

## Models for Multicenter Catalysts. 3.<sup>1,2</sup> Facile Hydride Rearrangements in A-Frame and Related Complexes and the Structure of $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$ , the Product of $\text{H}_2$ Addition at One Metal Center in the A-Frame Pocket

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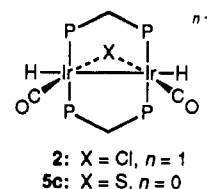
The reactions of several binuclear diiridium and heterobinuclear rhodium/iridium complexes with  $\text{H}_2$  are discussed. The compounds  $[\text{RhIr}(\text{CO})_2(\mu\text{-X})(\text{DPM})_2]^{n+}$  ( $\text{X} = \text{Cl}$ ,  $n = 1$ ;  $\text{X} = \text{S}$ ,  $n = 0$ ;  $\text{DPM} = \text{bis}(\text{diphenylphosphino})\text{methane}$ ) react with  $\text{H}_2$  to give dihydrides in which the hydrido ligands are shown by NMR spectroscopy to be primarily bound to the iridium center with one hydrido ligand in each case also interacting weakly with the rhodium atom. The X-ray structure determination of  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2][\text{BF}_4]$  supports this bonding proposal. These mixed-metal species model key intermediates in the hydride rearrangements observed in the related homobinuclear diiridium complexes  $[\text{Ir}_2(\text{CO})_2(\mu\text{-X})(\text{DPM})_2]^{n+}$  ( $\text{X} = \text{Cl}$ ,  $n = 1$ ;  $\text{X} = \text{S}$ ,  $n = 0$ ), and a mechanism for these hydride rearrangements is proposed. Of these A-frame complexes only  $[\text{Ir}_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2][\text{BF}_4]$  reacts further with excess  $\text{H}_2$ , yielding two isomeric tetrahydrides. The complex  $[\text{Ir}_2(\text{CO})_2(\mu\text{-I})(\text{DPM})_2][\text{BF}_4]$  reacts somewhat differently with  $\text{H}_2$  than do the related sulfido- and chloro-bridged A-frames, leading to a dihydride that does not undergo rearrangement. This dihydride reacts further with  $\text{H}_2$ , yielding only one tetrahydride species, which readily reductively eliminates HI to give the known trihydride  $[\text{Ir}_2\text{H}(\text{CO})_2(\mu\text{-H})_2(\text{DPM})_2]^+$ . The neutral complex  $[\text{RhIrCl}_2(\text{CO})_2(\text{DPM})_2]$  reacts with  $\text{H}_2$ , yielding a cationic dihydride identical with that of its A-frame counterpart. The neutral iodide  $[\text{Ir}_2\text{I}_2(\text{CO})_2(\text{DPM})_2]$  also reacts with  $\text{H}_2$  to give a cationic dihydride analogous to that observed when  $\text{H}_2$  is reacted with  $[\text{Ir}_2(\text{CO})_2(\mu\text{-I})(\text{DPM})_2][\text{BF}_4]$  but rapidly interconverts at room temperature with the neutral dihydride  $[\text{Ir}_2(\text{H})_2\text{I}_2(\text{CO})_2(\text{DPM})_2]$  which has one hydrido ligand on each metal, mutually adjacent to one another. These hydrido ligands are chemically inequivalent with one being trans to a carbonyl group while the other is opposite an iodo ligand. The structure of  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$  has been determined by X-ray crystallography. It crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 14.171(2)$  Å,  $b = 22.638(3)$  Å,  $c = 9.642(2)$  Å,  $\alpha = 94.18(1)^\circ$ ,  $\beta = 107.38(2)^\circ$ ,  $\gamma = 105.84(1)^\circ$ ,  $V = 2799.4$  Å<sup>3</sup>, and  $Z = 2$ . Refinement has converged to  $R = 0.053$  and  $R_w = 0.081$  based on 7935 unique observations and 364 parameters varied. This binuclear, DPM-bridged complex has a slightly distorted square planar Rh(I) center and an octahedral Ir(III) center, the latter of which has both hydrido ligands attached. These hydrido ligands are bound in the inside pocket of the complex with one being in a position to interact weakly with the Rh atom.

### Introduction

Homogeneous hydrogenation catalysts based on mononuclear Rh(I) phosphine complexes have been much studied and are reasonably well understood.<sup>3</sup> However, much less is known about catalysts that contain more than one metal center, owing to the added complexity introduced when more than one reactive site is present in the molecule. Reports of catalytic alkyne hydrogenation by the binuclear complexes  $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2][\text{BPh}_4]$ ,<sup>4</sup>  $[\text{Rh}_2\text{H}_2(\text{CO})_2(\text{DPM})_2]$ ,<sup>5</sup>  $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\text{DPM})_2]$ ,<sup>6</sup> and  $[\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\text{DPM})_2]$ <sup>7</sup> ( $\text{DPM} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), and the suggestions<sup>1,8</sup> that the metals may be involved in a cooperative manner, prompted us to probe the function of the adjacent metals in hydrogenation reactions catalyzed by  $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2]^+$  and related A-frame species.

In this paper we concentrate on the binuclear hydrides obtained in reactions with  $\text{H}_2$  since such species are pivotal to our understanding of multicenter hydrogenation catalysts. Our original studies involved the diiridium species  $[\text{Ir}_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2][\text{BF}_4]$ <sup>1</sup> and  $[\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\text{DPM})_2]$ ,<sup>2</sup> since these complexes yielded isolable hydride products whereas this was not true

of the catalytically active dirhodium analogues. In both of these diiridium species studied, the thermodynamically favored dihydride products had the hydrido ligands on the outsides of the A-frames as shown:<sup>1,2</sup>



We were interested in establishing unequivocally the site of initial attack by  $\text{H}_2$  and in determining how a presumed concerted oxidative addition of  $\text{H}_2$  at one metal center gave rise to the products diagrammed. The results of this investigation are reported herein. Also reported are the analogous reactions involving a series of related binuclear complexes not containing bridging anionic ligands, since a previous comparison of  $[\text{Ir}_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2]^+$  (1) and *trans*- $[\text{IrCl}(\text{CO})(\text{DPM})_2]$  had shown rather dramatic differences,<sup>1</sup> which proved useful in establishing the involvement of the bridging halide ligand in 1.

### Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under dinitrogen. Reactions were performed under standard Schlenk conditions with use of dinitrogen that had been passed through columns containing Radox and 4A molecular sieves to remove traces of oxygen and water, respectively. Iridium(III) chloride hydrate was obtained from Johnson-Matthey, and bis(diphenylphosphino)methane was purchased from Strem Chemicals. Carbon monoxide (Matheson) and dihydrogen (Linde) were used as received. The compounds  $[\text{Ir}_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2][\text{BF}_4]$ ,<sup>9</sup>  $[\text{Ir}_2\text{I}_2(\text{CO})_2(\mu\text{-CO})(\text{DPM})_2]$ ,<sup>10</sup>  $[\text{Ir}_2(\text{CO})_2(\mu\text{-I})(\text{DPM})_2][\text{BF}_4]$ ,<sup>10</sup>  $[\text{RhCl}(\text{CO})_2]$ ,<sup>11</sup> and  $[\text{Ir}(\text{DPM})_2(\text{CO})][\text{Cl}]$ <sup>12</sup> were prepared by the reported procedures.  $[\text{RhIrCl}_2(\text{CO})_2(\text{DPM})_2]$  was

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Table I. Spectral Data<sup>a</sup>

compd	IR, cm <sup>-1</sup>		NMR, <sup>d</sup> δ	
	solid <sup>b</sup>	soln <sup>c</sup>	<sup>31</sup> P{ <sup>1</sup> H}	<sup>1</sup> H
[Ir <sub>2</sub> (H) <sub>4</sub> Cl(CO) <sub>2</sub> (DPM) <sub>2</sub> ][BF <sub>4</sub> ] (3a,b)	2059 (vs), 2022 (vs), 1957 (med) <sup>e</sup> 2213 (w), 2130 (med) <sup>f</sup>	2071 (vs), 2036 (st), 1965 (st) <sup>e</sup> 2146 (br, med) <sup>f</sup>	(a) -8.83 (m)  (b) -6.58 (s)	(a) 5.14 (m, 2 H), 4.85 (m, 2 H), -10.12 (t, 1 H, <sup>2</sup> J <sub>P-H</sub> = 13.2), -13.86 (t, 1 H, <sup>2</sup> J <sub>P-H</sub> = 10.4), -14.75 (br, 1 H), -16.52 (br, 1 H) <sup>g</sup> (b) 5.78 (m, 2 H), 3.87 (m, 2 H), -10.70 (br, 2 H), -12.88 (br, 2 H) <sup>g</sup>
[RhIr(CO) <sub>2</sub> (μ-Cl)(DPM) <sub>2</sub> ][BF <sub>4</sub> ] (6)	1974 (vs), 1993 (vs) <sup>e</sup>	2002 (st), 1982 (vs) <sup>e</sup>	17.66 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 111.0) 12.76 (m)	7.2-7.8 (m, 40 H), 3.65 (m, 2 H), 4.14 (m, 2 H) <sup>h</sup>
[RhIr(CO) <sub>2</sub> (μ-S)(DPM) <sub>2</sub> ] (7)	1932 (vs), 1906 (vs) <sup>e</sup>	1948 (st), 1920 (vs) <sup>e</sup>	14.42 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 131.3) 6.88 (m)	7.0-7.9 (m, 40 H) 5.20 (m, 2 H), 3.41 (m, 2 H)
[RhIr(H) <sub>2</sub> (CO) <sub>2</sub> (μ-Cl)(DPM) <sub>2</sub> ][BF <sub>4</sub> ] (8a)	2058 (st), 2048 (st), 1955 (vs, br) <sup>e</sup> 2242 (w), 2215 (w) <sup>f</sup>	2070 (st), 1973 (vs, br) <sup>e</sup> 2225 (w) <sup>f</sup>	23.14 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 109.3) -7.14 (m)	7.0-7.8 (m, 40 H), 4.29 (m, 2 H), 3.76 (m, 2 H) -8.62 (m, 1 H), -17.86 (t, 1 H, <sup>2</sup> J <sub>P-H</sub> = 11.0) <sup>h</sup>
[RhIr(H) <sub>2</sub> (CO) <sub>2</sub> (μ-Cl)(DPM) <sub>2</sub> ][Cl] (8b)	2056 (st), 1980 (med), 1946 (vs, br) <sup>e</sup> 2245 (w), 2222 (w) <sup>f</sup>	2069 (st), 1973 (vs, br) <sup>e</sup> 2223 (w) <sup>f</sup>	23.36 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 109.2) -6.96 (m)	7.0-7.8 (m, 40 H), 4.26 (m, 2 H), 3.92 (m, 2 H), -8.62 (m, 1 H), -17.86 (t, 1 H, <sup>2</sup> J <sub>P-H</sub> = 11.0) <sup>h</sup>
[RhIr(H) <sub>2</sub> (CO) <sub>2</sub> (μ-S)(DPM) <sub>2</sub> ] (9)		2019 (st), 1924 (vs, br) <sup>e</sup>	21.32 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 151.4) -4.31 (m)	6.7-8.1 (m, 40 H), 5.17 (m, 2 H), 2.90 (m, 2 H), -9.10 (dt, 1 H, <sup>1</sup> J <sub>Rh-H</sub> = 12.5, <sup>2</sup> J <sub>P-H</sub> = 12.2), -11.85 (t, 1 H, <sup>2</sup> J <sub>P-H</sub> = 12.8)
[Ir <sub>2</sub> (H) <sub>2</sub> (CO) <sub>2</sub> (μ-I)(DPM) <sub>2</sub> ][BF <sub>4</sub> ] (11a)	1937 (vs) <sup>e</sup>	1942 (st) <sup>e</sup>	-8.93 (s)	4.96 (m, 2 H), 4.48 (m, 2 H), -13.18 (quintet, 2 H, <sup>2</sup> J <sub>P-H</sub> = 6.4)
[Ir <sub>2</sub> (H) <sub>2</sub> (CO) <sub>2</sub> (μ-I)(DPM) <sub>2</sub> ][I] (11b)	1955 (vs) <sup>e</sup>	1960 (vs, br) <sup>e</sup>	-9.13 (s)	4.94 (m, 2 H), 4.45 (m, 2 H), -13.26 (quintet, 2 H, <sup>2</sup> J <sub>P-H</sub> = 6.4) <sup>h</sup>
[Ir <sub>2</sub> (H) <sub>4</sub> (CO) <sub>2</sub> (I)(DPM) <sub>2</sub> ][BF <sub>4</sub> ] (12)		2034 (vs), 1779 (st) <sup>e</sup> 2124 (w) <sup>f</sup>	-6.42 (s)	7.0-8.0 (m, 40 H), 6.52 (br, 2 H), 4.58 (br, 2 H), -10.62 (br, 2 H), -13.16 (br, 2 H) <sup>g</sup>
[RhIrCl <sub>2</sub> (CO) <sub>2</sub> (DPM) <sub>2</sub> ] (13)	1960 (vs) <sup>e</sup>	1980 (vs), 1970 (vs), 1756 (st) <sup>e</sup>	17.16 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 125.7) -6.96 (m)	6.8-8.0 (m, 40 H), 4.01 (m, 2 H), 4.29 (m, 2 H)
[Ir <sub>2</sub> I <sub>2</sub> (H) <sub>2</sub> (CO) <sub>2</sub> (DPM) <sub>2</sub> ] (15)	2002 (vs), 1982 (st) <sup>e</sup> 2230 (w), 2105 (w) <sup>f</sup>	2071 (vs), 2010 (vs) <sup>e</sup> 2220 (w), 2112 (w) <sup>f</sup>	-11.19 (m), -14.82 (m)	5.70 (m, 2 H), 5.20 (m, 2 H), -8.90 (t, 1 H, <sup>2</sup> J <sub>P-H</sub> = 13.0), -13.59 (t, 1 H, <sup>2</sup> J <sub>P-H</sub> = 8.8) <sup>h</sup>

<sup>a</sup> Abbreviations used: st = strong, vs = very strong, med = medium, w = weak, s = singlet, m = multiplet, dm = doublet of multiplets, br = broad, t = triplet, dt = doublet of triplets. <sup>b</sup> Nujol mull. <sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub> solution except compounds 11a and 12 (THF). <sup>d</sup> In CD<sub>2</sub>Cl<sub>2</sub> solution except compounds 11a and 12 (THF-d<sub>6</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR vs 85% H<sub>3</sub>PO<sub>4</sub>. <sup>e</sup> <sup>ν</sup>(CO). <sup>f</sup> <sup>ν</sup>(M-H). <sup>g</sup> -60 °C. <sup>h</sup> -40 °C.

prepared by a modification of a previously reported procedure.<sup>13</sup> The NMR spectra (<sup>1</sup>H, <sup>1</sup>H{<sup>31</sup>P}, <sup>31</sup>P{<sup>1</sup>H}) were run on a Bruker WH-400 spectrometer. Spin-saturation-transfer experiments were conducted with a Bruker WH-200 NMR spectrometer. Infrared spectra were recorded on a Nicolet 7199 Fourier transform interferometer either as solids in Nujol mulls on KBr plates or as solutions in KCl cells with 0.5-mm window path lengths. Analyses were performed by the microanalytical service within the department but were not obtained for the hydrides presented herein due to facile H<sub>2</sub> loss in most cases. Conductivity measurements were made on approximately 10<sup>-3</sup> M solutions with a Yellow Springs Instrument Co. Model 31 conductivity bridge.

**H/D Exchange.** Approximately 5 mg of the sample was placed in an NMR tube under N<sub>2</sub> and cooled to liquid-nitrogen temperature. Acetone-d<sub>6</sub> that had previously been saturated with H<sub>2</sub>/D<sub>2</sub> (1:1) was transferred into this tube and the sample placed under ca. 600 Torr of H<sub>2</sub>/D<sub>2</sub> (1:1 v/v). The NMR tube was flame-sealed, and the exchange was followed by warming to room temperature and monitoring the H<sub>2</sub> and HD resonances at δ 4.5 in the <sup>1</sup>H NMR spectrum with the Bruker WH-400 spectrometer.

**Preparation of Compounds.** (a) [Ir<sub>2</sub>(H)<sub>4</sub>Cl(CO)<sub>2</sub>(DPM)<sub>2</sub>][BF<sub>4</sub>] (Isomers 3a and 3b). An atmosphere of hydrogen was placed over a solution of [Ir<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>][BF<sub>4</sub>] (1) 50.0 mg, 0.0376 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the solution was stirred for 15 min, during which time the color changed from dark red to pale yellow. The solution was taken to dryness under a rapid flow of hydrogen, leaving a pale yellow powder. The <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra indicated the presence of the two species 3a and 3b (established as tetrahydrides on the basis of integration of the <sup>1</sup>H resonances) in an approximate 5:1 ratio, respectively. Spectroscopic data for these and all subsequent compounds are given in Table I.

(b) [RhIrCl<sub>2</sub>(CO)<sub>2</sub>(DPM)<sub>2</sub>] (13). The dry solids [Ir(DPM)<sub>2</sub>(CO)]-[Cl] (200 mg, 0.195 mmol) and [RhCl(CO)<sub>2</sub>]<sub>2</sub> (38.0 mg, 0.098 mmol) were combined and dissolved in 25 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the resulting solution was stirred for 18 h. During this time the color of the solution changed from yellow to orange. The solution was refluxed under a dinitrogen flow for 1 h, causing the orange color to intensify. A 40-mL volume of diethyl ether was added, resulting in the precipitation of a bright orange microcrystalline solid, which was collected, washed with diethyl ether, and dried in vacuo. Typical isolated yields were 75-80%. Compound 13 was found to be a nonelectrolyte in CH<sub>2</sub>Cl<sub>2</sub> solutions (Λ<sub>m</sub> = 4.8 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>). Anal. Calcd for IrRhCl<sub>2</sub>P<sub>4</sub>O<sub>2</sub>C<sub>52</sub>H<sub>44</sub>: C, 52.45; H, 3.72; Cl, 5.95. Found: C, 51.57; H, 3.77; Cl, 5.37.

(c) [RhIr(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>][BF<sub>4</sub>] (6). Compound 13 (200 mg, 0.168 mmol) was suspended in 20 mL of THF; then AgBF<sub>4</sub> (32.7 mg, 0.168 mmol), dissolved in 5 mL of THF, was added to the suspension. An immediate color change to dark orange occurred, and after an additional 30 min of stirring the volume was reduced to approximately 15 mL; then 30 mL of diethyl ether was added to cause complete precipitation. The solvent was removed, the product was redissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the solution was filtered to remove the silver salts. The product was reprecipitated by the addition of 30 mL of diethyl ether, collected, and dried in vacuo. Yields were approximately 80% of a dark orange microcrystalline solid. Compound 6 was determined to be a 1:1 electrolyte in CH<sub>2</sub>Cl<sub>2</sub> solutions (Λ<sub>m</sub> = 59.7 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>). Anal. Calcd for IrRhClP<sub>4</sub>O<sub>2</sub>F<sub>4</sub>C<sub>52</sub>BH<sub>44</sub>: C, 50.28; H, 3.57; Cl, 2.85. Found: C, 50.02; H, 3.53; Cl, 3.20.

(d) [RhIr(CO)<sub>2</sub>(μ-S)(DPM)<sub>2</sub>] (7). To a solution of [RhIrCl<sub>2</sub>(CO)<sub>2</sub>(DPM)<sub>2</sub>] (13; 50.0 mg, 0.0420 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added Na<sub>2</sub>S·9H<sub>2</sub>O (12.0 mg, approximately 10% excess) dissolved in 5 mL of methanol. The solution immediately turned dark red. After it was stirred for 15 min, the solution was concentrated to 5 mL, whereupon a dark red microcrystalline solid precipitated. The solid was collected, recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH, and washed with MeOH and then with diethyl ether. Isolated yields were 90-95%. Anal. Calcd for IrRhSP<sub>4</sub>O<sub>2</sub>C<sub>52</sub>H<sub>44</sub>:

(13) Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *Organometallics* 1983, 2, 1889.

C, 54.22; H, 3.85. Found: C, 53.58; H, 3.96.

(e) **[RhIr(H)<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>][BF<sub>4</sub>]** (**8a**). An atmosphere of hydrogen was placed over a solution of [RhIr(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>][BF<sub>4</sub>] (**6**; 50.0 mg, 0.0403 mmol) in 8 mL of CH<sub>2</sub>Cl<sub>2</sub>, causing an immediate color change from orange to yellow-orange. After the mixture was stirred for 10 min, 20 mL of diethyl ether was added, precipitating a light yellow solid. The solvent was removed and the solid dried under a rapid flow of hydrogen. Isolated yields were approximately 95%. Compound **8** was determined to be a 1:1 electrolyte in CH<sub>2</sub>Cl<sub>2</sub> solutions ( $\Lambda_m = 58.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ).

(f) **[RhIr(H)<sub>2</sub>(CO)<sub>2</sub>(μ-S)(DPM)<sub>2</sub>]** (**9**). An atmosphere of hydrogen was placed over a solution of [RhIr(CO)<sub>2</sub>(μ-S)(DPM)<sub>2</sub>] (**7**; 20.0 mg, 0.0174 mmol) in 3 mL of CH<sub>2</sub>Cl<sub>2</sub>. Over a period of 5–10 min the color of the solution changed from red to orange. Addition of 10 mL of diethyl ether caused precipitation of a flocculent yellow-brown solid, which proved susceptible to decomposition except under a hydrogen atmosphere. For this reason only solution characteristics were obtained for compound **9**.

(g) **[Ir<sub>2</sub>(H)<sub>4</sub>(CO)<sub>2</sub>(I)(DPM)<sub>2</sub>][BF<sub>4</sub>]** (**12**). A sample of [Ir<sub>2</sub>(CO)<sub>2</sub>(μ-I)(DPM)<sub>2</sub>][BF<sub>4</sub>] (10.0 mg, 0.00703 mmol) was dissolved in THF-*d*<sub>6</sub> in an NMR tube under dinitrogen. Hydrogen was introduced, causing an immediate color change from dark orange to yellow. <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra, recorded within 10 min of H<sub>2</sub> addition, indicated the formation of a single tetrahydride species. Compound **12** was not obtained in solid form due to facile H<sub>2</sub> and HI loss.

(h) **[Ir<sub>2</sub>(H)<sub>2</sub>(CO)<sub>2</sub>(μ-I)(DPM)<sub>2</sub>][BF<sub>4</sub>]** (**11a**). Removing the hydrogen atmosphere from the sample of **12a** prepared as in (g), replacing it with dinitrogen, and warming slightly led to immediate formation of a dihydride species, **11a**, as monitored by <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectroscopy. Variable amounts of [Ir<sub>2</sub>H(CO)<sub>2</sub>(μ-H)<sub>2</sub>(DPM)<sub>2</sub>][BF<sub>4</sub>], resulting from HI loss from **12a**, were also detected by NMR (identified by comparison of the <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra with those of an authentic sample<sup>14</sup>) and caused a slight color change from yellow to orange-yellow.

(i) **[RhIr(H)<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>][Cl]** (**8b**). Compound **8b** was prepared by the same method as in (e) for compound **8a**, except [RhIrCl<sub>2</sub>(CO)<sub>2</sub>(DPM)<sub>2</sub>] (**13**) was used instead of [RhIr(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>][BF<sub>4</sub>] (**6**); yield 95%. Compound **8b** was determined to be a 1:1 electrolyte in CH<sub>2</sub>Cl<sub>2</sub> solutions ( $\Lambda_m = 44.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ).

(j) **[Ir<sub>2</sub>(H)<sub>2</sub>I<sub>2</sub>(CO)<sub>2</sub>(DPM)<sub>2</sub>]** (**15**). Approximately 20 mg of [Ir<sub>2</sub>I<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(DPM)<sub>2</sub>] was dissolved in CD<sub>2</sub>Cl<sub>2</sub> in an NMR tube under dinitrogen. Hydrogen was introduced, causing the solution to immediately change color from orange to yellow. <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra revealed the formation of two dihydride species in a 7:3 ratio. The minor product was identified as [Ir<sub>2</sub>(H)<sub>2</sub>(CO)<sub>2</sub>(μ-I)(DPM)<sub>2</sub>][I] (**11b**) by comparison of its spectral parameters to those of [Ir<sub>2</sub>(H)<sub>2</sub>(CO)<sub>2</sub>(μ-I)(DPM)<sub>2</sub>][BF<sub>4</sub>] (**11a**), and the major species has been formulated as **15**, on the basis of its spectral parameters. The products were precipitated by the addition of 10 mL of hexanes, yielding a yellow powder that proved susceptible to facile H<sub>2</sub> loss unless kept under a hydrogen atmosphere.

**X-ray Data Collection.** Crystals of [RhIr(H)<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>][BF<sub>4</sub>]-CH<sub>2</sub>Cl<sub>2</sub> were obtained by slow diffusion of diethyl ether into a saturated CH<sub>2</sub>Cl<sub>2</sub> solution of the compound. A suitable crystal was wedged into a capillary tube, which was flame-sealed as a precaution against loss of solvent of crystallization. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22 °C using graphite-monochromated Mo K $\alpha$  radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range 20.0° ≤ 2θ ≤ 23.7°. Automatic peak search and reflection indexing programs established a triclinic crystal system. This system and the lack of systematic absences were consistent with the space groups *P*1 and *P* $\bar{1}$ ; the centrosymmetric space group was chosen and later was verified by successful refinement of the structure.

Intensity data were collected on the CAD4 diffractometer in the bisecting mode employing the  $\theta/2\theta$  scan technique to  $2\theta = 50.00^\circ$ . The scan range was determined as a function of  $\theta$  to compensate for  $\alpha_1 - \alpha_2$  wavelength dispersion, and backgrounds were scanned for 25% of the peak width on either side of the peak scan. The intensities of three standard reflections were measured every 1 h of exposure time in order to monitor possible crystal decomposition. The mean decrease in the intensities of the standards was 5.1%, and a correction was applied to the data with the assumption of linear decay. Data reduction was executed with  $p = 0.04$  to downweight intense reflections,<sup>15</sup> and corrections for Lorentz and polarization effects and for absorption were applied by using the method of Walker and Stuart.<sup>16</sup> See Table II for crystal data and details of the intensity collection.

**Table II.** Crystallographic Data for [RhIr(H)<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>][BF<sub>4</sub>]-CH<sub>2</sub>Cl<sub>2</sub>

chem formula: IrRhCl <sub>3</sub> P <sub>4</sub> F <sub>4</sub> C <sub>53</sub> BH <sub>48</sub>	fw: 1286.32
$a = 14.171 (2) \text{ \AA}$	space group: <i>P</i> $\bar{1}$ (No. 2)
$b = 22.638 (3) \text{ \AA}$	$T = 22 \text{ }^\circ\text{C}$
$c = 9.642 (2) \text{ \AA}$	$\lambda = 0.71069 \text{ \AA}$
$\alpha = 94.18 (1)^\circ$	$\rho_{\text{calcd}} = 1.578 \text{ g cm}^{-3}$
$\beta = 107.38 (2)^\circ$	$\mu = 29.63 \text{ cm}^{-1}$
$\gamma = 105.84 (1)^\circ$	transmissn coeff: 0.812–1.251
$V = 2799.4 \text{ \AA}^3$	$R(F_o) = 0.053$
$Z = 2$	$R_w(F_o) = 0.081$

**Structure Solution and Refinement.** The structure was solved in the space group *P* $\bar{1}$  by using Patterson techniques to locate the metal atoms and by successive least-squares and difference Fourier calculations to obtain the other atom positions. All hydrogen atoms were located; the methylene and phenyl protons were placed in their idealized positions by using C–H distances of 0.95 Å, whereas those bound to Ir were placed in positions obtained from difference Fourier maps since attempts to refine these atoms failed. The thermal parameters of the iridium-bound hydrogens were fixed at 4.0 Å<sup>2</sup> whereas all others were input as 1.2 times the thermal parameter of the attached carbon atom. The BF<sub>4</sub><sup>−</sup> anion was badly disordered, displaying only three well-defined (although smeared out) maxima in the difference Fourier maps. It appeared that the boron and one fluorine were disordered on each side of the plane defined by the three fluorines, so they were input as such. Attempts to refine these two disordered atoms failed, presumably because of the large amount of residual electron density in the vicinity, so these atoms were input and fixed in subsequent refinements, with two half-occupancy fluorine positions and only one boron position.

The high thermal parameters for the carbon and chlorine atoms of the CH<sub>2</sub>Cl<sub>2</sub> molecule suggest some degree of disorder of this group but are not unusual for such a molecule. The occupancy of this solvent molecule may be somewhat less than 1 but high correlation of the occupancy factor and the thermal parameters did not allow a better estimate from least-squares refinements. In addition, facile loss of CH<sub>2</sub>Cl<sub>2</sub> upon drying of the solid prevented reliable determination of the amount of solvent by either elemental analyses or <sup>1</sup>H NMR spectroscopy.

Refinement was carried out by full-matrix least-squares methods<sup>17</sup> minimizing the function  $\sum w(|F_o| - |F_c|)^2$ , with  $w = 4F_o^2/\sigma^2(F_o^2)$ . Atomic scattering factors and anomalous dispersion terms used in the structure determination programs were those supplied in the Enraf-Nonius structure determination package.

The positional and isotropic thermal parameters for the final model are given in Table III. Selected bond distances and angles are given in Tables IV and V, respectively. Refinement in the space group *P* $\bar{1}$  converged at  $R = 0.053$  and  $R_w = 0.081$ . Additional information is available as supplementary material.

## Results

The spectral parameters of the new products are presented in the Discussion section and are tabulated in Table I. The results of the transformations observed are summarized in Scheme I.

## Discussion

(a) **A-Frame Complexes.** We have previously shown<sup>1</sup> that the A-frame complex [Ir<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>]<sup>+</sup> (**1**) reacts readily with H<sub>2</sub>, giving first the dihydride [Ir<sub>2</sub>(H)<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>]<sup>+</sup> (**2**), which subsequently reversibly adds another 1 equiv of H<sub>2</sub> to give a tetrahydride species, [Ir<sub>2</sub>(H)<sub>4</sub>Cl(CO)<sub>2</sub>(DPM)<sub>2</sub>]<sup>+</sup> (cation of **3**). Although only one tetrahydride product was originally observed and reported, subsequent studies (reported herein) indicate that two isomers of **3** are in fact produced. Before discussing the natures and origins of these tetrahydride isomers, however, it is instructive to first consider the dihydride **2** and the facile hydride rearrangements that occur in this and related A-frame dihydrides. In order to obtain a global understanding of these rearrangements, we will first summarize the salient features of our two previous reports on this chemistry and then relate this work to the present study.

In our initial report<sup>1</sup> we proposed the structure shown earlier for **2**, in which the hydride ligands were not adjacent but instead

(14) McDonald, R.; Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1987**, *26*, 3333.

(15) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

(16) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 1581.

(17) All computing was carried out on a Digital PDP11/23 PLUS computer using the programs of the Enraf-Nonius Structure Determination Package and some local programs by R. G. Ball.

Table III. Positional Parameters and Isotropic Thermal Parameters<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>	atom	x	y	z	B, Å <sup>2</sup>
Ir	0.19224 (2)	0.32121 (2)	0.09488 (4)	2.667 (7)	C(34)	-0.342 (1)	0.1535 (8)	-0.016 (2)	8.3 (4)*
Rh	0.10502 (5)	0.17897 (3)	0.05200 (7)	2.79 (1)	C(35)	-0.351 (1)	0.1475 (8)	-0.157 (2)	9.0 (5)*
Cl(1)	0.2028 (2)	0.2414 (1)	-0.0886 (2)	3.41 (5)	C(36)	-0.259 (1)	0.1527 (7)	-0.193 (2)	7.0 (3)*
Cl(2) <sup>b</sup>	0.3056 (5)	0.5594 (3)	0.2346 (7)	13.9 (2)	C(41)	-0.0781 (7)	0.1212 (4)	-0.294 (1)	3.6 (2)*
Cl(3) <sup>b</sup>	0.1866 (5)	0.4864 (4)	0.3841 (8)	14.7 (3)	C(42)	-0.0692 (9)	0.0642 (6)	-0.280 (1)	5.5 (3)*
P(1)	0.0294 (2)	0.3207 (1)	-0.0544 (3)	3.06 (5)	C(43)	-0.092 (1)	0.0201 (6)	-0.403 (1)	6.4 (3)*
P(2)	-0.0459 (2)	0.1779 (1)	-0.1287 (3)	3.10 (5)	C(44)	-0.124 (1)	0.0326 (6)	-0.540 (1)	6.5 (3)*
P(3)	0.3434 (2)	0.3163 (1)	0.2685 (2)	2.76 (5)	C(45)	-0.135 (1)	0.0889 (7)	-0.563 (2)	7.0 (3)*
P(4)	0.2619 (2)	0.1733 (1)	0.2078 (3)	2.93 (5)	C(46)	-0.112 (1)	0.1340 (6)	-0.435 (1)	6.3 (3)*
F(1)	0.6223 (6)	0.2604 (7)	0.350 (1)	19.8 (4)	C(51)	0.3524 (6)	0.3240 (4)	0.4604 (9)	3.1 (2)*
F(2)	0.7715 (7)	0.2646 (5)	0.524 (1)	19.8 (3)	C(52)	0.2742 (8)	0.3354 (5)	0.507 (1)	4.3 (2)*
F(3)	0.633 (1)	0.2478 (6)	0.556 (1)	24.7 (5)	C(53)	0.2850 (9)	0.3419 (6)	0.657 (1)	5.1 (2)*
F(4) <sup>c</sup>	0.666	0.177	0.430	25.0*	C(54)	0.3703 (9)	0.3373 (6)	0.756 (1)	5.3 (3)*
F(5) <sup>c</sup>	0.740	0.322	0.433	25.0*	C(55)	0.445 (1)	0.3254 (6)	0.712 (1)	6.3 (3)*
O(1)	0.3055 (6)	0.4357 (3)	-0.0051 (8)	5.6 (2)	C(56)	0.4395 (8)	0.3196 (5)	0.565 (1)	5.0 (2)*
O(2)	-0.0076 (6)	0.0661 (4)	0.1369 (9)	5.9 (2)	C(61)	0.4575 (6)	0.3773 (4)	0.268 (1)	3.2 (2)*
C(1)	0.02651 (7)	0.3931 (4)	0.028 (1)	3.6 (2)	C(62)	0.5240 (8)	0.3682 (5)	0.198 (1)	4.8 (2)*
C(2)	0.0358 (7)	0.1101 (5)	0.105 (1)	4.0 (2)	C(63)	0.600 (1)	0.4190 (6)	0.182 (1)	6.1 (3)*
C(3)	-0.0329 (7)	0.2528 (4)	-0.197 (1)	3.5 (2)	C(64)	0.6124 (9)	0.4770 (6)	0.244 (1)	5.9 (3)*
C(4)	0.3703 (6)	0.2436 (4)	0.234 (1)	3.3 (2)	C(65)	0.5439 (9)	0.4889 (6)	0.313 (1)	5.6 (3)*
C(5) <sup>b</sup>	0.235 (3)	0.565 (1)	0.381 (2)	20 (1)	C(66)	0.4684 (8)	0.4383 (5)	0.325 (1)	4.9 (2)*
C(11)	-0.0649 (7)	0.3248 (5)	0.033 (1)	3.7 (2)*	C(71)	0.2671 (7)	0.1614 (4)	0.393 (1)	3.5 (2)*
C(12)	-0.0443 (8)	0.3283 (5)	0.185 (1)	4.6 (2)*	C(72)	0.1862 (8)	0.1658 (5)	0.443 (1)	4.6 (2)*
C(13)	-0.1182 (9)	0.3291 (6)	0.252 (1)	5.7 (3)*	C(73)	0.1893 (9)	0.1553 (6)	0.587 (1)	5.9 (3)*
C(14)	-0.2149 (9)	0.3269 (6)	0.163 (1)	5.9 (3)*	C(74)	0.269 (1)	0.1394 (6)	0.678 (1)	6.2 (3)*
C(15)	-0.2393 (9)	0.3227 (6)	0.016 (1)	5.9 (3)*	C(75)	0.345 (1)	0.1327 (7)	0.632 (2)	7.3 (4)*
C(16)	-0.1656 (8)	0.3214 (5)	-0.052 (1)	4.7 (2)*	C(76)	0.349 (1)	0.1447 (7)	0.486 (2)	6.8 (3)*
C(21)	0.0372 (7)	0.3865 (4)	-0.155 (1)	3.5 (2)*	C(81)	0.3045 (7)	0.1130 (4)	0.136 (1)	3.6 (2)*
C(22)	0.663 (8)	0.4452 (5)	-0.078 (1)	4.9 (2)*	C(82)	0.235 (1)	0.0596 (7)	0.051 (2)	7.1 (3)*
C(23)	0.0858 (9)	0.4966 (6)	-0.141 (1)	5.3 (3)*	C(83)	0.265 (1)	0.0098 (8)	0.000 (2)	8.4 (4)*
C(24)	0.077 (1)	0.4910 (6)	-0.287 (1)	6.1 (3)*	C(84)	0.360 (1)	0.0176 (7)	0.016 (2)	7.8 (4)*
C(25)	0.052 (1)	0.4325 (7)	-0.364 (2)	7.3 (3)*	C(85)	0.438 (2)	0.073 (1)	0.100 (2)	10.9 (6)*
C(26)	0.0304 (9)	0.3794 (6)	-0.301 (1)	5.4 (3)*	C(86)	0.410 (1)	0.1211 (8)	0.161 (2)	8.5 (4)*
C(31)	-0.1659 (8)	0.1642 (5)	-0.083 (1)	4.1 (2)*	B	0.692	0.275	0.462	25.0*
C(32)	-0.1616 (8)	0.1705 (5)	0.060 (1)	5.0 (2)*	H(1)	0.120	0.266	0.182	4.0
C(33)	-0.254 (1)	0.1662 (7)	0.090 (1)	6.6 (3)*	H(2)	0.167	0.353	0.223	4.0

<sup>a</sup> Estimated standard deviations in this and subsequent tables are given in parentheses and correspond to the least significant digit. Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $\frac{1}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$ . <sup>b</sup> The atoms Cl(2), Cl(3), and C(5) are those of the CH<sub>2</sub>Cl<sub>2</sub> solvent molecule. <sup>c</sup> Atoms F(4) and F(5) are half-occupancy. See text for a discussion of BF<sub>4</sub><sup>-</sup> disorder.

Table IV. Selected Distances<sup>a</sup> (Å) in [RhIr(H)<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>][BF<sub>4</sub>]

(a) Bonded			
Ir-H(1)	1.81	P(1)-C(21)	1.830 (6)
Ir-H(2)	1.56	P(2)-C(3)	1.846 (6)
Ir-Cl(1)	2.501 (1)	P(2)-C(31)	1.834 (7)
Ir-P(1)	2.322 (1)	P(2)-C(41)	1.828 (6)
Ir-P(3)	2.328 (1)	P(3)-C(4)	1.820 (6)
Ir-C(1)	1.938 (6)	P(3)-C(51)	1.808 (6)
Rh-Cl(1)	2.468 (1)	P(3)-C(61)	1.820 (6)
Rh-P(2)	2.313 (1)	P(4)-C(4)	1.825 (6)
Rh-P(4)	2.325 (1)	P(4)-C(71)	1.810 (6)
Rh-C(2)	1.800 (6)	P(4)-C(81)	1.806 (6)
P(1)-C(3)	1.807 (6)	O(1)-C(1)	1.103 (7)
P(1)-C(11)	1.801 (6)	O(2)-C(2)	1.134 (7)
(b) Nonbonded			
Ir-Rh	3.0651 (5)	P(3)-P(4)	3.073 (2)
P(1)-P(2)	3.070 (2)	Rh-H(1)	2.18

<sup>a</sup> Additional distances are given in the supplementary material.

were located cis to the bridging chloride ligand, one on each metal. Although this is not a structure expected from concerted oxidative addition of H<sub>2</sub> at one Ir center, it is the only dihydride observed, forming essentially instantaneously upon reaction of **1** with H<sub>2</sub>. Our proposal was based on the reluctance of **2** to lose H<sub>2</sub>, implying that the hydride ligands were not mutually adjacent, and on the subsequent reaction of this species with alkyne to yield [Ir<sub>2</sub>(RC=C(H)R)<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>]<sup>+</sup>. The structure determination of the neutral dichloride, obtained by Cl<sup>-</sup> addition to this product, confirmed that the metalloolefin moieties were located on the *outsides* of the complex exactly as proposed for the hydride ligands in the precursor **2**.<sup>1</sup>

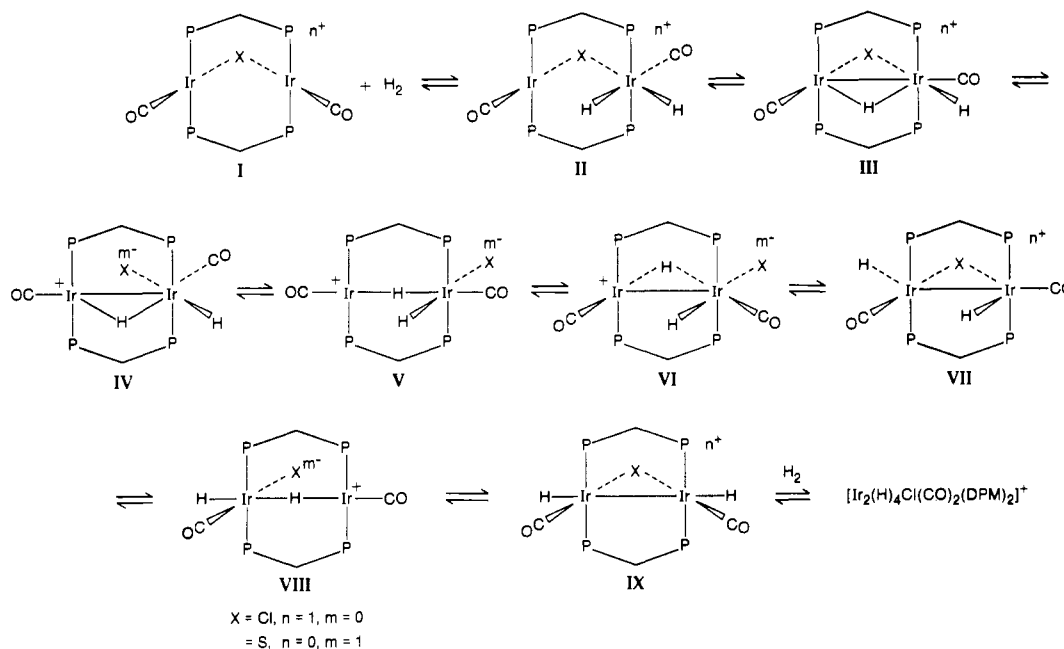
Table V. Selected Angles<sup>a</sup> (deg) in [RhIr(H)<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>][BF<sub>4</sub>]

Cl(1)-Ir-P(1)	92.55 (5)	C(3)-P(1)-C(11)	105.8 (3)
Cl(1)-Ir-P(3)	91.18 (5)	C(3)-P(1)-C(21)	104.4 (3)
Cl(1)-Ir-C(1)	96.0 (2)	C(11)-P(1)-C(21)	103.8 (3)
P(1)-Ir-P(3)	171.67 (5)	Rh-P(2)-C(3)	111.9 (2)
P(1)-Ir-C(1)	93.6 (2)	Rh-P(2)-C(31)	118.8 (2)
P(3)-Ir-C(1)	93.5 (2)	Rh-P(2)-C(41)	112.4 (2)
Cl(1)-Ir-H(1)	95.9	C(3)-P(2)-C(31)	102.9 (3)
Cl(1)-Ir-H(2)	162.6	C(3)-P(2)-C(41)	103.7 (3)
P(1)-Ir-H(1)	84.7	C(31)-P(2)-C(41)	105.8 (3)
P(3)-Ir-H(1)	87.5	Ir-P(3)-C(4)	112.7 (2)
P(1)-Ir-H(2)	85.8	Ir-P(3)-C(51)	118.4 (2)
p(3)-Ir-H(2)	88.4	Ir-P(3)-C(61)	111.8 (2)
C(1)-Ir-H(1)	168.0	C(4)-P(3)-C(51)	104.0 (3)
C(1)-Ir-H(2)	101.3	C(4)-P(3)-C(61)	105.3 (3)
H(1)-Ir-H(2)	66.7	C(51)-P(3)-C(61)	103.5 (3)
Cl(1)-Rh-P(2)	87.70 (5)	Rh-P(4)-C(4)	112.8 (2)
Cl(1)-Rh-P(4)	88.36 (5)	Rh-P(4)-C(71)	116.4 (2)
Cl(1)-Rh-C(2)	157.6 (2)	Rh-P(4)-C(81)	113.3 (2)
P(2)-Rh-P(4)	172.09 (6)	C(4)-P(4)-C(71)	104.3 (3)
P(2)-Rh-C(2)	90.7 (2)	C(4)-P(4)-C(81)	102.9 (3)
P(4)-Rh-C(2)	90.3 (2)	C(71)-P(4)-C(81)	105.9 (3)
Ir-Cl(1)-Rh	76.18 (4)	Ir-C(1)-O(1)	176.7 (6)
Ir-P(1)-C(3)	112.1 (2)	Rh-C(2)-O(2)	179.1 (7)
Ir-P(1)-C(11)	117.6 (2)	P(1)-C(3)-P(2)	114.4 (3)
Ir-P(1)-C(21)	112.0 (2)	P(3)-C(4)-P(4)	114.9 (3)

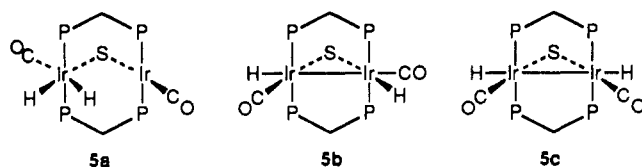
<sup>a</sup> Additional angles are given in the supplementary material.

Reaction of the related sulfido-bridged A-frame [Ir<sub>2</sub>(CO)<sub>2</sub>(μ-S)(DPM)<sub>2</sub>] (**4**) with H<sub>2</sub><sup>2</sup> again yielded a dihydride species (**5c**) having a structure like that of **2**, and the large hydride-hydride coupling constant derived from the high-field resonance in the

Scheme I



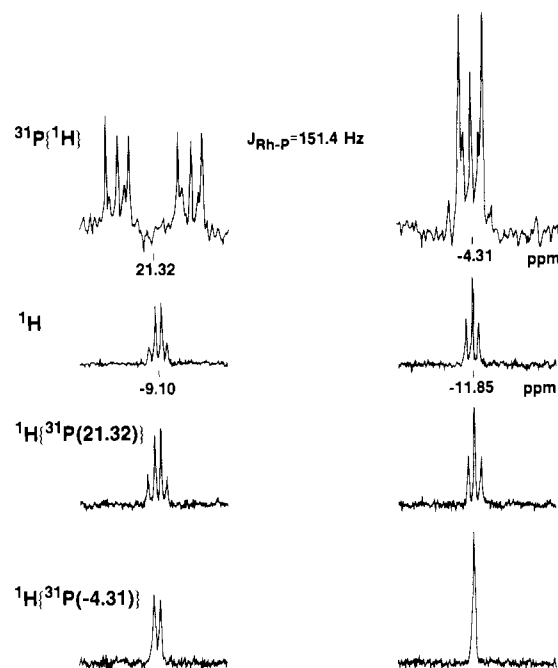
$^1\text{H}$  NMR spectrum suggested that both hydride ligands were nearly collinear with the Ir–Ir bond. This caused us to rein-



vestigate the  $^1\text{H}$  NMR spectrum of **2**, which had originally been reported<sup>1</sup> as a poorly resolved triplet, and we now find that this resonance is very much like that of **5c**, except poorly resolved due to somewhat smaller coupling constants. Unfortunately, because of the poor resolution we are unable to derive the coupling constants, as was done for **5c**.<sup>2</sup>

Significantly, the formation of **5c** is much slower than that of the analogous chloride **2**, taking hours instead of being instantaneous. As a consequence, two precursors of **5c**, namely **5a** and **5b**, were also observed.<sup>2</sup> The initial species (**5a**) was proposed to be an Ir(III)–Ir(I) dimer resulting from oxidative addition at one metal center. However, owing to the extreme fluxionality of **5a**, a suitable low-temperature limiting spectrum, which would allow us to carry out appropriate NMR decoupling experiments in order to unambiguously characterize this species, was not obtained. Compound **5a** rearranged with time to the unsymmetrical compound **5b**, which subsequently yielded **5c**.

In an attempt to isolate and characterize a species analogous to **5a**, having both hydrides associated with one metal, we turned in this study to the closely related heterobimetallic compounds  $[\text{RhIr}(\text{CO})_2(\mu\text{-X})(\text{DPM})_2]^{n+}$  (cation of **6**,  $X = \text{Cl}$ ,  $n = 1$ ; **7**,  $X = \text{S}$ ,  $n = 0$ ), on the assumption that oxidative addition of  $\text{H}_2$  should be favored at the Ir center and that because of stronger Ir–H bonds compared to Rh–H,<sup>18</sup> the hydride ligands would remain associated with Ir. These heterobinuclear A-frames are readily prepared either by abstraction of one  $\text{Cl}^-$  ion from  $[\text{RhIrCl}_2(\text{CO})_2(\text{DPM})_2]$  by using  $\text{AgBF}_4$  or by exchange of both  $\text{Cl}^-$  ions with  $\text{S}^{2-}$  through use of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ . The infrared spectra of **6** and **7** are similar to those of the respective homobimetallic analogues, having two terminal carbonyl bands (**6**, 1993, 1974  $\text{cm}^{-1}$ ; **7**, 1932, 1906  $\text{cm}^{-1}$ ). As in the homobimetallic analogues of both Rh<sup>19,20</sup> and Ir,<sup>7,9</sup> the



**Figure 1.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (top) and  $^1\text{H}$  NMR spectra (hydride region) of compound **9**, including selective  $^{31}\text{P}$  decoupling of the  $^1\text{H}$  NMR spectrum.

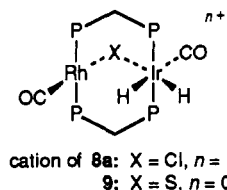
sulfide-bridged species has lower carbonyl stretches than the chloride-bridged one, indicating more electron-rich metal centers. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **6** and **7** are typical of rhodium/iridium heterobimetallic DPM complexes, having an AA'BB'X spin system, and display a multiplet resonance for the phosphorus nuclei on the iridium center and a doublet of multiplets ( $^1J_{\text{Rh-P}} = 111.0$  Hz (**6**), 131.3 Hz (**7**)) for the phosphorus atoms on rhodium.

Reaction of compounds **6** and **7** with  $\text{H}_2$  yields the dihydrides **8a** and **9**, respectively. As anticipated, both hydride ligands have remained coordinated to the iridium center in each case, although

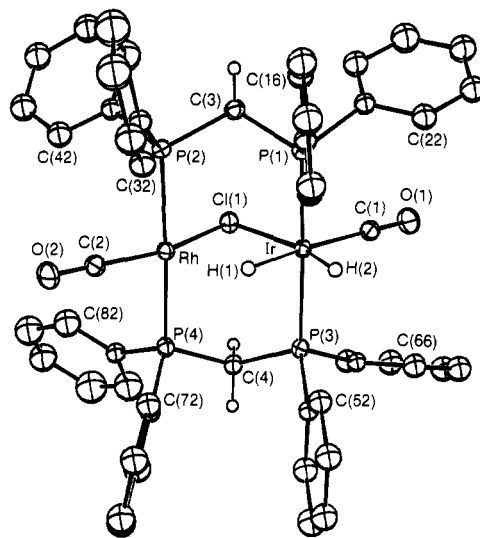
(18) (a) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 82, and references therein.

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NMR and X-ray (vide infra) studies indicate that one is also weakly interacting with Rh. The  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra for **9**, with and without selective  $^{31}\text{P}$  decoupling, are shown in Figure 1; those obtained for **8a** are very similar. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum displays two sets of resonances such as for compounds **6** and **7**; the resonance at  $\delta -4.31$  (multiplet) corresponds to the phosphorus nuclei bound to Ir, whereas that at  $\delta 21.32$  (doublet of multiplets;  $^1J_{\text{Rh-P}} = 151.4$  Hz) clearly corresponds to the rhodium-bound phosphorus nuclei. The  $^1\text{H}$  NMR spectrum displays two high-field resonances, each being integrated as one hydrogen. The resonance at  $\delta -11.85$  is a triplet ( $^2J_{\text{P-H}} = 12.8$  Hz), whereas that at  $\delta -9.10$  is an apparent quartet ( $J \approx 12.5$  Hz). Selective phosphorus decoupling clearly establishes the connectivities involving these hydride ligands. Decoupling the Rh-bound  $^{31}\text{P}$  resonances gives rise to no observable change in the  $^1\text{H}$  resonance at  $\delta -11.85$  and results in only a very slight sharpening of the resonance at  $\delta -9.10$ , whereas decoupling the Ir-bound  $^{31}\text{P}$  resonance causes the triplet  $^1\text{H}$  resonance to collapse to a singlet and the quartet to collapse to a doublet, retaining only coupling to rhodium of 12.5 Hz. Clearly both hydride ligands are bound to Ir. However, the hydride ligand giving rise to the low-field resonance is also bound to Rh as demonstrated by the significant coupling to this nucleus. It appears, however, that this hydride ligand does not display appreciable coupling to the two phosphorus nuclei on Rh. Although this seems unusual, we note that in the rather similar complexes  $[\text{M}_2(\text{CO})_2(\mu\text{-H})_2(\text{DPM})_2]$  the dirhodium complex again displayed no coupling of the hydride ligands to phosphorus,<sup>21</sup> whereas obvious coupling ( $^2J_{\text{P-H}} = 6.6$  Hz) was observed for the diiridium analogue.<sup>14</sup> Furthermore, the related mixed-metal complex  $[\text{RhIr}(\text{CO})_3(\mu\text{-H})_2(\text{DPM})_2]^{2+}$  has been found to exhibit coupling of the bridging hydrides to the Ir-bound phosphines of 11.1 Hz, but coupling to the Rh-bound phosphorus atoms was not resolved and was estimated at less than 3.5 Hz.<sup>22</sup> It is also significant that the  $^1J_{\text{Rh-H}}$  value of 12.5 Hz for **9** is somewhat lower than for other bridging hydrides in binuclear species,<sup>21,23</sup> where values of ca. 20–25 Hz appear typical. In an analogous trinuclear complex,  $[\text{Rh}_3(\text{H})_2(\text{CO})_2(\mu\text{-Cl})_2(\mu\text{-Ph}_2\text{PCH}_2)_2\text{AsPh}_2]^{2+}$ , in which the two hydride ligands are coordinated to the central rhodium while they interact weakly with the terminal rhodium atoms, the coupling of the hydrides to the central metal was 24.7 Hz but only 10.9 Hz to the terminal rhodium atoms.<sup>24</sup> Moreover, in analogous  $\text{Ir}_2\text{Rh}$  and  $\text{IrRh}_2$  complexes coupling constants ( $J_{\text{Rh-H}}$ ) involving the hydride ligands and the weakly interacting Rh nuclei of between 8.7 and 14.1 Hz were reported,<sup>25</sup> much as in **8a** and **9**. The high-field triplet in **9** therefore results from coupling of the terminal hydride to the two chemically equivalent phosphorus nuclei on iridium, and the apparent quartet is actually a doublet of triplets ( $^1J_{\text{Rh-H}} = 12.5$  Hz,  $^2J_{\text{P-H}} \approx 12.2$  Hz) due to coupling to rhodium and the two iridium-bound phosphorus nuclei. As in almost all previous examples of diphosphine-bridged A-frame hydrides of iridium, no H–H coupling is observed.<sup>1,9,14</sup> In the chloride-bridged analogue (**8a**) the spectra differ only slightly, in that small (but still un-



**Figure 2.** Perspective view of the  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2]^+$  cation showing the numbering scheme. Thermal parameters are shown at the 20% level except for hydrogens, which are shown artificially small for the methylene and hydride groups but are not shown for other groups.

resolved) additional coupling to the rhodium phosphines is also observed.

It appears as though oxidative addition of  $\text{H}_2$  to the iridium center at the inside or "pocket" of the A-frame occurs in both compounds **6** and **7**, followed by movement of one of the hydride ligands to a semibringing position. This supports our earlier proposal<sup>2</sup> of an initial Ir(III)/Ir(I) species resulting from  $\text{H}_2$  attack at one metal center of  $[\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\text{DPM})_2]$ . The preference of the Ir sites of compounds **6** and **7** to oxidatively add  $\text{H}_2$  instead of Rh is not surprising in view of previous observations of  $\text{H}_2$  addition to the diiridium species<sup>1,2,7</sup> but not to the dirhodium analogues. Although the structures of compounds **8a** and **9** can be considered as either of two extremes, involving either a classical hydride bridge or independent Rh(I)/Ir(III) centers having terminal hydride ligands, the above NMR evidence suggests an intermediate structure having an unsymmetrical Ir–H–Rh bridge, not unlike agostic<sup>26</sup> C–H–M interactions. Such a view is consistent with a recent discussion of interactions of various X–H bonds with transition metals (X = main-group or transition-metal element) by Crabtree and Hamilton.<sup>27</sup> Furthermore, this proposal is consistent with the X-ray structure as determined for **8a**. A view of the molecule is shown in Figure 2. As shown, both hydride ligands are coordinated to Ir to give a slightly distorted square planar Rh(I) center and an octahedral Ir(III) center. The positions shown for the hydride ligands were derived from a difference Fourier map, but since these atoms could not be refined acceptably, their positions are approximate. Therefore, the long Ir–H(1) distance (1.81 Å), which could in principle reflect the semibringing nature of this ligand, may be fortuitous. In any case the positions of these hydride ligands clearly result from  $\text{H}_2$  attack at the inside of the complex, between the metals. The Ir–C(1) distance (1.938 (6) Å), which is opposite H(1), is significantly longer than the Rh–C(2) distance (1.800 (6) Å), consistent with the high trans influence of a hydride ligand. Analogous differences are also observed for the bridging chloro ligand, although in this case they are less dramatic. Around the Ir center the angles are consistent with octahedral coordination, while at Rh the coordination is slightly distorted from square planar, with Rh moving inward toward H(1) slightly, resulting in Cl–Rh–C(2) and P(2)–Rh–P(4) angles of 157.6 (2) and 172.09 (6)°, respectively. The resulting Rh–H(1) interaction (approximately 2.18 Å) is clearly weak but is not inconsistent with some interaction, which from the NMR study is positively established. All parameters involved are closely comparable to those of the trinuclear  $\text{Rh}_3$  complex alluded to

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earlier.<sup>24</sup> In particular, the Rh–H distances involving the weak interactions in this Rh<sub>3</sub> species are just more than 2.0 Å and the corresponding Rh–Rh distances (2.967 (1), 2.948 (1) Å) are also similar to our Rh–Ir distance of 3.0651 (5) Å, although it appears that, on the basis of the shorter distances in the trirhodium species, the weak Rh–H interactions in the trinuclear species are somewhat stronger than in compound **8a**. The Rh–Ir distance in **8a** is almost exactly equal to the intraligand P–P separations, again suggesting that the interaction between Rh and the “IrH<sub>2</sub>” moiety is not strong. Little appears to have changed in the metal inner coordination spheres upon coordination of H<sub>2</sub> (on the basis of a comparison with the structure of [Rh<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(DPM)<sub>2</sub>][BF<sub>4</sub>]<sup>28</sup>), apart from movement of C(1)O(1) and possibly a slight compression of the Rh–Ir distance.

The infrared spectrum in solution for compound **8a** displays two terminal carbonyl bands at 2070 and 1973 cm<sup>-1</sup> as well as a weak Ir–H stretch at 2225 cm<sup>-1</sup>. In the sulfide-bridged analogue **9**, the corresponding carbonyl bands are observed at 2019 and 1924 cm<sup>-1</sup> but no Ir–H stretch is obvious. Again the sulfide-bridged species exhibits lower carbonyl stretching frequencies than the chloride-bridged species. The slight coupling of the bridging hydride ligand to the rhodium-bound phosphines in the chloro-bridged **8a** may suggest that in this case the interaction with rhodium is stronger than in the sulfide-bridged case. Consistent with this suggestion, reductive elimination of H<sub>2</sub> from **8a** occurs less readily than from **9**, requiring prolonged reflux in THF for **8a**, while only a rapid dinitrogen purge under ambient conditions is necessary to induce H<sub>2</sub> loss from **9**.

On the basis of this work and on that previously reported for compounds **1** and **4** we can now propose a scheme describing the reaction of these A-frames with H<sub>2</sub>. This is shown in Scheme I. First we propose oxidative addition of H<sub>2</sub> at one metal center on the *inside* of the A-frame pocket to yield the Ir(III)/Ir(I) dimer II. This was the species proposed as the initial product (**5a**) observed at low temperature in the reaction of **4** with H<sub>2</sub>. Although this adduct was never unequivocally identified, complexes **8a** and **9** represent models of such a species and are closely related to the next product, III, having one hydride ligand in the bridging position. These hydride-bridged species are pivotal to our understanding of the H<sub>2</sub> activation and subsequent hydride rearrangement in the presence of adjacent metals. Not only do these products clearly indicate that H<sub>2</sub> attack occurs on the inside of the A-frame pocket but they also model a key intermediate in the migration of the hydride ligands over the metal framework in at least two processes. The initial product of H<sub>2</sub> addition to the sulfide-bridged compound **4** was found to be fluxional, with the hydride ligands rapidly migrating between the two metal centers. Species III presents a possible intermediate in this migration, in which each hydride moves stepwise from one metal to another via a hydride bridge. This intermediate is also a key species in the movement of the hydride ligands from the face of the dimer opposite the bridging X ligand (X = Cl, S), as in II, to that observed in the final species IX (complexes **2** and **5c**, respectively), in which both hydrides are adjacent to X. We propose that this rearrangement also occurs stepwise, via cleavage of one of the Ir–X bonds to give intermediate IV. We have previously proposed such a bridge-breaking mechanism to explain the facile reaction of **2** with alkynes.<sup>1</sup> This step is consistent with the much more facile rearrangement observed for the chloro-bridged dimer compared to that for the sulfido-bridged analogue, since the latter would involve the formation of a dipolar intermediate by heterolytic cleavage of the covalent Ir–S bond in **5**, whereas formation of **2** involves cleavage of a dative Cl→Ir bond. This proposal is also consistent with the more facile rearrangement of **5** in polar solvents,<sup>2</sup> which would stabilize the dipolar intermediate. Having broken the halide or sulfide bridge, the hydride ligand is now able to “tunnel” between the two metals through an intermediate such as V to give VI, in which the hydride is on the same face of the complex as the ligand X. Such a tunneling process has been proposed by Puddephatt and co-workers in related Pt<sub>2</sub> complexes<sup>29</sup>

and should be a reasonably facile process since the flexible DPM ligands can easily accommodate the metal–metal separation of ca. 3.2–3.4 Å (twice the sum of the Ir and H covalent radii) necessary for a linear Ir–H–Ir intermediate. In support of this proposal, the structure of [Ir<sub>2</sub>(H)(Cl)(RC≡C(H)R)<sub>2</sub>(CO)<sub>2</sub>(μ-H)(DPM)<sub>2</sub>]<sup>+</sup> (R = CO<sub>2</sub>Me)<sup>30a</sup> has been shown to have an Ir–Ir separation of 3.289 Å, and although the hydrides were not located, the NMR study and the dispositions of the other ligands in the X-ray study indicate that one hydride ligand is terminally bound while the other is bridging with an Ir–H–Ir unit that is close to linear.<sup>30b</sup> Subsequent transformation of VI can occur by movement of the chloro or sulfido group back to the bridging position, displacing the hydride ligand to an adjacent terminal site and yielding VII, the structure proposed<sup>2</sup> for the intermediate isomer **5b** in the reaction of **4** with H<sub>2</sub>. Subsequent rearrangements yielding IX are analogous to those already described but now involve the second hydride ligand.

It appears, on the basis of the vastly different rates of rearrangement for the chloro and sulfido complexes and on the faster rate for the sulfido species in polar solvents, that the steps involving cleavage of the Ir–X bonds to give intermediates such as IV–VI and VIII are rate determining.

As noted earlier, compound **2** (shown as IX in Scheme I; X = Cl) reacts further with H<sub>2</sub> to yield two isomers of [Ir<sub>2</sub>(H)<sub>4</sub>Cl(CO)<sub>2</sub>(DPM)<sub>2</sub>]<sup>+</sup> in a 5:1 ratio. Only the major isomer **3a** had been previously reported, and its structure had not been formulated.<sup>1</sup> We are now in a position to propose structures for both isomers. Compound **3a** displays a <sup>31</sup>P{<sup>1</sup>H} NMR spectrum typical of an unsymmetrical species having an AA'BB' spin system, and the <sup>1</sup>H NMR spectrum shows that all four hydride ligands are chemically inequivalent. At –60 °C the <sup>1</sup>H NMR spectrum shows four distinct resonances; the two at δ –10.12 (<sup>2</sup>J<sub>P–H</sub> = 13.2 Hz) and –13.86 (<sup>2</sup>J<sub>P–H</sub> = 10.4 Hz) are resolved as triplets while the other two are unresolved. Raising the temperature causes the three low-field resonances to broaden considerably, while the upfield resonance resolves into a triplet (<sup>2</sup>J<sub>P–H</sub> = 11.1 Hz) at 0 °C. The fourth resonance is never resolved between ambient temperature and –80 °C. At –60 °C selective <sup>31</sup>P decoupling of the <sup>1</sup>H NMR spectrum indicates that two hydride atoms are apparently located on each metal. Decoupling the downfield portion of the <sup>31</sup>P signal causes the two triplets to become singlets, and decoupling the upfield portion causes the remaining two resonances to sharpen considerably. The minor species (**3b**) observed in this mixture displays a singlet in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum due to four chemically equivalent phosphorus atoms, and the <sup>1</sup>H NMR spectrum displays two different hydride environments (being integrated as two protons each) and exhibits fluxional behavior. At –80 °C the <sup>1</sup>H NMR spectrum appears as two broad unresolved resonances, the more upfield of which broadens and collapses into the base line as the solution is warmed. In the solution infrared spectrum, the two tetrahydride species together display three terminal carbonyl bands (2071, 2036, 1965 cm<sup>-1</sup>) and a broad hydride band (2146 cm<sup>-1</sup>). The last band was confirmed as such by preparation of the analogous tetra-deuterides by using D<sub>2</sub> instead of H<sub>2</sub>. The IR spectrum of the deuteride analogues contains carbonyl stretches at 2063, 1984, and 1960 cm<sup>-1</sup>. Apparently the intermediate band has shifted appreciably upon deuteration, suggesting strong vibronic coupling involving mutually trans H and CO ligands,<sup>31</sup> consistent with the structure proposed for **3a**. The low frequency of the carbonyl stretch at ca. 1960 cm<sup>-1</sup> appears unusual for formally Ir(III) metal centers.

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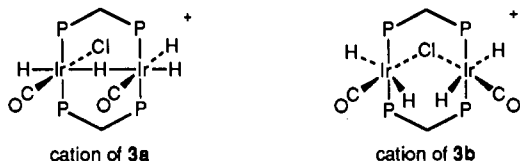
(30) (a) Vaartstra, B. A.; Cowie, M. Manuscript in preparation. (b) Summary of crystal data for [Ir<sub>2</sub>(H)(Cl)(CH<sub>3</sub>O<sub>2</sub>CC≡C(H)CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>(μ-H)(DPM)<sub>2</sub>]<sup>+</sup>·3THF: cell parameters *a* = 18.675 (5) Å, *b* = 15.775 (3) Å, *c* = 26.371 (4) Å, β = 96.38 (2)°; space group P2<sub>1</sub>/c; no. of unique data used 6026; final no. of parameters refined 590; *R* = 0.055; *R*<sub>w</sub> = 0.064. Selected bond lengths (Å): Ir–Cl = 2.395 (3); Ir–CO = 1.86 (1), 1.91 (1); Ir–O = 1.11 (1), 1.17 (1); metallolefin C=C = 1.28 (1), 1.34 (2).

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We propose that **3a** and **3b** result from oxidative addition of  $H_2$  either in the A-frame pocket of complex **2** or on the outside of the species. Attack from the outside leads to **3a**, while attack



in the pocket leads to the symmetrical species **3b**. Both proposed structures involve octahedral Ir(III) centers with a bridging hydride ligand in **3a** and a bridging chloride ligand in **3b**. The structure for **3a** has precedent in the structure noted earlier<sup>30</sup> for  $[Ir_2(H)(Cl)(RC=CHR)_2(\mu-H)(CO)_2(DPM)_2]^+$ , in which the hydride ligands opposite the Ir–Ir bond in **3a** are replaced by the metalloolefin moieties. Furthermore, this complex resulted from the addition of  $H_2$  to  $[Ir_2(RC=CHR)_2(CO)_2(\mu-Cl)(DPM)_2]^+$ , a species very reminiscent of **2**. Although the decoupling study at  $-60^\circ C$  suggested that two hydride ligands were on each metal, we assume that the bridged hydride of structure **3a** is interacting more strongly with the iridium which carries only one terminal hydride ligand, so no appreciable coupling to the phosphines on the other metal is observed. This situation is not unlike that described earlier for compound **9**, in which coupling of the bridging hydride to rhodium, but not to the Rh-bound phosphines, was observed, and is also similar to that observed in a dihydrido dialkenyl complex in which coupling of the hydride to one set of phosphines was stronger than to the other set.<sup>30</sup> Formation of both **3a** and **3b** was probably preceded by cleavage of one Ir–Cl bond to yield coordinative unsaturation, allowing  $H_2$  attack at one metal. Our failure to observe the analogous tetrahydride in the case of the sulfide-bridged analogue is consistent with its reluctance to cleave one of the Ir–S bonds. Further support for the structures shown for **3a** and **3b** comes from the reaction of **2** with  $D_2$ . The  $^1H$  NMR spectrum shows only one hydride resonance ( $\delta -10.70$ ) for **3b**, consistent with  $D_2$  attack in the pocket of **2**, and displays one strong hydride resonance ( $\delta -16.52$ ) for **3a**, together with three weak ones. In isomer **3a** the three hydride or deuteride ligands associated with one metal can interchange, causing H/D scrambling, whereas the fourth isolated hydride remains undiluted by deuterium and so appears as a strong resonance.

These DPM-bridged tetrahydride complexes can be contrasted with the closely related bis(diphenylphosphino)propane-bridged complex  $[Ir_2Cl_2(CO)_2(DPPP)_2]$ .<sup>32</sup> Apparently the large metal–metal separation in this species does not allow appreciable interaction between the metals and consequently  $H_2$  addition proceeds first at one metal, to give an Ir(I)/Ir(III) dihydride, and then at the other, yielding the Ir(III)/Ir(III) tetrahydride.

Unfortunately, the low-temperature limiting spectra for **3a** and **3b** could not be obtained due to instrumental and solvent limitations. The possibility that  $H_2$  loss was involved in the fluxionality was ruled out when placing  $D_2$  above solutions of **3a** and **3b** had no effect on their respective hydride integrations in the  $^1H$  NMR spectrum after 15 min. On a longer time scale, however, exchange does occur, as observed by monitoring HD formation in the  $^1H$  NMR spectrum of a sample of **1** in the presence of  $H_2/D_2$  (1:1 v/v). Although no HD is observed initially upon mixing, after 3 h the  $H_2$ :HD ratio is 3:5 while a control sample containing only  $H_2$ ,  $D_2$ , and acetone- $d_6$  showed no HD formation. This can be compared to the same experiment involving compound **5c**, where the  $H_2$ :HD ratio is 3:1 immediately after mixing and 1:1 after 3 h. If HD formation is a result of the formation of dihydride/dideuteride species, the rate of formation of HD for **5c** would indicate that Ir–S bond cleavage apparently does occur, although not to give a stable product. At the same time the slow rate involving **1** reflects the stability of the coordinatively saturated tetrahydride (or hydride/deuteride) formed.

Although one might anticipate that the reaction of the A-frame

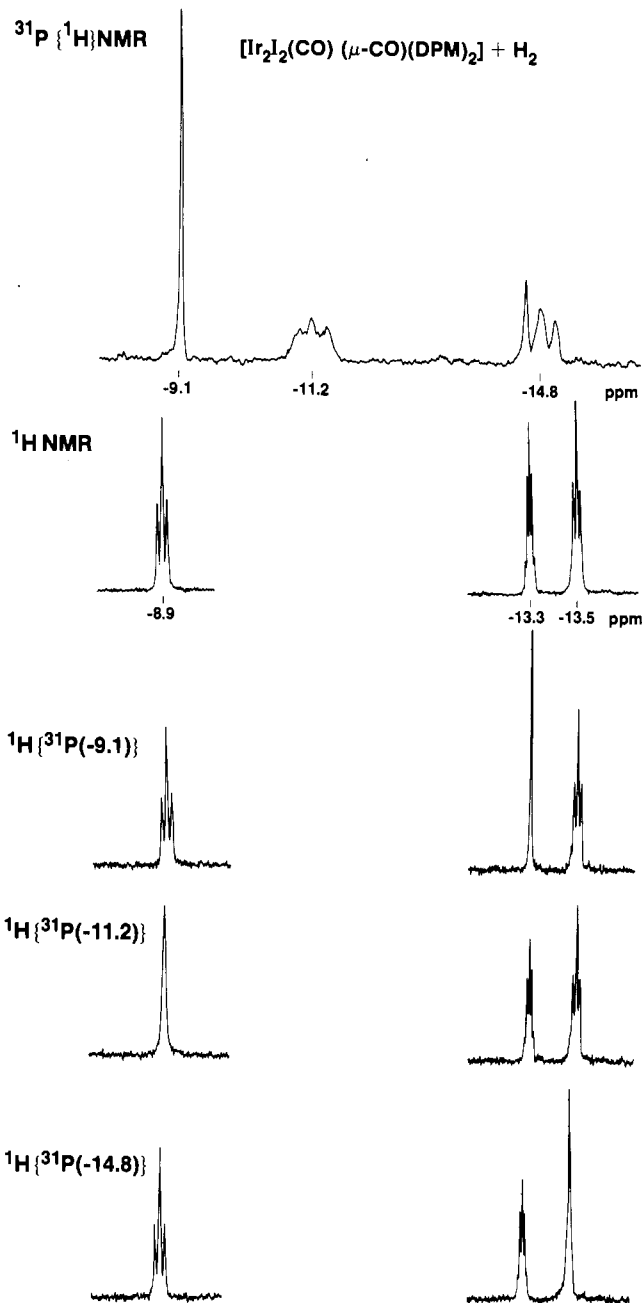
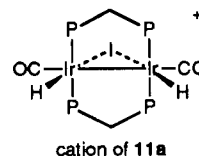


Figure 3.  $^{31}P\{^1H\}$  NMR spectrum (top) and  $^1H$  NMR spectra (hydride region) of compounds **11b** and **15**, including selective  $^{31}P$ -decoupled  $^1H$  NMR spectra.

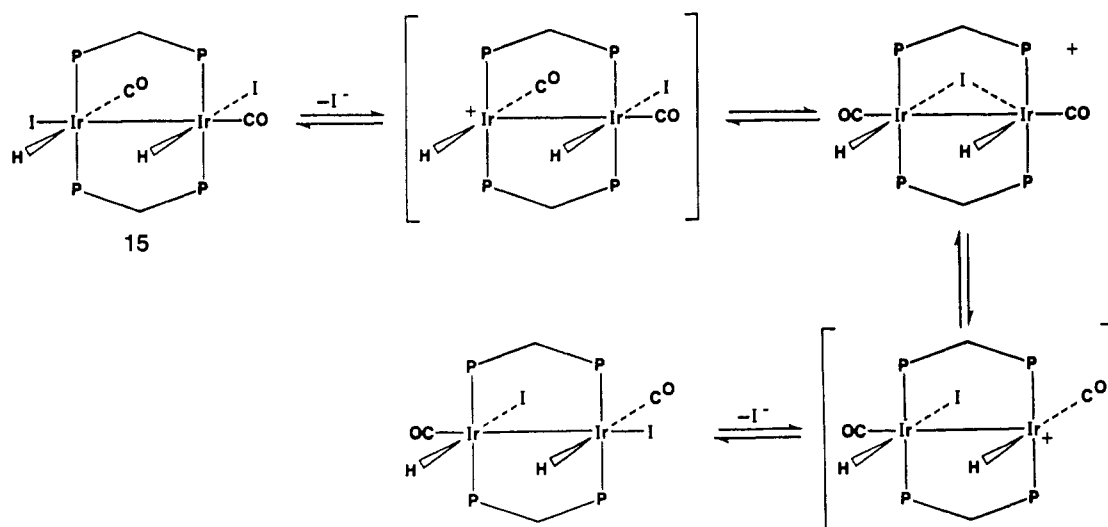
$[Ir_2(CO)_2(\mu-I)(DPM)_2][BF_4]$  (**10**) would parallel that observed with the closely related **1** and **4**, this appears not to be the case. As with the chloro-bridged species **1**, only one dihydride product is observed, but it does not appear to be a rearrangement product but instead appears to be analogous to the initial sulfide/dihydride **5a**, in which the hydride ligands occupy the A-frame pocket. The  $^{31}P\{^1H\}$  NMR spectrum, which appears as a singlet over the temperature range  $-80$  to  $+22^\circ C$ , and the  $^1H$  NMR spectrum, which displays a quintet at  $\delta -13.18$  ( $^2J_{P-H} = 6.4$  Hz), indicate that the hydride ligands are coupled to the four equivalent phosphorus nuclei on the NMR time scale. Unlike the chloro- and sulfido-bridged analogues the IR spectrum for **11a** displays only a single carbonyl stretch at  $1937\text{ cm}^{-1}$ . This may indicate that a species such as that shown for **11a** may be a better rep-



(32) Wang, H.-H.; Pignolet, L. H.; Reedy, P. E., Jr.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1987**, *26*, 377.

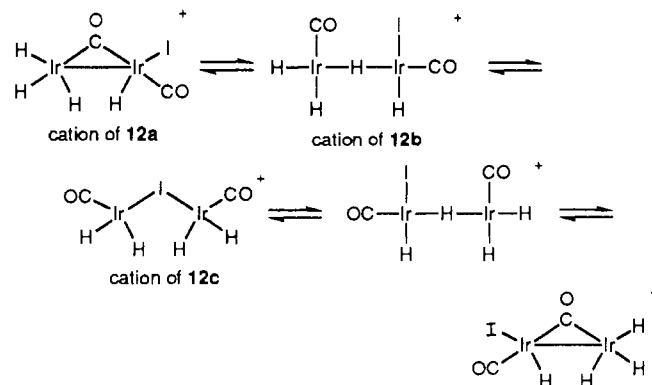


Scheme II



resentation for the ground-state configuration. Such a structure, in which the hydride ligands were exchanging metals through an intermediate such as III in Scheme I, is consistent with the NMR data. If this species is sufficiently stable, it may offer an explanation for the failure of this hydride product to rearrange to a product such as IX. Also consistent with such a proposed structure, the reductive elimination of  $H_2$  from **11a** is much less facile than from **5a**, requiring several hours in refluxing THF under an  $N_2$  purge (compound **5a** merely required an  $N_2$  purge under ambient conditions for 30 min).

As with the chloride A-frame, compound **10** also forms a tetrahydride species upon reaction with excess  $H_2$ . The  $^1H$  NMR spectrum of the resulting light yellow solution indicates the presence of a single tetrahydride species (**12**), which displays two broad hydride resonances, even at  $-80$  °C, integrated as two protons each. This tetrahydride is fluxional in solution as evidenced by a broadening and collapse into the base line of the most upfield resonance as the temperature is raised. The  $^{31}P\{^1H\}$  NMR spectrum remains a singlet ( $\delta -6.42$ ) at all temperatures studied ( $-80$  to  $+22$  °C), indicating a time-averaged symmetric species. The major species in solution would appear to have a bridging carbonyl ligand as evidenced by a low-frequency carbonyl stretch ( $\nu(CO)$  at  $2030, 1779$   $cm^{-1}$ ). It is proposed that this species results from oxidative addition of  $H_2$  at one metal center, adjacent to one of the hydrido ligands of **11a**, with accompanying movement of the iodo and carbonyl groups to give isomer **12a**. The fluxionality of **12a** to give a time-averaged symmetrical species might be envisioned as occurring via intermediates such as **12b** and **12c**, as shown. This process is not greatly different from those proposed



earlier for the chloro- and sulfido-bridged complexes. The proposed structures all have octahedral Ir(III) centers and are related by a "merry-go-round" migration of all ligands in the equatorial plane.

Along with  $H_2$  loss from **12** to give **11a**, reductive elimination

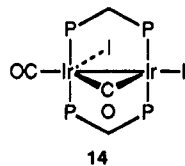
of HI from **12**, forming significant amounts of  $[Ir_2H(CO)_2(\mu-H)_2(DPM)_2]^+$ , proved unavoidable. This trihydride was identified by comparison of its  $^{31}P\{^1H\}$  and  $^1H$  NMR spectra to those of an authentic sample previously characterized.<sup>14</sup> The presence of this species and the absence of rearranged products similar to **2** and **5c** lead us to believe that tunneling of the hydrido ligands does indeed occur at some stage (probably via a species like **12b**), but that immediate reductive elimination of HI then readily occurs. It should be noted that reductive elimination of HCl from the chloride tetrahydride **3** has also been observed, but only when **3** is refluxed in THF or higher boiling solvents. Although it is clear that the A-frame iodide complex reacts quite differently from the sulfide and chloride analogues, it is not immediately obvious why this should be so. The steric bulk of the large iodide bridge atom is, however, expected to be an important factor.

Although the possibility of one or more  $\eta^2-H_2$  ligands was considered for compound **12**, as well as for the previously discussed tetrahydrides (**3a** and **3b**), the apparent relaxation times ( $T_1$ ) measured at various temperatures are found to be typical of classical hydrides,<sup>33</sup> so these species are formulated as such.

**(b) Neutral, Non-A-Frame Complexes.** We had previously shown that reactions involving the A-frame **1** and the neutral precursor *trans*- $[IrCl(CO)(DPM)_2]$  differed substantially,<sup>1</sup> and a comparison of these two systems proved to be extremely useful in establishing an understanding of the function of the bridging group in the A-frame species. We therefore undertook a study of the neutral precursors to the A-frames **6** and **10**, namely  $[RhIrCl_2(CO)_2(DPM)_2]$  (**13**) and  $[Ir_2I_2(CO)_2(DPM)_2]$  (**14**). The mixed-metal dichloride reacts readily with  $H_2$ , yielding **8b**, a species identical with the product **8a** from the A-frame reaction, apart from the chloride counterion. In addition to having almost superimposable spectroscopic parameters with **8a**, conductivity measurements for **8b** indicate that it is a normal 1:1 electrolyte. This species loses  $H_2$  somewhat more readily than the  $BF_4^-$  salt (requiring only slight warming in  $CH_2Cl_2$  with  $N_2$  purge) probably due to the coordinating ability of the  $Cl^-$  ion. This result differs from that previously reported for the diridium analogue, in which a neutral dihydride was obtained under the same conditions.<sup>1</sup>

The neutral diiodide complex **14** has been shown to have the unusual structure in which one carbonyl ligand is bridging,<sup>10</sup> and surprisingly the iodo ligands (and the carbonyls) are mutually *cis*, rather than *trans* as in the chloro analogue, *trans*- $[IrCl(CO)(DPM)_2]$ . Compound **14** reacts immediately with  $H_2$ , yielding two dihydride species in a 7:3 ratio as shown by the NMR spectra in Figure 3. This reaction is readily reversed merely by exchanging the  $H_2$  atmosphere with  $N_2$ . The minor species **11b** has

(33) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.



spectroscopic parameters identical with those of **11a** and is formulated as such, apart from the  $I^-$  counterion.

The major product in the reaction of **14** with  $H_2$  displays a  $^{31}P\{^1H\}$  NMR spectrum typical of an unsymmetrical species having an AA'BB' spin system. The  $^1H$  NMR spectrum at  $-40^\circ C$  exhibits a triplet for each of two hydride ligands ( $\delta -8.90$ ,  $^2J_{P-H} = 13.0$  Hz;  $\delta -13.59$ ,  $^2J_{P-H} = 8.8$  Hz), and selectively decoupling each of the  $^{31}P$  resonances (as revealed in Figure 3) establishes that each hydride is coordinated to a different metal. The ease by which  $H_2$  is reductively eliminated from the product suggests mutually adjacent hydride ligands. The infrared bands ( $\nu(CO)$  2002, 1982  $cm^{-1}$ ;  $\nu(Ir-H) = 2230, 2105$   $cm^{-1}$ ) are remarkably similar to those of the dichloro complex  $[Ir_2(H)_2Cl_2(CO)_2(DPM)_2]$ ,<sup>1</sup> which results from the reaction of *trans*- $[IrCl(CO)(DPM)]_2$  with hydrogen. We therefore propose that compound **15** has the same geometry, as shown in Scheme II. Note that formation of **15** from **14** requires iodide loss and recoordination in order to go from a cis to a trans arrangement of ligands, suggesting formation of **11b** as an intermediate. Spin saturation transfer experiments on the  $^1H$  NMR signals of the mixture of **11b** and **15** in fact show that both species are in equilibrium. Saturation of the most downfield hydride resonance of **15** causes the intensities of both the high-field triplet of **15** and the quintet of **11b** to diminish. It should be noted that the saturation transfer is more pronounced upon the quintet resonance of **11b**, as observed in a greater intensity decrease for this resonance versus that of the upfield triplet of **15**. This suggests species **11b** as the intermediate that exchanges the two hydride environments, since site exchange of either of the hydrides in **15** with each other or with the hydrides of **11b** will both involve transfer of spin information to the quintet resonance of **11b**. This supports the equilibria described in Scheme II and proposed for the analogous chloro species.<sup>1</sup> However, the NMR data suggest that the A-frame iodide **11b** is significantly more stable than the chloride, since the chloride A-frame was not observed in the NMR spectra above  $-40^\circ C$ . This result again suggests that the stability of this species may be responsible for the failure of **11a** to rearrange (*vide supra*). As one might expect with the presence of compound **11b**, if this solution is left for long periods of time under  $H_2$  the tetrahydride species **12** (iodide salt) and the product of its reductive elimination of HI,  $[Ir_2H(CO)_2(\mu-H)_2(DPM)_2]^+$  (*vide supra*), are observed.

## Conclusions

The A-frame complexes  $[Ir_2(CO)_2(\mu-X)(DPM)_2]^{n+}$  (**1**,  $X = Cl$ ,  $n = 1$ ; **4**,  $X = S$ ,  $n = 0$ ) have been shown to react with  $H_2$ , producing dihydrides in which the hydrido ligands are not mutually cis but have rearranged to positions adjacent to the anionic bridging group.<sup>1,2</sup> On the basis of the intermediates observed in the much slower reaction of  $[Ir_2(CO)_2(\mu-S)(DPM)_2]$  (**4**) with  $H_2$ ,<sup>2</sup> and of the results of the mixed-metal analogues  $[RhIr(CO)_2(\mu-X)(DPM)_2]^{n+}$  (cation of **6**,  $X = Cl$ ,  $n = 1$ ; **7**,  $X = S$ ,  $n = 0$ ) in the presence of  $H_2$ , a feasible mechanism for the rearrangement of the hydrido ligands is proposed, key features of which include the cleavage of one of the bonds between the bridging anionic group and the metal and subsequent tunneling of the hydride ligands between the two metal centers. Furthermore, it has been established that the initial oxidative addition of  $H_2$  occurs at a single metal center in the A-frame pocket of these complexes before stepwise rearrangement takes place. The iodo A-frame  $[Ir_2(CO)_2(\mu-I)(DPM)_2][BF_4]$  (**10**) also undergoes  $H_2$  attack in the pocket, but subsequent rearrangement would appear to result only in reductive elimination of HI upon generation of a species containing mutually adjacent hydrido and iodo ligands. The reaction of the neutral iodo complex  $[Ir_2I_2(CO)_2(DPM)_2]$  (**14**) with  $H_2$  leads to the neutral dihydride  $[Ir_2(H)_2I_2(CO)_2(DPM)_2]$  (**15**), analogous to that obtained in the reaction of *trans*- $[IrCl(CO)(DPM)]_2$  with  $H_2$ . This neutral species is interconverting with  $[Ir_2(H)_2(CO)_2(\mu-I)(DPM)_2][I]$  (**11b**), which is in fact a necessary precursor to **15** in order that the ligand arrangement no longer be mutually cis with respect to the iodo and carbonyl groups.

This work has again demonstrated the usefulness of bridging halide or pseudohalide bridging ligands as a source of incipient coordinative unsaturation allowing unusual ligand mobility and also allowing for further reaction with incoming substrates. Additional studies are under way to utilize this metal cooperativity in the modeling of homogeneous hydrogenation of unsaturated organic substrates.

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**Supplementary Material Available:** Tables of crystal data and details of the intensity collection, anisotropic thermal parameters, additional bond lengths and angles, and hydrogen atom parameters (5 pages); a listing of the observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.