3668 *Inorg. Chem.* **1988**, *27*, 3668–3672

Table III. Important Bond Lengths and Angles for the Two Independent Molecules of $(CO)_5W(C_{12}H_9N_2\{O\}C_{12}H_9)$

molecule A		molecule B	
	Bond Distances (Å)		
W(1)–N(1)	2.258 (10)	W(2)–N(3)	2.32 (6)
N(1)–N(2)	1.297 (11)	N(3)–N(4)	1.300 (15)
N(1)–C(6)	1.448 (16)	N(3)–C(35)	1.459 (17)
N(2)–O(6)	1.251 (13)	N(4)–O(35)	1.262 (16)
N(2)–C(18)	1.498 (14)	N(4)–C(47)	1.469 (11)
W(1)–C(1)	2.033 (16)	W(2)–C(30)	2.027 (15)
W(1)–C(2)	1.971 (15)	W(2)–C(31)	1.995 (10)
W(1)–C(3)	2.011 (17)	W(2)–C(32)	2.042 (18)
W(1)–C(4)	2.047 (19)	W(2)–C(33)	2.046 (17)
W(1)–C(5)	2.019 (16)	W(2)–C(34)	2.042 (21)
	Bond Angles (deg)		
C(2)–W(1)–N(1)	178.0 (6)	C(31)–W(2)–N(3)	176.7 (6)
W(1)–N(1)–C(6)	122.7 (6)	W(2)–N(3)–C(35)	122.3 (7)
W(1)–N(1)–N(2)	119.7 (8)	W(2)–N(3)–N(4)	122.2 (7)
Nn2)–N1)–C(6)	117.4 (9)	N(4)–N(3)–C(35)	115.5 (7)
N(1)–N(2)–O(6)	121.1 (9)	N(3)–N(4)–O(35)	120.3 (8)
C(18)–N(2)–O(6)	115.1 (7)	C(47)–N(4)–O(35)	115.7 (10)
N(1)–N(2)–C(18)	123.4 (9)	N(3)–N(4)–C(47)	124.0 (11)

for a complex with an azoxy ligand. Azoxy molecules are apparently not sufficiently strong ligands to compete for a coordination site. Thus, it is likely that the azoxy ligand in **14** is formed within the coordination sphere by addition of nitrosobiphenyl to a coordinated biphenylylnitrene ligand.

We have shown in this work that organic nitroso reagents rapidly react with $(CO)_5W{=}C(OMe)Ph$ and probably with other Fischer-type carbene complexes as well, and the reaction products are consistent with the metathesis reaction (1a). However, it is clear that nitrene complexes of the type $(CO)_5W{=}NR$ are too unstable to be characterized. Binuclear nitrene complexes should be considerably more stable, and experiments are in progress to prepare such species.

Experimental Section

The complex $(CO)_5W{=}C(OMe)(Ph)$[4] and *o*-nitrosobiphenyl[11] were prepared by the literature procedure. PhNO, 2,4,6-$(Bu^t)_3C_6H_2NO$, $[Bu^tNO]_2$, and *p*-azoxyanisole were purchased from Aldrich Chemical Co. and used as received. All manipulations were performed in standard Schlenk glassware under prepurified N_2 or in a nitrogen-filled drybox with the use of predried solvents. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Reaction of 1 with Nitrosobenzene. A 0.5-mL C_6D_6 solution of **1** (0.050 g, 0.11 mmol) was added to a 0.5-mL C_6D_6 solution of PhNO (0.024 g, 0.22 mmol). This gave an immediate darkening of the initial red color, and ^1H NMR analysis showed that the δ 4.08 methoxy resonance of **1** had been completely replaced by the characteristic resonances of methyl benzoate (δ 3.50) and the imidate **3** (δ 3.79). TLC chromatography (SiO_2) also showed the formation of aniline, azobenzene and methyl benzoate, which were identified by their characteristic mass and IR spectra.

Reaction of 1 with 2,4,6-$(Bu^t)_3C_6H_2NO$. This reaction was conducted exactly as described above by using 2,4,6-$(Bu^t)_3C_6H_2NO$ (0.060 g, 0.22 mmol). NMR monitoring showed complete reaction over a period of 4 days. Chromatography of the reaction mixture on a SiO_2 TLC plate with 2:1 hexane/CH_2Cl_2 as eluent gave **6** (18.4 mg, 62%), **7** (6.5 mg, 11%), and **8** (3.4 mg, 5%) which were identified by their characteristic IR, ^1H NMR, and mass spectra. The methyl benzoate product was quantified by NMR integration and was observed by TLC chromatography, but no attempt was made to isolate this volatile liquid in pure form.

6. ^1H NMR ($CDCl_3$): δ 1.24 (s, 9 H), 1.43 (s, 18 H), 2.85 (broad s, 2 H), 7.17 (s, 2 H). IR (KBr): ν_{N-H} = 3516 (m), 3445 (m); ν_{C-H} = 2957 (s), 2803 (s); other bands at 1618 (m), 1510 (m), 1433 (s), 1238 (s) cm^{-1}. *m/z* 261 (M^+), 246 ($M^+ - NH_2$).

7. ^1H NMR ($CDCl_3$): δ 1.32 (s, 36 H), 1.39 (s, 18 H), 3.35 (s, 2 H), 7.22 (s, 2 H), 7.36 (s, 2 H). IR (KBr): ν_{N-H} = 3450 (m); ν_{C-H} = 2960 (s), 2750 (s); other bands at 1510 (m), 1430 (m), 1235 (m) cm^{-1}. *m/z* 520 (M^+), 492, 462, 446.

8. ^1H NMR ($CDCl_3$): δ 1.37 (s, 36 H), 1.55 (s, 18 H), 7.22 (s, 2 H), 7.36 (s, 2 H), 8.18 (s, 2 H). IR (KBr): ν_{C-H} = 2965 (s), 2870 (s); ν_{CO} = 1694 (s); other bands at 1609 (m), 1464 (m), 1383 (m), 1366 (m), 1242 (m) cm^{-1}. *m/z* 491 (M^+–Bu^t), 435 (M^+–$2Bu^t$), 410, 308.

Reaction of 1 with Bu^tNO. A 0.5-mL $CDCl_3$ solution of **1** (0.050 g, 0.113 mmol) was added to $[Bu^tNO]_2$ (0.030 g, 0.167 mmol). The solution was filtered into an NMR tube in the drybox, and the reaction was monitored by ^1H NMR spectroscopy over a 5–day period, during which time the methoxy resonance of **1** diminished and was replaced by that of methyl benzoate, the azoxy compound **9** [δ 1.48 (s, 9 H), 1.29 (s, 9 H)],[12] and $(CO)_5W(Bu^tNO)$ (**10**; δ 1.44). The last complex was isolated as a black crystalline solid by −30 °C chromatography on SiO_2 and was spectroscopically and crystallographically characterized.[7]

Reaction of 1 with *o*-Nitrosobiphenyl. This reaction was conducted exactly as described above by using *o*-nitrosobiphenyl (0.040 g, 0.22 mmol) and **1** (0.050 g, 0.11 mmol). NMR monitoring showed that the δ 4.08 methoxy resonance of **1** ceased to decrease in intensity after 18 h (69% conversion). Chromatography of the reaction mixture on a SiO_2 TLC plate eluting with 1:1 hexane/CH_2Cl_2 gave carbazole (**11**; 6.6 mg, 52%), the azo compound **12** (1.7 mg, 6%), the azoxy compound **13** (1.0 mg, 4%), and the azoxy complex **14** (2.2 mg, 4%). The yields given are based on the amount of **1** consumed. The organic products were identified by their characterstic mass, IR, and NMR spectra. The methyl benzoate product was quantified by NMR integration and was observed by TLC chromatography, but no attempt was made to isolate this volatile liquid in pure form.

11. ^1H NMR (acetone-d_6): δ 10.34 (broad s, 1 H), 8.2–7.0 (m). IR (KBr): ν_{N-H} = 3420 (s); ν_{C-H} v 2959 (w), 2926 (w), 2860 (w); other bands at 1450 (m), 1327 (m)8 1290 (m), 1096 (m), 1021 (m) cm^{-1}. *m/z* 167 (M^+), 139, 83.

12. ^1H NMR (acetone-d_6): δ 7.6–6.6 (m). IR (KBr): ν_{C-H} = 2952 (w), 2919 (w), 2840 (w); other bands at 1460 (m), 1426 (m), 1260 (m) cm^{-1}. *m/z* 334 (M^+), 181, 167, 152.

13. ^1H NMR (acetone-d_6): δ 7.6–6.6 (m). IR (KBr): ν_{C-H} = 2952 (w), 2919 (w), 2952 (w); other bands at 1481 (m), 1460 (m), 1426 (m), 1261 (m) cm^{-1}. *m/z* 349 (M^+), 333, 167.

14. Anal. Calcd for **14**·$^1/_2$(pentane) (shown by ^1H NMR), $C_{31.5}H_{24}N_2O_6W$: C, 53.33; H, 3.38. Found: C, 53.03; H, 3.79. ^1H NMR (acetone-d_6): δ 8.0–7.0 (m, 16 H), 5.77 (d, 2 H, J_{H-H} = 7.83 Hz), 5.63 (d, 2 H, J_{H-H} = 8.1 Hz). IR (pentane): ν_{CO} = 2068 (w), 1941 (s), 1937 (s), 1923 (m) cm^{-1}. *m/z*(FD) 673 (M^+).

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Registry No. **1**, 37823-96-4; **2**, 93-58-3; **3**, 6780-39-8; **4**, 103-33-3; **6**, 961-38-6; **7**, 116212-35-2; **8**, 116212-36-3; **9**, 16649-52-8; **10**, 116301-27-0; **11**, 86-74-8; **12**, 13710-27-5; **13**, 7334-10-3; **14**, 116301-28-1; **14**·$^1/_2$(pentane), 116301-29-2; 2,4,6-$(Bu^t)_3C_6H_2NO$, 24973-59-9; $[Bu^tNO]_2$, 31107-20-7; PhNO, 586-96-9; *o*-nitrosobiphenyl, 21711-71-7.

Supplementary Material Available: For **14**, tables of complete bond lengths and angles, anisotropic thermal parameters for non-H atoms, and positional and isotropic thermal parameters for H atoms (6 pages); a listing of structure factors (30 pages). Ordering information is given on any current masthead page.

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Oxidative Addition of H_2 to the A-Frame Complex $[Ir_2(CO)_2(\mu\text{-}S)(Ph_2PCH_2PPh_2)_2]$: A Reinvestigation

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"A-Frame" complexes, such as $[Rh_2(CO)_2(\mu\text{-}S)(DPPM)_2]$,[3] $[Ir_2(CO)_2(\mu\text{-}S)(DPPM)_2]$,[4] $[Rh_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$,[5] and

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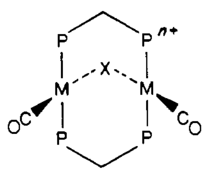
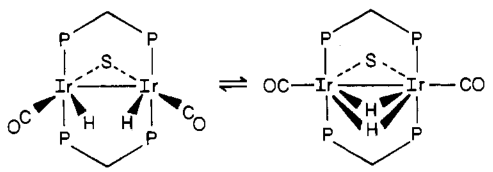
$[Ir_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$[6] (DPPM = $Ph_2PCH_2PPh_2$), diagrammed as



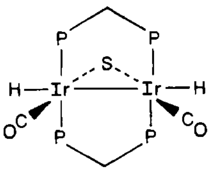
M = Rh, Ir: X = S, *n* = 0;
X = Cl, *n* = 1

have attracted interest since the original suggestion[3] that the coordination sites in the "pocket" between the metals might function together as the "active site" in which substrate molecules could be bound and activated by both metals, possibly with the metals acting in some cooperative manner. Although several such complexes were found to be active as hydrogenation catalysts,[3b,4,7–9] little has yet been determined about the involvement of the adjacent metals in catalysis. Clearly, in order to obtain a better understanding of the functions of the metals, it is of interest to establish the nature of possible catalytic intermediates, which for hydrogenation reactions will undoubtedly involve metal hydrides.

An early study on the reactivity of $[Ir_2(CO)_2(\mu\text{-}S)(DPPM)_2]$ with H_2 showed the presence of two dihydride species in the 100-MHz ^1H NMR spectrum.[4] One resonance (a quintet) was believed to result from a rapid equilibrium between species **2a** and **2b**, while the second resonance (analyzed as a triplet of triplets) was believed to be due to **4**, although no definitive assignment of structures was possible at that time. A subsequent study in which the related complex $[Ir_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$ reacted with H_2 to give a species analogous to **4** and a tetrahydride species[10] caused us to question how rearrangement to **4** had occurred and whether the sulfide-bridged complex also yielded a tetrahydride analogous to the chloride-bridged complex. In this paper we report a reinvestigation of the reaction of $[Ir_2(CO)_2(\mu\text{-}S)(DPPM)_2]$ with H_2 using improved spectroscopic techniques.



2a **2b**



4

Experimental Section

Iridium trichloride hydrate (Johnson-Matthey), 1,5-cyclooctadiene (COD) (Aldrich), bis(diphenylphosphino)methane (DPPM) (Strem), and gases, H_2 and D_2 (Matheson CP), were used as purchased. Sodium sulfide was washed with distilled water before use. THF, benzene, and toluene were distilled from sodium/benzophenone, ethanol was distilled from magnesium turnings, and acetone was dried over $CaSO_4$ or molecular sieves and distilled prior to use. $[Ir_2(CO)_2(\mu\text{-}S)(DPPM)_2]$ (**1**) was prepared by the reported procedure.[4] The ^1H, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker WH-400 instruments, and infrared spectra were obtained by using a Mattson Sirius 100 or Nicolet 7199 FT spectrometer. Solid samples were run as Nujol mulls on NaCl or KBr plates, solutions were run in KCl cells with 0.5 mm path length windows, and solvent was subtracted. The reactions were typically done by suspending 100 mg of compound **1** in approximately 5 mL of solvent under N_2 with stirring. The N_2 atmosphere was displaced by H_2, causing the dark purple mixture to turn to a clear yellow solution almost immediately. Three products were observed with time in the ^1H and $^{31}P\{^1H\}$ NMR spectra, the last of which could be isolated in the solid by precipitation with hexanes; however, this solid decomposed rapidly on exposure to air. Spectroscopic data for the products are summarized in Table I.

H/D Exchange Promoted by Compounds 1 and 4. Approximately 5 mg of the sample was placed in an NMR tube, which was connected to a high-vacuum line. Acetone-d_6 was vacuum-transferred into this tube, and the sample was placed under ca. 600 Torr of H_2/D_2 (1:1 v/v). The NMR tube was flame-sealed, and the exchange was followed by monitoring the H_2 and HD resonances at δ 4.5 in the ^1H NMR spectrum.

Results and Discussion

Initially, the reaction of $[Ir_2(CO)_2(\mu\text{-}S)(DPPM)_2]$ (**1**) with hydrogen was studied in benzene, although the results are almost identical in toluene and THF and are similar in acetone. Upon addition of hydrogen, reaction occurred immediately, as indicated by a change in color of the solution from purple to yellow. The complex initially formed (**2**) was identified by its $^{31}P\{^1H\}$ and ^1H NMR and IR spectra (see Table I). The $^{31}P\{^1H\}$ NMR spectrum showed a singlet at δ −4.0, indicating a symmetrical species in which all four phosphorus nuclei were chemically equivalent. At the same time, the ^1H NMR spectrum of **2** displayed the DPPM methylene resonances at δ 2.76 and 5.53 and a quintet for the hydride resonance at δ −10.46 ($^2J_{P-H}$ = 5.6 Hz). All three resonances integrated as two protons each, establishing **2** as a dihydride species in which the hydride ligands were coupled to four equivalent phosphorus nuclei. The IR spectrum (acetone solution) showed two strong bands for the terminal carbonyl ligands (1915, 2012 cm^{-1}) but nothing attributable to an Ir–H stretch. This assignment was confirmed by an almost indistinguishable IR spectrum of the corresponding deuteride, obtained upon reaction of **1** with D_2.

Further reaction for 2 h yielded two additional species. The first (**3**) was present in trace amounts at this stage and displayed two multiplets in the $^{31}P\{^1H\}$ NMR spectrum, at δ −6.8 and −13.2, and also showed two new hydride resonances (each a triplet) in the ^1H NMR spectrum, at δ −10.07 and −11.68, together with the methylene resonances at δ 5.31 and 3.04; again, integration indicated that this species, which had not been observed in the previous study,[4] is a dihydride. The $^{31}P\{^1H\}$ NMR results indicated that this species is unsymmetrical, having chemically different phosphorus environments, and the ^1H NMR parameters indicated that the two hydride ligands are also inequivalent, with each displaying coupling to two phosphorus nuclei. In addition, selective decoupling of each phosphorus resonance of **3** caused each triplet in the ^1H NMR spectrum to collapse in turn to a singlet, thereby unambiguously establishing that each hydride ligand is coordinated to a different metal.

Also observed together with **3** was compound **4**, which after 2 h was present at approximately one-tenth the concentration of the initial product **2**. Complex **4** was characterized by a singlet in the $^{31}P\{^1H\}$ NMR spectrum, indicating a symmetrical species, and resonances in the ^1H NMR spectrum due to the methylene groups (δ 4.82, 2.82) and two hydride ligands (δ −10.18). Although the hydride resonance was previously identified as a triplet of triplets in a poorer resolution spectrum, a close inspection of the current spectrum (at 400 MHz) shows that it is a second-order pattern in which the inner two lines of the pseudoquintet are broader than the central and two outer lines, having widths at half-height of 8.4 and 3.5 Hz, respectively (see insert in Figure 1 for an enlargement of this resonance). This spectrum is invariant with temperature over the range +25 to −80 °C (THF) and has

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Table I. Spectroscopic Data[a]

		IR (ν(CO)), cm^{-1}		NMR		
no.	compd	solid[b]	soln[c]	$^{31}P\{^1H\}$[d] δ[e]	^1H δ (benzene-d_6)	^1H δ (acetone-d_6)
1	$[Ir_2(CO)_2(\mu\text{-}S)(DPPM)_2]$	1918 (st), 1902 (vs)	1934 (st), 1915 (vs)	4.8 (s)	5.53 (m, 2 H), 3.15 (m, 2 H)	5.36 (m, 2 H), 3.79 (m, 2 H)
2	$[Ir_2H_2(CO)_2(\mu\text{-}S)(DPPM)_2]$		2012 (st), 1915 (vs)	−4.0 (s)	5.53 (m, 2 H), 2.76 (m, 2 H) −10.46 (quintet, 2 H); $^2J_{H-P}$ = 5.6 Hz	5.22 (m, 2 H), 3.42 (m, 2 H) −10.89 (quintet, 2 H); $^2J_{H-P}$ = 7 Hz
2c	$[Ir_2H_2(CO)_2(\mu\text{-}S)(DPPM)_2]$			0.9 (m), −8.9 (m)		−10.5 (br, 1 H), −11.3 (br, 1 H)
3	$[Ir_2H_2(CO)_2(\mu\text{-}S)(DPPM)_2]$		1987 (st), 1918 (sh)[f]	−6.8 (m), −13.2 (m)	5.31 (m, 2 H), 3.04 (m, 2 H) −10.07 (tr, 1 H); $^2J_{H-P}$ = 14 Hz −11.68 (tr, 1 H); $^2J_{H-P}$ = 11 Hz	5.06 (m, 2 H), 3.71 (m, 2 H) −10.85 (tr, 1 H)[g] −12.03 (tr, 1 H); $^2J_{H-P}$ = 12 Hz
4	$[Ir_2H_2(CO)_2(\mu\text{-}S)(DPPM)_2]$	1956 (st), 1926 (st)	1961 (vs), 1932 (st)	−8.5 (s)	4.82 (m, 2 H), 2.82 (m, 2 H) −10.18 (m, 2 H)	4.88 (m, 2 H), 3.53 (m, 2 H) −10.45 (m, 2 H)

[a] Abbreviations used: st = strong, vs = very strong, sh = shoulder, br = broad, s = singlet, m = multiplet, tr = triplet. [b] Nujol mull. [c] Acetone solution. [d] In benzene-d_6 except for **2c**, which is obtained in acetone-d_6. [e] Vs 85% H_3PO_4. [f] Shoulder appears on the 1932-cm^{-1} band of species **4**. [g] Coupling not obtained due to overlap with compound **2**.

been successfully simulated on the basis of an AA′XX′X″X‴ spin system with $^2J_{H-P}$ = 13.4 Hz, $^3J_{H-P}$ = 2.4 Hz, and $^3J_{H-H}$ = 13.5 Hz. Although the value of $^3J_{H-H}$ appears, at first glance, to be unusually large for three-bond coupling, we propose that effective transmission of coupling through the Ir–Ir bond occurs. In a series of related platinum hydride complexes, $[Pt_2HL(DPPM)_2]^+$ (L = phosphine), the three-bond coupling ($J_{H-Pt-Pt-L}$) between the axial H and L groups, which are opposite the Pt–Pt bond, was found to be 3–4 times that of the two-bond coupling between the hydride and the adjacent phosphorus nuclei of the DPPM ligands.[11] The hydride–hydride coupling in the present system might also be expected to be large if the H–Ir–Ir–H linkage were also close to being linear.

With time, the concentrations of **3** and **4** increased at approximately the same rate at the expense of **2**, yielding **2**:**3**:**4** ratios of ca. 15:1:3 after 6 h and ca. 2:3:3 after 24 h. After several days under H_2, only compound **4** remained. Figure 1 shows the $^{31}P\{^1H\}$ and the ^1H NMR spectra of a mixture of all three isomers after approximately 30 h under H_2; selective phosphorus decoupling unambiguously allows correlation of the species in the ^1H and the $^{31}P\{^1H\}$ NMR spectra. The rate of conversion of **2** to **4** is enhanced by heating and is also much increased in polar solvents, occurring approximately 16 times faster in a 1:1 (v/v) mixture of nitromethane/CH_2Cl_2 than in CH_2Cl_2 alone and occurring at approximately the same rate with heating to 40 °C in benzene or CH_2Cl_2. We have monitored the above reaction of **1** with both H_2 and D_2 in acetone and find no evidence, at any stage of the reaction, for Ir–H or Ir–D stretches in the IR spectra; the carbonyl regions in these spectra recorded under H_2 and under D_2 are essentially superimposable. Our failure to observe Ir–H stretches is not too surprising however, since the intensities of such stretches can be variable and the stretches not infrequently are absent.[12]

In the absence of hydrogen, compound **2** disappears first with the reappearance of **1**, while compounds **3** and **4** initially remain. Heating this solution to about 60 °C in the absence of H_2 causes compounds **3** and **4** to disappear within approximately 1 h.

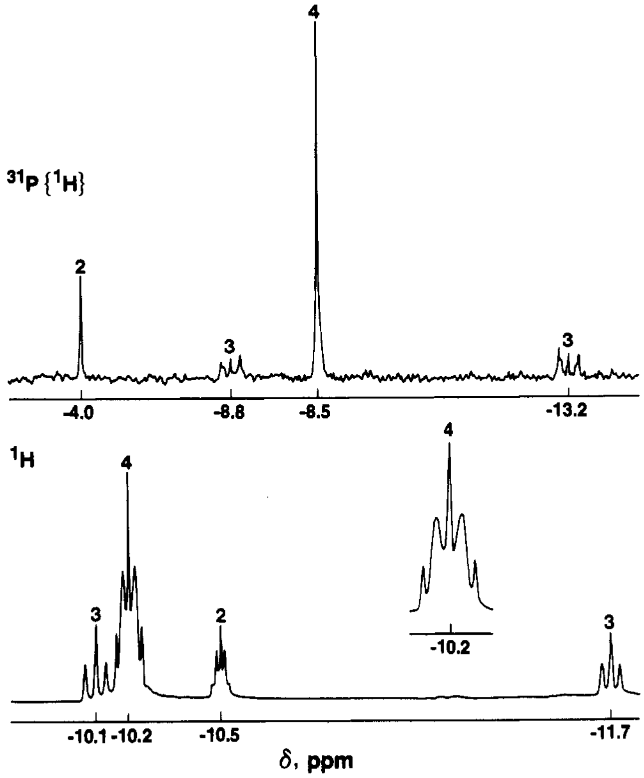

Figure 1. The $^{31}P\{^1H\}$ NMR spectrum (top) and the corresponding hydride region of the ^1H NMR spectrum of compound **1** under H_2 showing the three products. An enlargement of the hydride resonance for **4** is shown as an insert on the ^1H NMR spectrum.

On the basis of the information given above and related work involving $[Ir_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$,[10] we can now suggest the natures of these hydride species with some confidence. Compound **2** was previously proposed to be a stereochemically nonrigid species such as **2a** or **2b**. Rapid equilibration of the hydride ligands between the two metal centers would result in a quintet in the ^1H NMR and a singlet in the $^{31}P\{^1H\}$ NMR spectra. In acetone the fluxionality of **2** has now been confirmed by the broadening and collapse of the quintet upon cooling and the emergence of two hydride resonances at δ −10.5 and −11.3 at −90 °C, although our proposed static structure differs from either of those (**2a**, **2b**) initially proposed.[4] While a true low-temperature-limiting spectrum, showing spin–spin coupling was not obtained, the spectrum at −90 °C indicates that the two hydrides are in different chemical environments and are not equivalent as in **2a** and **2b**. The $^{31}P\{^1H\}$ NMR spectrum at this temperature is consistent with an unsymmetrical species having two chemically inequivalent Ir centers. We propose structure **2c** to rationalize the −90 °C spectra. This structure corresponds to the kinetic product in the hydrogenation of **1**, and it forms by the oxidative addition of H_2 to a single metal center in the binuclear complex. Equilibration of the two hydrides in **2c** may occur by rearrangement involving structures such as **2a** or **2b** or by intramolecular reductive elim-

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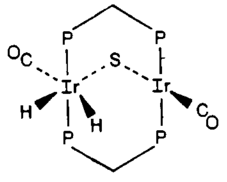
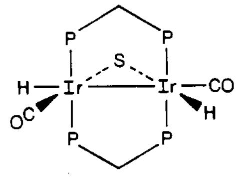
ination/oxidative addition involving **2c** and a species denoted simply as (**1** + H_2). The IR spectrum of **2**, showing one carbonyl band at 2012 cm^{-1} and the other at 1915 cm^{-1}, is also consistent with the structure **2c** having one Ir(III) and one Ir(I) center, respectively. The similarities in the IR spectra of **2** and its deuteride are somewhat surprising, considering that the carbonyl stretching frequency for the H_2 adduct of Vaska's compound is 21 cm^{-1} lower than that for the D_2 adduct (1982 vs. 2003 cm^{-1}).[13] This suggests that in compound **2** neither hydride ligand is exactly trans to the carbonyl group, so no resonance interaction between the carbonyl and hydride ligands is observed. From the variable-temperature NMR data, ΔG^* for the exchange process of **2c** can be estimated[14] at 36.0 kJ mol^{-1}. By comparison, values between 47 and 68 kJ mol^{-1} were obtained for processes of A-frame inversion in somewhat analogous hydride-bridged diplatinum complexes.[15] Species analogous to **2c** have been observed in at least two cases in which transfer of one hydride ligand to the adjacent metal, with concomitant metal–metal bond formation, was somehow inhibited.[16,17]



2c

The second species observed, **3**, has two chemically inequivalent hydride ligands that are on different metals, with each hydride showing coupling to only two phosphorus nuclei. We propose the intermediate structure for **3** in which rearrangement at only one Ir center has taken place. This appears to be the most logical structure that agrees with the spectroscopic parameters, having two chemically different hydride ligands, with one on each metal, resulting in two different phosphorus environments, yielding an AA′BB′-type $^{31}P\{^1H\}$ NMR spectrum. Furthermore, a structure such as **3** represents the intermediate species in the stepwise rearrangement of **2** to **4** (vide infra). This species is an Ir(II)/Ir(II) complex having resulted from the transfer of one hydride ligand in **2c** to the adjacent metal, accompanied by rearrangement and Ir–Ir bond formation. Such hydride transfer, yielding metals in the same oxidation state, appears to be favored in related binuclear systems in which metal–metal bond formation is not inhibited.[10,18]



3

We suggest that the final species (**4**) is also an Ir(II)/Ir(II) compound having the symmetric structure as shown earlier, in which rearrangement at *both* metal centers has occurred to give a species in which the hydride ligands are no longer adjacent but are on the outside of the complex, and probably almost collinear with the Ir–Ir bond. As noted, such a structure is supported by the ^1H NMR spectrum of **4** and the large coupling (13.5 Hz) between the two hydride ligands, as derived from the NMR simulation. This structure, in which the hydride ligands are not mutually adjacent, explains the reluctance of **4** to lose H_2 (vide supra). In addition, the proposed structure is also analogous to that which has been proposed for the chloride-bridged dihydride $[Ir_2(H)_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$, on the basis of spectroscopic and chemical evidence and of an X-ray structure of a product resulting from alkyne insertion into both Ir–H bonds.[10] Furthermore, it is worthy of note that although the hydride resonance for this chloride-bridged hydride species was originally reported to be an unresolved triplet,[10] further studies show it to be a poorly resolved pseudoquintet, not unlike that of **4**. Species **4** appears to be the thermodynamically favored product, and as noted, rearrangement to this isomer is greatly accelerated if the solution is heated under H_2.

Our proposal of oxidative addition of H_2 at one metal center, followed by transfer of one hydride ligand to the other metal and concomitant Ir–Ir bond formation, is rather similar to a proposal, by Poilblanc and co-workers,[18] for H_2 addition to a binuclear thiolato-bridged complex. Furthermore, the cis–trans isomerism observed in the thiolato-bridged species is not unlike the isomerism of **2c** to **4** described in our work. Although Poilblanc proposed a mechanism which did not involve breaking of bonds to the bridging thiolate groups to explain the isomerization, it appears that in our sulfide-bridged A-frame, cleavage of one Ir–S bond occurs to give a dipolar intermediate.[19] This proposal is consistent with the more facile rearrangement observed for the chloro-bridged A-frame,[10] since it should be easier for bridge cleavage to occur for monoanionic than for dianionic ligands. In addition, this proposal is also consistent with the more facile rearrangement of the sulfide-bridged dihydride, which occurs in a polar solvent.

Structures **2c**, **3**, and **4** are also consistent with the relative ease of H_2 loss in these species. Species **2c**, in which the hydride ligands are adjacent and therefore appropriately placed for a concerted reductive elimination, loses H_2 quite readily. Compounds **3** and **4** lose H_2 more reluctantly, since significant rearrangement at the metal centers, to give a species such as **2c** in which the hydride ligands are adjacent, is required. The mechanisms of hydride rearrangements in this and halide-bridged A-frames will be the focus of a subsequent paper.[19]

Compound **1** was also reacted with an equimolar mixture of H_2 and D_2 in acetone, while a control sample containing only H_2, D_2, and acetone was also prepared. Immediately after mixing, the sample containing **1** showed HD formation at an HD:H_2 ratio of about 1:3 (as determined by integration of the NMR resonances). After 4 days the HD:H_2 ratio was 1:1 in the solution containing **1**, while the control showed no HD formation. Although formation of HD can be rationalized on the basis of an intermolecular process involving separate dihydride and dideuteride species, it is tempting to suggest the presence of small, undetected amounts of a single dihydride–dideuteride species analogous to the tetrahydride $[Ir_2(H)_4(CO)_2(Cl)(DPPM)_2][BF_4]$.[10,20] As noted, both chloride- and sulfide-bridged A-frames react with 1 equiv of H_2 to give dihydrides having structures like **4**, so it seems reasonable that reaction of **1** with 2 equiv of H_2, yielding a tetrahydride, should also be possible, as was observed for the chloride analogue. Assuming a tetrahydride intermediate, the H/D exchange can occur in several ways. Oxidative addition of H_2 at one metal center and D_2 addition to the other would yield a species analogous to that observed in the reaction of H_2 with $[Ir(\mu\text{-}S\text{-}t\text{-}Bu)(CO)(P(O\text{-}t\text{-}Bu)_3)]_2$,[16] and ligand scrambling followed by reductive elimination could yield HD. Otherwise, D_2 addition to one of the rearranged species, **3** or **4**, could occur with subsequent HD elimination. It is of interest to note that the latter mechanism appears to operate for formation of the tetrahydride

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(20) Although only one tetrahydride species was initially observed, we have subsequently observed two isomers of this species. Their characterizations will appear in ref 19.

from $[Ir_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$,[19] and on the basis of analogies in the two systems, we favor this route for the sulfide-bridged species also. In an attempt to determine whether or not species **4** was involved in HD formation, this species was also reacted with a H_2/D_2 mixture under the same conditions as for **1**. The results indicate that the H_2:HD ratios obtained by starting from either **1** or **4** are essentially indistinguishable.

Conclusions

Ligand attack in A-frame complexes can occur either at one of the two enclosed sites proximal to the adjacent metal or on the "outside" of the complex at either of the two sites distant from the adjacent metal; examples of each have been reported.[21-23] If the metals are to interact with substrate in a cooperative manner, it is essential that the substrate be bound in close proximity to both metals. We have clearly shown that H_2 attack on the sulfide-bridged A-frame, **1**, occurs at one of the enclosed sites, suggesting the possibility of metal–metal cooperativity in the subsequent chemistry of related species. We see no evidence of attack at either distal site. Although H_2 attack probably occurs at one metal to give a species such as **2c**, exchange of hydride ligands between the two metals, within the enclosed "pocket" of the complex, is extremely facile.

Subsequently, much slower rearrangement takes place, first at one metal to give an unsymmetrical dihydride (**3**) in which one hydride ligand is in the pocket and the other occupies one of the outside sites and then at the second metal to give **4**, in which both hydride ligands occupy the outside sites of the A-frame. This rearrangement may occur via cleavage of one of the Ir–S bonds to yield a dipolar intermediate.

The production of HD from mixtures of H_2 and D_2 in the presence of either **1** or **4** suggests the involvement of a dihydride–dideuteride species analogous to the tetrahydride previously observed in the reaction of $[Ir_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$ with H_2.[10,20]

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Band Structure Calculation of Extended Poly(copper phthalocyanine) One-Dimensional and Two-Dimensional Polymers

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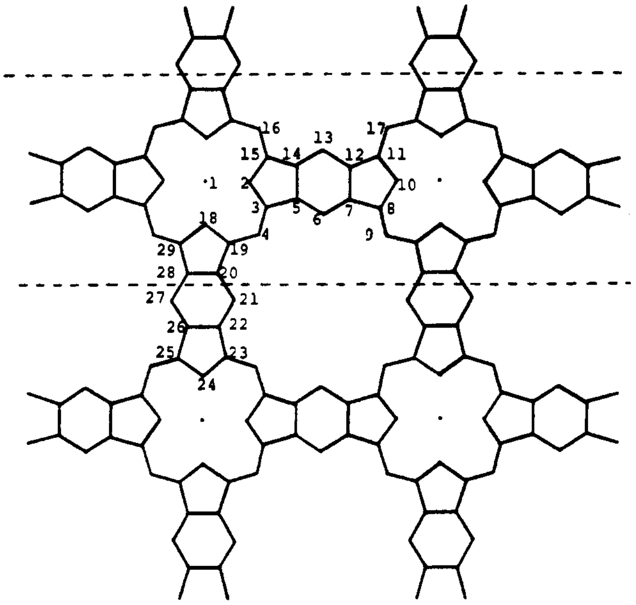
A variety of metallophthalocyanine (MPc) polymers have been experimentally[1-4,9] and theoretically[5-8] studied due to the interest in them as potential conductors and semiconductors. Among them, the linearly stacked chains have been studied most extensively. In these conducting polymeric Pc's the electrons are delocalized along the π–π stacked Pc chains and the corresponding bandwidths are large (≈1 eV according to ref 5). A less obvious question is the mechanism of electron transport between the individual conducting macromolecular chains.



BOND DISTANCES (Å)	
Cu1–N2	1.97
N2 –C3	1.37
C3 –N4	1.33
C3 –C5	1.48
C5 –C6	1.39
C5 –C14	1.30

BOND ANGLES			
1	2	3	125
2	3	4	130
3	4	19	122
2	3	5	108
15	2	3	108
3	5	14	108
14	5	6	120
5	6	7	120

Figure 1. Labeling of the atoms in the square (4/*mm*) unit cell of the poly(copper phthalocyanine) layer $CuC_{20}N_8$. Unit cell dimension: a = 10.773 Å. The dotted line indicates the limits of the one-dimensional polymer **1a**. For polymer **1b**, C atoms 21, 22, 26, and 27 were included in the calculation, together with the four corresponding H's.

We suggest that the obtainment of fused-ring Pc polymers, from one-dimensional models (**1a**, **1b**), to two-dimensional systems such

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