged. Our interpretation of these results is that at 25 °C complex **5** rapidly exchanges the Rh bound CO's with free CO in solution *on the time scale of the* ^{13}C *NMR measurement.* Although a detailed line-shape analysis has not been performed, a rate constant of ~500 s^{-1} can be estimated for this exchange at the coalescence temperature (25 °C).

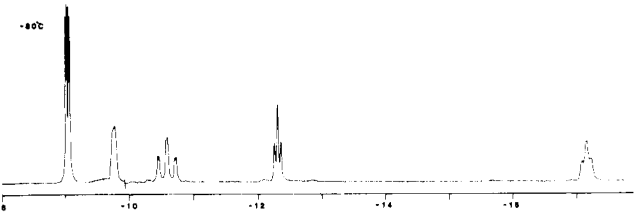
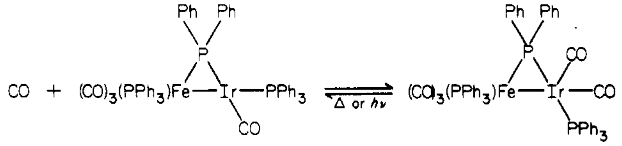


Figure 4. ^1H NMR spectrum of $FeIrH_4(\mu\text{-}PPh_2)(CO)_3(PPh_3)_2$, **10**, in solution at -80 °C.

$^{31}P\{^1H\}$ NMR spectra also show that the **2** ⇄ **5** interconversion is rapid on the ^{31}P NMR time scale at 25 °C. The -40 °C $^{31}P\{^1H\}$ NMR spectrum of a solution that contains an approximately equimolar mixture of **2** and **5**, formed by appropriate adjustment of the CO pressure over the solution, shows separate resonances for both compounds. However, upon warming, these resonances broaden and by 25 °C have coalesced into broad resonances evidencing a rapid **2** ⇄ **5** interconversion via the reversible addition/elimination of CO (eq 3). Upon further warmup to 52 °C the resonances have begun to sharpen into a single set of signals at δ 133 (μ-PPh_2), 70 (Fe–PEt_3), and 32 (Rh–PEt_3).

An equilibrium analogous to that shown in eq 3 also occurs for the FeIr complex except that here the equilibrium lies much further to the right. Thus the **1** → **7** conversion (eq 4) can only be induced by heating (110 °C, toluene solution) or irradiating (λ 366 nm) under reduced pressure. This conversion is conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy that shows the smooth decrease in intensity of resonances due to **1** upon heating and the growth of new resonances attributable to **7** (see below). The **1** → **7** conversion can be driven to ~90% completion, but exposure of solutions **7** to CO (1 atm or less) gives immediate regeneration of **1**. The $^{31}P\{^1H\}$ NMR spectrum of **7** (Table IV) shows the usual resonances attributed to the μ-PPh_2 bridging ligand, a PPh_3 bound to Ir, and a PPh_3 attached to Fe, consistent with the structure drawn in eq 3. The spectral data do not rule out the possibility of loss of CO from Fe rather than from Ir, to give a complex with the $(CO)_2(PPh_3)\overline{Fe(\mu\text{-}PPh_2)Ir}(CO)_2(PPh_3)$ formulation. However, this seems unlikely in view of the **2** ⇄ **5** conversion discussed above and the known propensity of Ir(I)

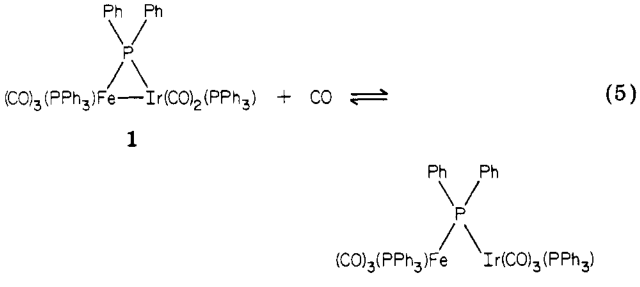


7	1

(4)

complexes to undergo reversible addition/elimination of CO.

The $FeIr(\mu-PPh_2)(CO)_5(PPh_3)_2$ complex **1** also reversibly *adds* CO. When solutions of **1** are placed under 1 atm CO, new $^{31}P\{^1H\}$ NMR signals grow in which can be assigned to the CO adduct **8** (eq 5). When the CO atmosphere is removed, **8** promptly converts back to **1**. Addition of CO must occur at Ir since addition to Fe would yield a six-coordinate, 20-electron Fe(O) complex, an unlikely possibility. The $^{31}P\{^1H\}$ NMR spectrum of **8** (Table IV) shows resonances attributable to PPh_3 on Fe, PPh_3 on Ir, and the phosphido bridge. The most noteworthy feature of the spectrum is the marked upfield shift in the resonance attributable to the $\mu-PPh_2$ ligand (δ 12.8 (dd)). The upfield position of this resonance implies the *absence* of an Fe–Ir bond in **8**. This is of course expected since each metal has 18 valence electrons without the necessity of a metal–metal bond. Thus the **1** → **8** conversion represents replacement of the Fe–Ir donor–acceptor bond by an Ir–CO bond. Significantly, even when left for prolonged periods under a CO atmosphere at 25 °C, complex **8** does not fragment via further addition of CO.



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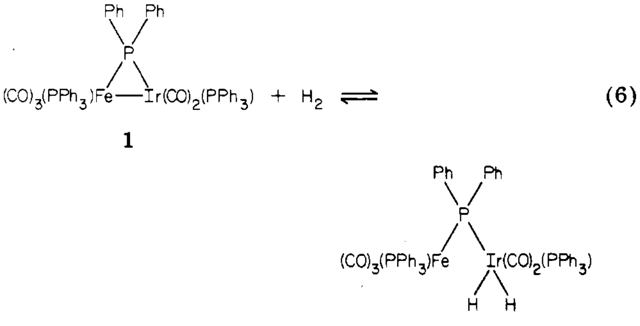
8

Reactions on 1 and 7 with H_2. Both complexes **1** and **7** react with H_2 at 25 °C and 1-atm pressure. Addition of H_2 to **1** gives $FeIrH_2(\mu-PPh_2)(CO)_5(PPh_3)_2$, **9**, in which H_2 has added to the Ir center and displaced the Fe-Ir bond (eq 6). The $^{31}P\{^1H\}$ NMR data of **9** (Table IV) is consistent with the structure drawn showing the characteristic resonances of the PPh_3 ligands bound to Fe and Ir and the $\mu-PPh_2$ bridge. The latter is shifted considerably upfield from its position in **1**, reflecting the necessary cleavage of the Fe–Ir bond in the **1** → **9** conversion.[10]



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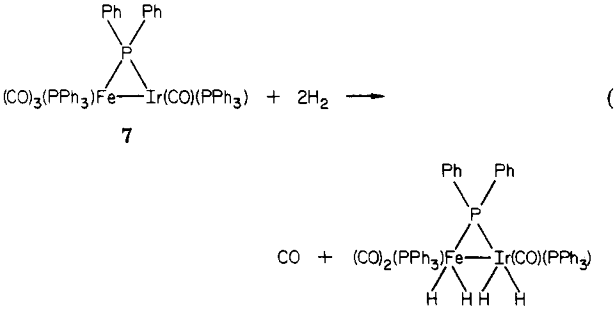
9

The ^1H NMR spectrum of **9** shows a doublet of doublets at δ −8.6 ($J_{^1H-^{31}P_{Ir}}$ = 17.6 Hz, $J_{^1H-^{31}P_{\mu}}$ = 7.7 Hz), implying equivalent hydride ligands which couple to two nonequivalent phosphorus nuclei. The specific coupling assignments given above were determined by appropriate selective decoupling experiments. Thus, the doublet at δ 1.9 in the $^{31}P\{^1H\}$ NMR spectrum of **9** due to the PPh_3 on Ir splits into a doublet of triplets with $J_{^{31}P_{Ir}-^1H}$ = 17.6 Hz when the spectrum is recorded with only the phenyl protons decoupled. This implies that both hydrides are attached to Ir as indicated in eq 6. A similar splitting was observed on the $\mu-PPh_2$ resonance, but the $Fe-PPh_3$ resonance remained unchanged when the hydride ligands were allowed to couple to the ^{31}P nuclei.

The tetracarbonyl complex $FeIr(\mu-PPh_2)(CO)_4(PPh_3)_2$, **7**, also adds H_2, but the spectroscopic data imply that two H_2 molecules add with loss of a CO ligand (eq 7). The instability of the product has precluded an unambiguous characterization, but the structure **10** is tentatively assigned on the basis of its spectroscopic properties. As before, this reaction is most conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy. When a toluene-d_8 solution of **7** is exposed to H_2 (1 atm, 25 °C), the $^{31}P\{^1H\}$ NMR resonances of **7** immediately disappear and resonances characteristic of $FeIr(\mu-PPh_2)(CO)_5(PPh_3)_2$, **1**, $FeIrH_2(\mu-PPh_2)(CO)_5(PPh_3)_2$, **9**, and those attributable to **10** grow in. The ratio of **10** to **1** and **9** combined is approximately 1:1, as determined by integration of the $^{31}P\{^1H\}$ NMR spectrum. The resonances attributable to **10** are listed in Table IV. Their assignment is based on reasoning similar to that outlined in the preceding paragraphs. Particularly relevant is the downfield position of the resonance attributable to the $\mu-PPh_2$ ligand, implying the presence of a metal–metal bond in **10**.[10]



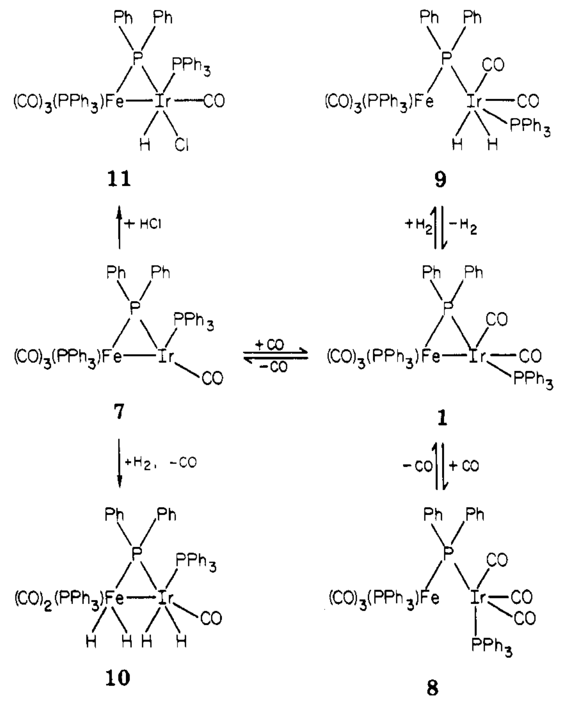
(7)

7

10

The −80 °C ^1H NMR spectrum of the above solution is shown in Figure 4. The hydride resonance at δ −8.6 (dd) is due to **9**. Four additional hydride signals are apparent at δ −9.8 (m), −10.6 (ddd, $J_{^1H-^{31}P_{Ir}} \simeq J_{^1H-^{31}P_{\mu}} \simeq$ 50 Hz; $J_{^1H-^1H}$ = 8 Hz), −12.3 (dd, $J_{^1H-^{31}P_{\mu}} \simeq J_{^1H-^{31}P_{Fe}} \simeq$ 19 Hz), and −17.2 (ddd, $J_{^1H-^{31}P_{\mu}} \simeq J_{^1H-^{31}P_{Ir}} \simeq$ 28 Hz; $J_{^1H-^1H}$ = 8 Hz). These four resonances each integrate with a relative intensity of one. The relative intensity data in conjunction with the $^{31}P\{^1H\}$ NMR spectrum which shows only one species to be present other than **1** and **9** implies that all four of these hydride resonances are due to one compound, i.e., a tetrahydride complex. The proposed structure drawn for **10** in eq 7 is supported by selective $^{31}P-^1H$ NMR decoupling experiments. Thus, irradiation of the ^{31}P NMR resonance attributable to the PPh_3 on Ir (δ 10.0 (d)) causes the ^1H NMR resonances at δ −10.6 and −17.2 to collapse into doublets, but the δ −9.8 and −12.3 resonances remain unchanged. Selective irradiation of the ^{31}P NMR resonance assigned to the PPh_3 ligand on Fe (δ 67.5 (d)) causes the δ −12.3 ^1H NMR resonance to collapse into a doublet but leaves the −10.6 and 17.2 signals unchanged. An instrumental noise spike at δ −9.5 prevents observation of the effect on the δ −9.8 resonance. Irradiation into the ^{31}P NMR resonance assigned to the $\mu-PPh_2$ bridge (δ 118 (dd)) causes the δ −10.6, −12.3, and −17.2 resonances to collapse into doublets; again, the effect on the δ −9.8 resonance could not be determined. These experiments imply that the δ −10.6 and −17.2 resonances are due to inequivalent hydrides bound to Ir, whereas the δ −12.3 resonance is due to a hydride on Fe. The instrumental problem does not allow an unambiguous assignment of the location of the

Scheme I

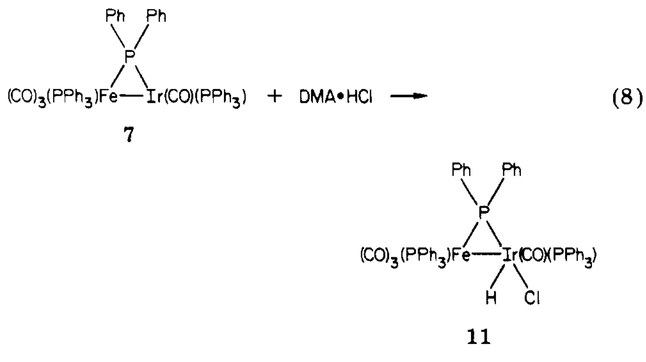


hydride that gives the δ −9.8 resonance, but a terminal position on Fe or a position bridging the Fe–Ir bond appear most likely.

The *tricarbonyl* formulation given for **10** is based on the δ 118 chemical shift of the ^{31}P NMR resonance of the phosphido bridge. Its downfield position argues for a metal–metal bond,[10] and the only way such a complex can have a metal–metal bond with four hydrides and not have greater than 18 electrons/metal is to have lost a CO ligand in the course of the reaction with H_2. Consistent with such CO loss is the formation of **1** and **9** during the reaction of **7** with H_2; **7** reacts with CO to form **1** (eq 4), and **1** adds H_2 to give **9** (eq 6).

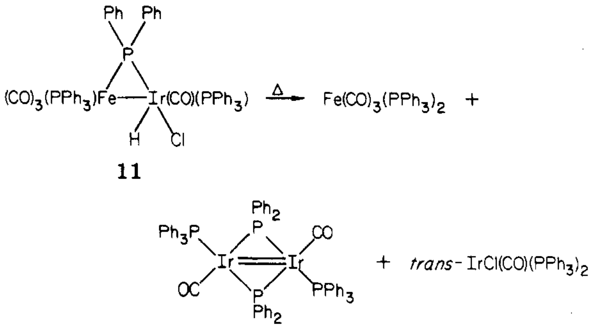
In contrast to the results discussed above, no evidence was obtained for reaction of the FeRh complexes **2** and **3** with H_2. Complex **2** was recovered unchanged following heating under 7 atm H_2 pressure and spectroscopic monitoring (^{31}P, IR) of a solution of **2** maintained under an H_2 atmosphere for a prolonged period also showed no evidence of reaction.

Reaction of 2 and 7 with HCl. Complexes **2** and **7** both react with HCl, with the most straightforward results obtained with **7**. When **7** is stirred in toluene solution in the presence of 1 equiv of the HCl adduct of dimethylacetamide (DMA·HCl), a rapid color change from orange to yellow results. The HCl adduct **11**, shown in eq 8, can be isolated as a yellow solid containing 5–10% unreacted **1** by evaporation of solvent from this solution. Complex **11** has been characterized spectroscopically. Its ^{1}H NMR spectrum shows a doublet of doublets at δ −19.6 ($J_{^1\text{H}-^{31}\text{P}_\mu}$ = 22.0 Hz, $J_{^1\text{H}-^{31}\text{P}_\text{Ir}}$ = 10.4 Hz), indicating coupling to two inequivalent phosphorus nuclei. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **11** shows the usual pattern of resonances with $\delta(\mu\text{-PPh}_2)$ 101.8 (ddd), $\delta(\text{Fe-PPh}_3)$ 61.2 (d), and $\delta(\text{Ir-PPh}_3)$ 18.7 (d). The downfield position of the phosphido-bridge resonance argues for the presence of a metal–metal bond in **11**,[10] and the terminal PPh_3 resonances fall in the ranges observed for the corresponding resonances in the other compounds discussed herein. The doublet at δ 18.7 attributable to the PPh_3 on Ir splits into a doublet of doublets when the hydride is allowed to couple to the phosphorus nuclei, thereby confirming its bonding to the Ir center. Alternative structures can be drawn for **11** with the chloride bridging the Fe–Ir bond or with the Cl^- ligand terminally bound to Fe. The present data do not exclude these possibilities although in the former case the Cl^- would be a four-electron donor. Such a complex would have 20 valence electrons at one of the metal centers, an unlikely situation.



(8)

The FeIr(HCl) adduct **11** is stable in solution up to ~100 °C. However, when heated in refluxing mesitylene (162 °C) under N_2, rapid decomposition occurs to yield a mixture of products, but mainly those shown in eq 9. The IR spectrum of the solution following 4 h reflux showed no bands due to **11** but instead four bands at 1990 (m), 1967 (s), 1920 (m), and 1890 (vs) cm^{-1}. The 1967-, 1890-, and 1920-cm^{-1} bands are due to *trans*-$\text{IrCl(CO)(PPh}_3)_2$, $\text{Fe(CO)}_3(\text{PPh}_3)_2$, and $\text{Ir}_2(\mu\text{-PPh}_2)_2(\text{CO})_2(\text{PPh}_3)_2$, respectively, by comparison to the spectra of authentic samples.[5b,14,15]



(9)

The $\text{FeRh}(\mu\text{-PPh}_2)(\text{CO})_4(\text{PPh}_3)_2$ complex reacts instantly at 25 °C with DMA·HCl, but no evidence for an intact binuclear product was obtained. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction solution showed principally two compounds to be present. One of these is *trans*-$\text{RhCl(CO)(PPh}_3)_2$ as evidenced by its characteristic doublet at δ 30.1 (d, $J_{^{31}\text{P}-^{103}\text{Rh}}$ = 126.0 Hz). The second compound shows two equal intensity doublets at δ 82.7 (d, $J_{^{31}\text{P}-^{31}\text{P}}$ = 33 Hz) and 55.9 (d, $J_{^{31}\text{P}-^{31}\text{P}}$ = 33 Hz) that couple to each other, but importantly no $^{31}\text{P}-^{103}\text{Rh}$ coupling is observed, implying the absence of Rh in this product. The δ 55.9 resonance splits into a doublet of doublets with $J_{^{31}\text{P}-^1\text{H}}$ = 366 Hz when the protons are allowed to couple to the phosphorus nuclei, implying this resonance is due to a PPh_2H ligand. The most reasonable formulation for this product that is consistent with the NMR data is trans-$\text{Fe(CO)}_3(\text{PPh}_3)(\text{PPh}_2\text{H})$. Consistent with this formulation, the IR spectrum of this product shows only a single ν_{CO} at 1883 cm^{-1}.

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Discussion

The new phosphido-bridged FeRh and FeIr complexes described herein are easily prepared by reaction of the corresponding *trans*-$IrCl(CO)(PPh_3)_2$ complex with the nucleophilic diphenylphosphido complex $[Fe(CO)_4(PPh_2)]^-$ (eq 1). Such "bridge-assisted substitution reactions" have considerable precedent for the synthesis of bridged binuclear complexes,[2a] although most reactions have involved the use of neutral PR_2 and AsR_2 derivatives such as $MCp(CO)_2PPh_2$ (M = Fe, Ru)[16] and $MCp(CO)_3AsMe_2$ (M = Cr, Mo, W).[17] The method employed here which utilizes a PPh_2H precursor complex should have considerable generality for the directed synthesis of phosphido-bridged compounds since PR_2H-substituted derivatives of many organometallic complexes should be readily obtainable. In situ generation of the nucleophilic metallo PR_2 reagent by proton abstraction from the PR_2H ligand with an organolithium reagent followed by addition of the appropriate metal halide complex should lead to the directed synthesis of specifically desired compounds. In work to be described separately, we have utilized this method for the preparation of a series of phosphido-bridged MoRh, MoIr, WRh, WPt, WPd, and Fe_2Rh complexes.[18]

The FeIr and FeRh complexes discussed herein have been characterized by a variety of spectroscopic methods but the most useful has clearly been ^{31}P NMR spectroscopy. This is particularly true of the complexes that contain Rh since the presence or absence of $^{103}Rh-^{31}P$ coupling indicates whether a given phosphorus ligand is bound to Rh. As indicated in Table IV and the discussion given in the Results, use has also been made of a chemical shift correlation for the PR_3 ligands terminally bound to Rh, Ir, and Fe. The PR_3 ligands bound to Fe all show resonances within the δ 61.3–84.7 range as do the PPh_3 ligands of $Fe(CO)_3(PPh_3)_2$ (δ 81.8).[19] Likewise, resonances of the PR_3 ligands on Rh fall within the δ 31.9–37.5 range. These are only slightly downfield from the resonances of *trans*-$RhCl(CO)(PEt_3)_2$ (δ 24.5) and *trans*-$RhCl(CO)(PPh_3)_2$ (δ 30.1). Similarly, the PPh_3 ligands on Ir are seen in the δ $-1.8 \rightarrow \delta$ 24.7 region where *trans*-$IrCl(CO)(PPh_3)_2$ also shows its ^{31}P NMR resonance (δ 22.5).

As noted earlier, the chemical shift of the μ-PPh_2 ligand is a useful indication of whether there is or is not significant metal–metal interaction in these new binuclear complexes.[10] Furthermore, the presence or absence of coupling of the bridging phosphorus ligand with the terminal phosphorus nuclei on the two metal centers also affords a method for easily determining whether the binuclear structure remains intact during reaction of these complexes with small molecules.

The results presented herein show that incorporation of Rh(I) and Ir(I) centers into phosphido-bridged binuclear complexes does not significantly alter the basic reactivity features of these metals as shown by their mononuclear complexes. Their reactions with H_2, CO, and HCl, e.g. Scheme I, demonstrate their ability to undergo reversible addition and oxidation-addition reactions without fragmentation of the complexes. Furthermore, the NMR data pertaining to the $FeRh(\mu\text{-}PPh_2)(CO)_4(PEt_3)_2 + CO \rightleftarrows FeRh(\mu\text{-}PPh_2)(CO)_5(PEt_3)_2$ equilibrium (eq 3) show that the rate of the reactions involved are quite fast, typical of such reactions of mononuclear Rh(I) complexes.

Several of the reactions discussed herein illustrate a unique feature of such metal–metal bonded compounds. The conversion of **7** into **1** and then to **8** (Scheme I) represents a total four-electron addition to the Ir center without requiring the dissociation of any ligand. The first CO addition, **7** → **1**, occurs at a coordinatively unsaturated Ir center, but the product **1** has the maximum 18-valence-electron configuration. The second ligand addition **1** → **8** 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. Such four-electron additions would seem to make complexes such as these useful in catalytic processes since many catalytic reactions require a total of four or more electron additions (e.g., hydrogenation—H_2(2), olefin(2); hydroformylation—H_2(2), CO(2), olefin(2)). Solutions of **7** do catalyze the hydrogenation and isomerization of 1-hexene at 25 °C and one atmosphere of H_2 although the reaction is very slow resulting in only two turnovers per hour.[20]

The reversibility of the **1** → **8** and **1** → **9** conversions also show that the bridging phosphido ligand serves the purpose intended it that it holds the metal centers together during such reactions. Indeed we have observed no fragmentation reactions when either $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ or $FeRh(\mu\text{-}PPh_2)(CO)_4(PEt_3)_2$ are stirred for prolonged periods under CO or H_2 at 25 °C and 1 atm pressure. Fragmentation reactions were only observed when **2** and **7** were allowed to react with HCl, with reaction of **7** with HCl proceeding through the intermediacy of the characterizable HCl adduct **11**, which is stable up to ~100 °C.

Summary

New heterobimetallic phosphido-bridged FeRh and FeIr complexes have been prepared and characterized, $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ by a complete single-crystal X-ray diffraction study. These complexes are either coordinatively unsaturated or can easily achieve open coordination sites by ligand dissociation or reversible metal–metal bond cleavage. They undergo a series of addition and oxidative-addition reactions, mainly at the Rh(I) and Ir(I) centers, and a series of binuclear H_2, CO, and HCl adducts have been characterized. This study demonstrates that the inherent reactivity features of Rh(I) and Ir(I) centers are maintained when these metals are incorporated into binuclear complexes and that such phosphido-bridged complexes do resist fragmentation, thereby offering promise for the design of stable polynuclear catalysts that contain these active metals.

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Registry No. **1**, 81987-86-2; **2**, 82135-57-7; **3**, 85185-77-9; **4**, 85185-78-0; **5**, 81987-90-8; **6**, 85185-79-1; **7**, 82135-58-8; **8**, 81987-87-3; **9**, 81987-88-4; **10**, 81987-89-5; **11**, 85185-80-4; *trans*-$Fe(CO)_3(PPh_3)(PPh_2H)$, 85185-81-5; $Li[Fe(CO)_4(PPh_2)]$, 82042-

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06-6; *trans*-IrCl(CO)$(PPh_3)_2$, 15318-31-7; *trans*-RhCl(CO)$(PEt_3)_2$, 15631-52-4; *trans*-RhCl(CO)$(PPh_3)_2$, 15318-33-9; Fe, 7439-89-6; Ir, 7439-88-5; Rh, 7440-16-6.

Supplementary Material Available: Listings of the positional and thermal parameters for the non-hydrogen atoms (Table A) and phenyl carbon atoms (Table B), calculated hydrogen atom parameters (Table C), and the structure factors (Table D) for 1 (29 pages). Ordering information is given on any current masthead page.

Dibenzo[*a*,*e*]cyclooctatetraene in a Proposed Test for Heterogeneity in Catalysts Formed from Soluble Platinum Group Metal Complexes

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The problem of distinguishing homogeneous from heterogeneous catalysis is discussed. A method based on dibenzo[*a*,*e*]cyclooctatetraene, a potent selective poison for homogeneous catalysts, is compared with filtration, nitrobenzene reduction, and Hg inhibition methods. $RhCl(PPh_3)_3$ (both free and polymer supported), $RuCl_2(PPh_3)_3$, $[Rh(nbd)(PPh_3)_2]PF_6$, and $[Ir(cod)(PMePh_2)_2]PF_6/CH_2Cl_2$ (cod = 1,5-cyclooctadiene) all show properties consistent with homogeneous catalysis, and Pd/C, colloidal Pd, and a system usually considered homogeneous, $RhCl_3(py)_3/NaBH_4$/dmf (py = pyridine), all show properties consistent with heterogeneous catalysis. The advantages and limitations of the method are discussed.

Over the past 20 years there has been considerable interest in catalysis of organic reactions[1] by metal complexes. Homogeneous catalysis can have important advantages over the well-known heterogeneous catalysts[2] such as Pd/C. An important question arises in these studies: how does one know that a catalyst really is homogeneous? Even if it has been prepared from a soluble metal complex, the metal itself may have been precipitated under the reaction conditions, to give either metal powder or a metal film or, especially in polar solvents, colloidal metal.[3] Visual inspection of the catalytic mixture can be helpful. If sufficient precipitation occurs, a metal film or powder may be noticed, but colloidal preparations are often bright and clear. It might be thought that filtration or centrifugation would be helpful. Unfortunately colloidal preparations pass through even micropore filters and, in general, survive centrifugation.

If colloids were unlikely to form under the conditions of "homogeneous" catalysis, the risk of error would be small. However, when one looks at a typical synthesis of colloidal platinum metals, one can see how close the conditions[4] (metal compound, ligand, reducing agent, polar solvent) often are to those typical in homogeneous catalysis.

Even if a colloid is present, the question still arises whether the catalytic activity observed is due to the homogeneous or heterogeneous component of the system. The inverse problem may also arise. A heterogeneous catalyst may dissolve under the reaction conditions and only the homogeneous component be active.

The question of homogeneity vs. heterogeneity is especially important when a reaction previously only known on a metal surface is effected by a supposed homogeneous system. We have discussed one such case in detail: alkane activation.[4]

The hydrogenation system $[Ir(cod)(Pc\text{-}Hx_3)(py)]PF_6/CH_2Cl_2$ (cod = 1,5-cyclooctadiene; c-Hx = cyclohexyl; py = pyridine) has certain properties in which it resembles heterogeneous catalysts: it reduces even hindered substrates and it is stable to air; therefore, the possibility that colloidal iridium might be the active species had to be considered. More recent results showing that the catalyst has very high regio- and stereoselectivity support its homogeneity.[5] The system also passed the light-scattering test which we are developing and which will be reported elsewhere.[6] Finally, the iridium system does not reduce $PhNO_2$. As we have discussed previously, nitrobenzene hydrogenation is very rapid on platinum group metal surfaces and we have proposed the absence of $PhNO_2$ reduction as a criterion for the absence of platinum group metal surfaces in catalytic systems. There are, however, many systems that are claimed to be homogeneous and yet reduce $PhNO_2$; probably many of these are authentically homogeneous, but we felt that among them might be some heterogeneous systems and that the group deserved further study.

In this paper we describe a proposed test for homogeneity relying on dibenzo[*a*,*e*]cyclooctatetraene (dct), a potent selective poison for homogeneous catalysts. It might better be described as a suicide inhibitor, for as an olefin, it resembles a common class of substrate in catalysis, but although it binds to the catalyst, it resists further transformation. As we found in earlier work[7] on dct it forms very strongly bound complexes with a variety of platinum group transition metals. In contrast to most

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