Cationic Binuclear "A-Frame" Complexes of Rhodium(I) and Iridium(I)

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Received January 26, 1979

The reaction of bis(diphenylphosphino)methane (DPM) or bis(diphenylarsino)methane (DAM) with an equimolar amount of $[Rh(CO)_2Cl_2]^-$ under CO in the presence of sodium tetraphenylborate yields the binuclear A-frame complexes $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(L_2)_2]B(C_6H_5)_4$ (L_2 = DPM, DAM). Both complexes readily lose CO in solution to give $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]B(C_6H_5)_4$. Exchange studies using ^{13}CO show that both terminal and bridging CO ligands are labile and that CO exchange and the interconversion of di- and tricarbonyl complexes occur via a bridge–terminal exchange process. Reaction of DPM with $[RhCl(c\text{-}C_8H_{12})]_2$ under CO yields $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][Rh(CO)_2Cl_2]$. Sulfur dioxide adds readily and reversibly to $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]B(C_6H_5)_4$ to give $[Rh_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-}Cl)(L_2)_2]B(C_6H_5)_4$ and on prolonged reaction $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$ is obtained. Reaction of $[IrCl(c\text{-}C_8H_{12})]_2$ with DPM and CO produced $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][Ir(CO)_2Cl_2]$ which on treatment with CO and sodium tetraphenylborate yielded $[Ir_2(CO)_2(\mu\text{-}CO)_2Cl(DPM)_2]B(C_6H_5)_4$. The infrared and ^1H, ^{13}C, and ^{31}P NMR spectra of the complexes are discussed.

Introduction

In the course of an earlier study of di(tertiary phosphine and arsine) complexes of rhodium(I) an attempt was made to prepare $[Rh(CO)Cl(DPM)]_2$ (DPM = bis(diphenylphosphino)methane) from $[Rh(CO)_2Cl_2]^-$. Unexpectedly a binuclear *cationic* complex was isolated.[2] Complete characterization proved extremely difficult owing to the overlap of infrared absorptions of the $[Rh(CO)_2Cl_2]^-$ anion with those of the cation and to the tendency to occlude varying amounts of solvent. Thus the exact number of carbonyl groups in the cation could not be determined. Equally frustrating was our inability to obtain a suitable single crystal for a crystallographic study. With the recent surge of interest in the use of polynuclear metal complexes for the study of multicenter catalysts in homogeneous media,[3] we began a further study of this complex and related iridium systems. We report here on these studies. A preliminary account has appeared.[4]

Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under dinitrogen. Although most complexes appear stable to air and moisture, standard Schlenk techniques (dinitrogen atmosphere) were routinely used in all preparative operations. Hydrated rhodium(III) chloride and chloro(cyclooctadiene)rhodium(I) (or -iridium(I)) dimer and the ligands bis(diphenylphosphino)methane (DPM) and bis(diphenylarsino)methane (DAM) were purchased from Strem Chemicals. Carbon monoxide and sulfur dioxide were Matheson CP grade. Carbon-13-labeled CO was generously provided by Dr. D. J. Darensbourg of the Tulane University Chemistry Department. Infrared spectra were obtained on Beckman IR-18A and Perkin-Elmer 521 instruments. Proton NMR spectra were obtained on a Jeol MH-100 spectrometer with chemical shifts referred to internal tetramethylsilane. Carbon-13 NMR spectra were obtained on a Jeol FX-60 spectrometer operating at 15.03 MHz in the Fourier transform mode with flip angle of 30° and a 5-s pulse repetition rate. Temperatures were measured with a thermocouple inserted directly into the probe. Phosphorus-31 NMR spectra were obtained by using a Varian HA-100 spectrometer, operating at 40.48 MHz, with Fourier transform capability: Digilab FTS/NMR 3 data system and pulse unit. Chemical shifts are referred to external tetramethylsilane (^{13}C) or 85% H_3PO_4 (^{31}P). Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, West Germany, and the analytical service of the University of Alberta Department of Chemistry.

$[Rh_2(CO)_3Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$. **Method A.** Carbon monoxide was bubbled through a solution of 0.20 g (0.76 mmol) of hydrated rhodium(III) chloride in refluxing ethanol (25 mL) containing 0.5 mL of H_2O until it became lemon yellow (ca. 4 h). The solution was then cooled to room temperature and solutions of 0.26 g (0.70 mmol) of bis(diphenylphosphino)methane in 3 mL of acetone or tetrahydrofuran and 0.24 g (0.70 mmol) of $NaB(C_6H_5)_4$

in 3 mL of ethanol were added in rapid succession while maintaining the flow of CO. Carbon monoxide was evolved and the product precipitated as yellow crystals. These were filtered off, washed with water, ethanol, and diethyl ether, and dried in vacuo.

Method B. Bis(diphenylphosphino)methane (0.384 g, 1.0 mmol) was added to a solution of $[Rh_2Cl_2(c\text{-}C_8H_{12})_2]$ (0.370 g, 1.5 mequiv) in dichloromethane (30 mL) under an atmosphere of carbon monoxide. $[Rh_2(CO)_3Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2][Rh(CO)_2Cl_2]$ was obtained as yellow crystals by slow evaporation of the solvent in a stream of CO or as a powder by dilution of a concentrated solution of the product with petroleum ether. Treatment of an ethanolic solution of the above complex under an atmosphere of CO with an excess of $NaB(C_6H_5)_4$ gave a product identical in all respects with the product of method A.

$[Rh_2(CO)_3Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$. This was prepared in analogous fashion to the previous complex from 0.20 g (0.76 mmol) of hydrated rhodium(III) chloride, 0.36 g (0.76 mmol) of bis(diphenylarsino)methane, and 0.24 g (0.70 mmol) of $NaB(C_6H_5)_4$. Recrystallization from tetrahydrofuran–diethyl ether under a carbon monoxide atmosphere yielded the complex as buff orange crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

$[Rh_2(CO)_2Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$. Dinitrogen was bubbled through a solution of $[Rh_2(CO)_3Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$ in tetrahydrofuran for 10 min. Addition of diethyl ether and petroleum ether precipitated the product as orange crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

$[Rh_2(CO)_2Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$. This was prepared as for the previous complex from $[Rh_2(CO)_3Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$ and obtained as orange crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

$[Rh_2(CO)_3Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]Cl$. Carbon monoxide was bubbled through a suspension of $[Rh(CO)Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)]_2$[2] in methanol whereupon the solid dissolved to give a bright yellow solution. Addition of diethyl ether and petroleum ether precipitated the product as yellow crystals which were filtered off, washed with diethyl ether, and dried in a stream of carbon monoxide.

$[Rh_2(CO)_2(SO_2)Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$. A solution of $[Rh_2(CO)_2Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$ in 5 mL of tetrahydrofuran was stirred under an atmosphere of SO_2 for 5 min whereupon it became red-orange. Addition of petroleum ether precipitated the product as orange crystals which were filtered off, washed with petroleum ether, and dried in a dinitrogen stream. Prolonged treatment of the above solution with SO_2 (>3 h) gave, as a brown, microcrystalline powder, the neutral complex $[Rh_2Cl_2(SO_2)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]$. A preliminary communication[5a] describing this complex has appeared.

$[Rh_2(CO)_2(SO_2)Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$. This was prepared in an analogous fashion to the previous complex and obtained as dark red crystals.

$[Ir_2(CO)_3Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2][Ir(CO)_2Cl_2]$. A solution of $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (0.387 g, 1.01 mmol) in ethanol or acetone (100 mL) was stirred under an atmosphere of CO, and $[Ir_2Cl_2(c\text{-}C_8H_{12})_2]$ (0.500 g, 149 mequiv) was added in small aliquots to form a deep, dark red solution. The solution slowly became paler, and after

Table I. Analytical Data on Complexes

no.	complex	% calcd					% found					mp,^{a} °C	% yield
		C	H	Cl	P	S	C	H	Cl	P	S		
1	[Rh$_2$(CO)$_3$Cl((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$]B(C$_6$H$_5$)$_4$	65.44	4.56	2.51	8.77		64.9	4.6	3.6	9.4		184 d	>90^b
2	[Rh$_2$(CO)$_3$Cl((C$_6$H$_5$)$_2$AsCH$_2$As(C$_6$H$_5$)$_2$)$_2$]B(C$_6$H$_5$)$_4$	58.19	4.07	2.23			57.7	4.1	2.5			168 d	90
3	[Rh$_2$(CO)$_2$Cl((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$]B(C$_6$H$_5$)$_4$	65.89	4.66	2.56	8.94		65.7	5.0	3.4	9.3		170 d	88
4	[Rh$_2$(CO)$_2$Cl((C$_6$H$_5$)$_2$AsCH$_2$As(C$_6$H$_5$)$_2$)$_2$]B(C$_6$H$_5$)$_4$	58.47	4.14	2.27			58.3	4.8	2.3			154 d	86
5	[Rh$_2$(CO)$_3$Cl((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$]Cl	56.35	3.93	6.28			55.5	4.2	6.3			187 d	85
6	[Rh$_2$(CO)$_2$(SO$_2$)Cl((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$]B(C$_6$H$_5$)$_4$	62.97	4.46	2.45		2.21	63.3	5.2	2.3		2.0	120 d	82
7	[Rh$_2$(CO)$_2$(SO$_2$)Cl((C$_6$H$_5$)$_2$AsCH$_2$As(C$_6$H$_5$)$_2$)$_2$]B(C$_6$H$_5$)$_4$	56.16	3.98	2.18		1.97	55.9	4.0	2.2		1.8	127 d	77
8	[Ir$_2$(CO)$_3$Cl((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$][Ir(CO)$_2$Cl$_2$]^c	41.50	2.79	6.68	7.78		41.2	2.85	7.0	7.9		>110 d	>59
9	[Ir$_2$(CO)$_4$Cl((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$]B(C$_6$H$_5$)$_4$	57.83	3.98	2.19	7.65		57.7	3.9	3.1	8.1		185 d	>77^b
10	[Ir$_2$(CO)$_3$Cl((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$]B(C$_6$H$_5$)$_4$	58.09	4.05	2.23	7.78		57.7	4.0	2.4	8.0			95
11	[Ir$_2$(CO)$_2$Cl(SO$_2$)((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$][Ir(CO)$_2$Cl$_2$]	39.84	2.72	6.53	7.61	1.97	40.8	2.9	6.6	7.3	1.9		97

^{a} d = decomposed. ^{b} Yield varies with the method of preparation and the solvent. ^{c} The solvated product analyzes as the bis(acetone) complex. Calcd: C, 42.90; H, 3.36; Cl, 6.33; P, 7.3. Found: C, 43.5; H, 2.9; Cl, 6.3; P, 7.4.

3 days the reaction mixture was filtered. The very pale yellow precipitate was successively washed with ethanol, recrystallized from dichloromethane, and dried in vacuo to give [Ir$_2$(CO)$_2$Cl((C$_6$H$_5$)$_2$-PCH$_2$P(C$_6$H$_5$)$_2$)$_2$][Ir(CO)$_2$Cl$_2$] as a pale brown powder.

When the mother liquor from the above reaction or a solution of the product in chloroform or dichloromethane was maintained under an atmosphere of CO and the resulting reaction mixture was treated with an ethanolic solution of NaB(C$_6$H$_5$)$_4$, [Ir$_2$(CO)$_4$Cl((C$_6$H$_5$)$_2$P-CH$_2$P(C$_6$H$_5$)$_2$)$_2$]B(C$_6$H$_5$)$_4$ was obtained as a pale yellow, crystalline precipitate. This precipitate could not be dried in vacuo without loss of CO. Slow evaporation of a solution of the above product in dichloromethane/ethanol (4:1) under a stream of dinitrogen gave, as reddish golden crystals, [Ir$_2$(CO)$_3$Cl((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$-H$_5$)$_2$)$_2$]B(C$_6$H$_5$)$_4$.

[Ir$_2$(CO)$_2$Cl(SO$_2$)((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$][Ir(CO)$_2$Cl$_2$]. A solution of [Ir$_2$(CO)$_3$Cl((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$][Ir(CO)$_2$Cl$_2$] in CH$_2$Cl$_2$ was stirred under an atmosphere of SO$_2$. The solution rapidly became very dark red. The mixture was slowly evaporated to dryness under a stream of SO$_2$ to yield the product as a red-orange crystalline solid.

Simulation of ^{31}P NMR Spectra. Because of the limited solubility of the complexes described herein, ^{31}P NMR spectra were obtained by Fourier transform techniques by using 500–4000 pulses. Consequently selective irradiation techniques could not be applied to determine the relationships between the various transitions. The spectra were solved by using the program NUMARIT developed by Martin and co-workers.[6] Because of the high symmetry of the rhodium complexes (AA'A''A'''XX') it was necessary to make the approximation that the phosphorus nuclei could be treated as two equivalent pairs related by a plane of symmetry. Using this approximation we found 68 of a maximum of 168 transitions were of significant intensity. The principal doublet of a second-order spectrum accounts for half of the total intensity and involves ten degenerate transitions in each half. Many of the other observed lines in each spectrum also consist of two or more degenerate or very close transitions. In order to solve the spectra it was necessary to initially assign observed values to a number of transitions. Because of the above limitations imposed by the system, a number of different arbitrary assignments of major transitions were tested before iteration was attempted. The results reported herein are those solutions which most closely simulated the observed spectra. In the case of [Rh$_2$(CO)$_3$(μ-Cl)-((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$]$^+$ it was determined that, by reassigning a number of relatively minor transitions, different solutions were obtained which were not considerably worse than the "best" solution. One of the principal variations between these solutions was in the Rh–Rh coupling constant. Consequently, in this case, a greater degree of uncertainty exists in this very significant parameter. Nevertheless, it can be stated with a high degree of confidence that the value of the Rh–Rh coupling constant and the long-range P–P coupling constant are nontrivial for this complex cation. Attempts to simulate the spectrum employing very low values of ^1J(Rh–Rh)[7] were singularly unsuccessful.

Results and Discussion

Analytical data for all complexes are presented in Table I while infrared and NMR spectral data are given in Tables II and III, respectively.

Table II. Infrared Spectral Data

complex	absorption maxima,^{a} cm^{-1}	assignment
1	1992 s, 1977 vs, 1863 s (Nujol mull) 2008 sh, 1991 vs, 1873 m (CH$_2$Cl$_2$ soln)	$\nu_{C\equiv O}$
2	1991 s, 1975 vs, 1864 s (Nujol mull) 2003 sh, 1989 vs, 1878 m (CH$_2$Cl$_2$ soln)	$\nu_{C\equiv O}$
3	1997 s, 1978 vs (Nujol mull) 2006 s, 1992 vs (CH$_2$Cl$_2$ soln)	$\nu_{C\equiv O}$
4	1987 s, 1970 vs (Nujol mull) 2003 s, 1992 vs (CH$_2$Cl$_2$ soln)	$\nu_{C\equiv O}$
5	1994 sh, 1969 vs, 1868 s (Nujol mull) 2002 sh, 1993 vs, 1875 m (CH$_2$Cl$_2$ soln)	$\nu_{C\equiv O}$
6	2023 sh, 2008 vs, 1987 sh (Nujol mull) 1228 s, 1068 s (Nujol mull)	$\nu_{C\equiv O}$ ν_{S-O}
7	2020 sh, 2006 vs, 1985 sh (Nujol mull) 1228 s, 1067 s (Nujol mull)	$\nu_{C\equiv O}$ ν_{S-O}
8	2048 vs, 1989 sh, 1975 vs, 1966 vs, 1816 s (Nujol mull)	$\nu_{C\equiv O}$
9	2047 m, 1998 vs, 1759 s (Nujol mull)	$\nu_{C\equiv O}$
10	1984 sh, 1968 vs, 1816 s (Nujol mull)	$\nu_{C\equiv O}$
11	2052 s, 2000 s, 1989 s, 1969 s (Nujol mull) 1224 m, 1073 m (Nujol mull)	$\nu_{C\equiv O}$ ν_{S-O}
12	1190 m, 1060 m (Nujol mull)	ν_{S-O}

^{a} Key: vs = very strong, s = strong, m = medium, sh = shoulder.

The reduction of hydrated rhodium(III) chloride with carbon monoxide in refluxing aqueous ethanol produces a yellow solution containing the [Rh(CO)$_2$Cl$_2$]$^-$ ion.[8] Successive reaction of this species with equimolar quantities of bis(diphenylphosphino)methane (DPM) and sodium tetraphenylborate yields yellow crystals of [Rh$_2$(CO)$_3$Cl(DPM)$_2$]B-(C$_6$H$_5$)$_4$ (**1**). A single-crystal X-ray diffraction study has shown **1** to be [Rh$_2$(CO)$_2$(μ-CO)(μ-Cl)(DPM)$_2$]B(C$_6$H$_5$)$_4$ and to contain a Rh–Rh bond.[4,9] The complex appears to be the first example wherein a metal–metal bond is simultaneously bridged by chloride and carbonyl ligands. Since the original study produced a species showing similar bands due to bridging and terminal carbonyls, that compound can now be formulated as [Rh$_2$(CO)$_2$(μ-CO)(μ-Cl)(DPM)$_2$][Rh(CO)$_2$Cl$_2$]. An identical product was also synthesized independently[5b] by the reaction of [Rh$_2$Cl$_2$(c-C$_8$H$_{12}$)$_2$] with DPM and CO. While this work was in progress, a report appeared on the closely related "A-frame" complex [Rh$_2$(CO)$_2$(μ-S)(DPM)$_2$].[10] The present compound can thus be considered an analogue of this latter species with a molecule situated in the postulated active site. Despite this, the bridging carbonyl does not appear to possess any unusual properties except for its ready exchangeability (vide infra). Thus, unlike the case of the similar palladium complexes [Pd$_2$Cl$_2$(μ-CO)(DPM)$_2$][11a] and [Pd$_2$Cl$_2$(μ-CO)(DAM)$_2$],[11b,c] the bridging CO stretching frequency (Table II) and the Rh–C–Rh' angle of 87.7 (4)°[4,9] are in the range associated with normal bridging carbonyl groups.[12]

Table III. NMR Chemical Shifts

com-plex	chemical shifts[a,b]	assignment	solvent	T, °C
1	26.0 m ($^1J_{Rh-P} = 118.3$, $^2J_{Rh-P} = -24.1$, $^1J_{Rh-Rh} = 128$ (±25) Hz)	P	CD$_2$Cl$_2$	−50
	203.9 ttq ($^1J_{C_b-Rh} = 41.0$, $^2J_{C_b-Rh-C_t} = 13.7$, $^2J_{C_b-Rh-P} = 6.8$ Hz)	CO (bridge)	CD$_2$Cl$_2$	−38
	188.6 m ($^1J_{C_t-Rh-C_b} = 13.6$, $|^1J_{C_t-Rh} + {^2}J_{C_t-Rh}| = 85.0$ Hz)	CO (terminal)		
2	197.5 m	CO (bridge)	CD$_2$Cl$_2$	−69
	187.4 m	CO (terminal)		
3	16.1 m ($|^1J_{Rh-P} + {^x}J_{Rh-P}| = 113.3$ Hz)	P	CD$_2$Cl$_2$	−30
	185.6 m ($^1J_{Rh-C} = 82.6$, $^1J_{Rh-P} = 125$, $^1J_{Rh-Rh} = 25$, $^2J_{Rh-P} = 14.6$ Hz)	CO (terminal)	CD$_2$Cl$_2$	30
4	184.5 d ($^1J_{Rh-C} = 75.2$ Hz)	CO (terminal)	CD$_2$Cl$_2$	30
5	25.8 m ($|^1J_{Rh-P} + {^x}J_{Rh-P}| = 98.0$ Hz)	P	CD$_2$Cl$_2$/CH$_3$OH	−63
	203.7 m	CO (bridge)	CD$_2$Cl$_2$/CH$_3$OH	−30
	187.6 m	CO (terminal)		
6	24.6 m ($|^1J_{Rh-P} + {^x}J_{Rh-P}| = 91.3$ Hz)	P	CD$_2$Cl$_2$	−50
	185.4 m	CO (terminal)	CD$_2$Cl$_2$	−63
7	184.4 d ($^1J_{Rh-C} = 81.0$ Hz)	CO (terminal)	CD$_2$Cl$_2$	−63
8	2.0 s	P	CD$_2$Cl$_2$	−50
9	−6.9 (AA'BB')($^2J_{P-Ir-P} \sim {^2}J_{P'-Ir-P'} = 30.0$, $^2J_{P-C-P} = 51.3$, $^4J_{P-C-P'} = 39.2$ Hz)	P$_A$	CD$_2$Cl$_2$	−50
	−15.8	P$_B$		
11	1.85 s	P	CD$_2$Cl$_2$	−50
12	19.6 m ($^1J_{Rh-P} = 129.2$, $^2J_{Rh-P} = -14.2$, $^1J_{Rh-Rh} = 167$ (±15), $^2J_{P-C-P} = 63.6$, $^2J_{P-Rh-P} = 35.0$, $^3J_{P-Rh-Rh-P} = -27.9$ Hz)	P	CD$_2$Cl$_2$	−50

a ^{31}P Chemical shifts relative to external H$_3$PO$_4$ and ^{13}C chemical shifts to external tetramethylsilane. Both positive downfield. b Key: s = singlet; d = doublet; ttq = triplet of triplets of quintets; m = second-order multiplet.
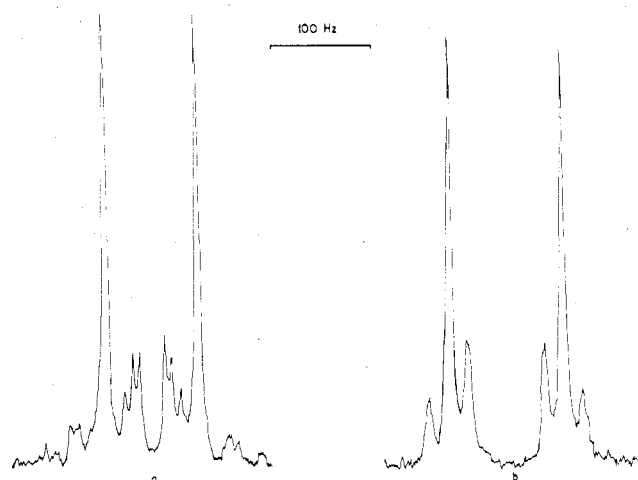

Figure 1. The ^{31}P {^{1}H} NMR spectrum of [Rh$_2$(CO)$_2$(μ-CO)(μ-Cl)(DPM)$_2$]B(C$_6$H$_5$)$_4$ (1) (a) and [Rh$_2$(CO)$_2$(μ-Cl)(DPM)$_2$]B(C$_6$H$_5$)$_4$ (3) (b) at −50 °C.

In solution, **1** readily loses carbon monoxide and thus can be recrystallized only in a CO atmosphere. If a solution of **1** in acetone or tetrahydrofuran is purged with dinitrogen or argon for several minutes, the color deepens to orange and orange crystals analyzing as [Rh$_2$(CO)$_2$Cl(DPM)$_2$]B(C$_6$H$_5$)$_4$ (**3**) can be obtained. As can be seen from Table II only terminal carbonyl absorptions are present. This, together with the fact that the terminal carbonyl bands in both **1** and **3** appear at very similar energies, strongly suggests that **3** should be formulated as [Rh$_2$(CO)$_2$(μ-Cl)(DPM)$_2$]B(C$_6$H$_5$)$_4$. This formulation has now been confirmed by a crystal structure study.[5c] Complex **3** can be reconverted to **1** by brief treatment with CO in acetone or tetrahydrofuran solution. In the conversion **1** → **3**, the loss of the bridging carbonyl ligand also occasions the loss of the metal−metal bond. Support for this postulate comes from the significantly smaller value of $^1J_{Rh-Rh}$ observed in **3** (Table III) and from the observation of a "proximity shifted" band[13] at 445 nm in the electronic spectrum of **3** (CH$_2$Cl$_2$ solution) which is absent in the spectrum of **1**. This band is comparable to that observed in the neutral dimer [Rh(CO)Cl(DPM)]$_2$ and indicates that **3** should have an analogous electronic structure. The conductivities of solutions in acetone (10^{-3} M) of [Rh$_2$(CO)$_2$-
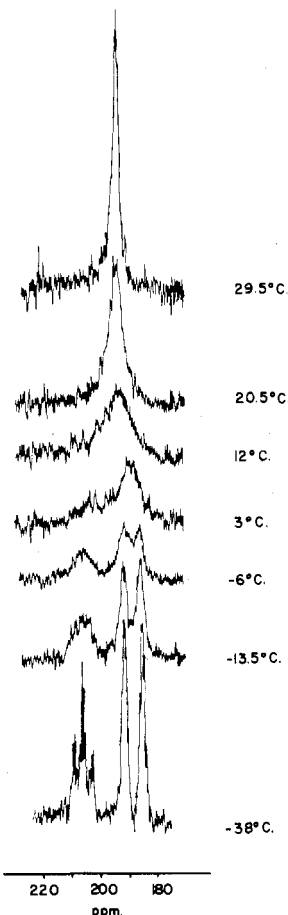

Figure 2. The ^{13}C {^{1}H} NMR spectrum of [Rh$_2$(^{13}CO)$_2$(μ-^{13}CO)-(μ-Cl)(DPM)$_2$]B(C$_6$H$_5$)$_4$ (1) under a ^{13}CO atmosphere at selected temperatures.

(μ-Cl)((C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)$_2$][Rh(CO)$_2$Cl$_2$] (114 Ω^{-1} cm^2 mol^{-1}) and **3** (99 Ω^{-1} cm^2 mol^{-1}) confirm that each complex is a 1:1 electrolyte.

The ^{31}P {^{1}H} and ^{13}C {^{1}H} NMR spectra of **1** are presented in Figures 1a and 2 (−38 °C), respectively, while the ^{31}P {^{1}H} spectrum of **3** is shown in Figure 1b. The ^{31}P spectra have been successfully analyzed as six-spin AA'A''A'''XX' systems
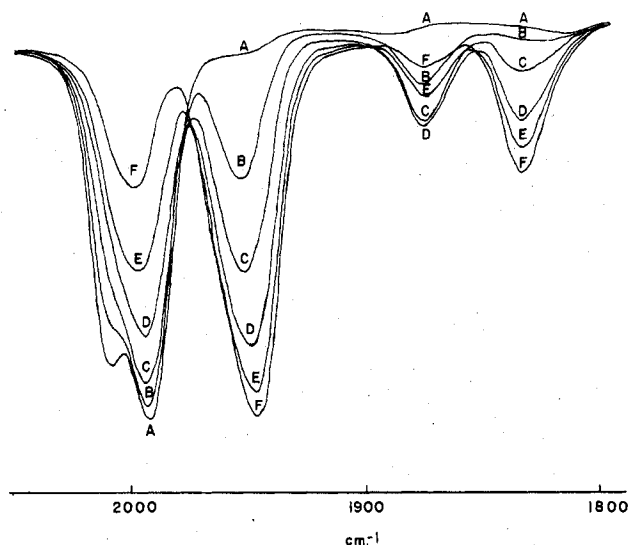
Figure 3. The infrared spectrum of the carbonyl region of a CH_2Cl_2 solution of $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$ and its reaction products with ^{13}CO: (A) $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$; (B–F) solution A treated with increasing amounts of ^{13}CO.

and the derived coupling constants are given in Table III. The spectrum of **1** was measured at −50 °C in order to eliminate the CO exchange (vide infra) which occurs at higher temperatures with the excess CO that must be present to prevent conversion to **3**. The ^{13}C NMR spectrum of a 90% enriched sample of **3** has been approximately analyzed as an AA′A″A‴MM′XX′ spin system and the derived coupling constants are given in Table III. The overlap of many of the expected lines makes these values only approximate, but it is clear that $^1J_{Rh-Rh}$ is much lower than in **1** in accord with the absence of strong metal–metal interaction discussed above.

Figure 2 presents the ^{13}C NMR spectrum of a 90% enriched sample of **1** under a ^{13}CO atmosphere at selected temperatures. Because of the limitations of our computer program it was only possible to perform a partial analysis of this nine-spin system. The spectrum at the low-temperature limit is nonetheless entirely consistent with the solid-state structure and indicates that structure is maintained under these conditions. Qualitatively $|{}^1J_{Rh-C_t} + {}^2J_{Rh-Rh-C_t}|$ appears larger than $|{}^1J_{Rh-C_b}|$ and their respective values of 84.0 and 41.0 Hz are comparable to those reported previously for rhodium carbonyl complexes.[14] Upon expansion, the resonance of the bridging carbonyl is perceived to be a first-order triplet of triplets of quintuplets $(J_1 = 41.0, J_2 = 13.7, J_3 = 6.8$ Hz). The highly ordered pattern is due to the precise ratio of these parameters (6:2:1). Inspection of the resonance for the terminal carbonyl demonstrates that J_2 is $^2J_{C_b-Rh-C_t}$ and that J_3 is therefore $^2J_{P-Rh-C_b}$. Upon warming of the solution, the carbonyl resonances collapse and reappear as a moderately broad singlet at 192.2 ppm indicating rapid intermolecular exchange of both bridging and terminal CO ligands.

Since CO exchange with **1** and the interconversion **1** ⇌ **3** is facile, it seems very likely that they occur by the same mechanism. We have investigated this process further by ^{13}CO labeling experiments. In agreement with the ^{13}C NMR results, passage of ^{13}CO through a dichloromethane solution of **1** at room temperature for 1–2 min results in the *essentially complete disappearance* of the original CO bands and the appearance of new absorptions at 1964 (sh), 1945 (s), and 1832 (m) cm⁻¹. Thus exchange of both terminal and bridging carbonyls has occurred. An identical spectrum is obtained by treating **3** with ^{13}CO in CH_2Cl_2 solution. Figure 3 details the spectral changes which occur in the carbonyl region when a CH_2Cl_2 solution of **3** is treated with incremental portions of

^{13}CO at −78 °C followed by recording the spectrum at room temperature. Comparison of spectrum B with that of the starting complex **3** (A) shows that the **1** which has formed initially is enriched in ^{13}CO almost exclusively at a terminal position while the bridging position contains predominantly ^{12}CO. It is further evident that the initial ^{13}CO enrichment occurs mainly in the terminal position responsible for the higher energy of the two terminal CO bands as the intensity of this band has diminished noticeably while the other has remained substantially the same.[15] As more ^{13}CO is added (spectra C–F) increasing enrichment occurs in the other positions as well. Because intermolecular exchange of CO between **1** and **3** and between each of these and free CO is rapid at 30 °C once substantial amounts of **1** are present,[4] the delay of ca. 3 min between removal of an aliquot from the cold solution and the recording of the infrared spectrum when the solution is at 30 °C allows equilibration between all of the variously labeled species which could be formed. Thus it is not clear from this experiment whether addition of CO to **3** occurs exclusively at a terminal position. To explore this question further, we treated a sample of **3** in dichloromethane with an approximately equimolar quantity of ^{13}CO at −78 °C and obtained the ^{13}C NMR spectrum at a probe temperature of −55 °C (1000 transients, ca 1.5 h contact with ^{13}CO). The only signal readily distinguishable above the noise level in the carbonyl region was centered at δ 185.4 and appeared as a doublet, each component of which appeared to be further split into a triplet of triplets. The major splitting of 82.0 Hz is clearly $^1J_{Rh-C}$ while the additional splitting can be attributed to $^2J_{Rh-C}$ (∼15 Hz) and $^xJ_{Rh-C}$ (∼8 Hz). The spectrum thus indicates the presence of **1** enriched predominantly at a terminal position. The absence of significant initial enrichment at the bridging position when **3** is converted to **1** with ^{13}CO as indicated by both these experiments argues strongly that the formation of **1** from **3** involves attack of CO on *one* rhodium with conversion of the terminal carbonyl originally on this center into a bridging ligand. The most reasonable process for CO exchange then presumably involves this type of bridge–terminal exchange (e.g., eq 1). Further support

$$\text{(1)}$$
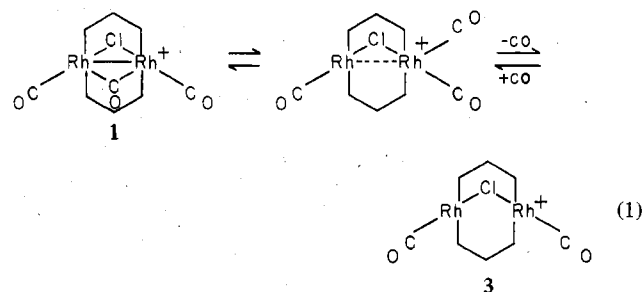
for the process is seen in the reaction of 1 equiv of *tert*-butyl isocyanide with **3** where the product is $[Rh_2(CO)(t\text{-}BuNC)(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$.[24] Again, conversion of a terminal carbonyl into a bridging carbonyl has occurred on addition of the new ligand.

Addition of equimolar quantities of bis(diphenylarsino)-methane (DAM) and sodium tetraphenylborate to the reduced solution containing $[Rh(CO)_2Cl_2]^-$ under a CO atmosphere yields buff-orange crystals of **2**. The conductivity of an acetone solution (10^{-3} M) of **2** is 84.8 Ω^{-1} cm² mol⁻¹ which, with the data in Tables I–III, indicates that the complex is $[Rh_2\text{-}(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$. For comparison a 10^{-3} M solution of $NaB(C_6H_5)_4$ in acetone has a conductivity of 111.0 Ω^{-1} cm² mol⁻¹. The ^{13}C {¹H} NMR spectrum of a 90% enriched sample obtained at −69 °C (Table III) is quite similar to that obtained for **1** but is less complex because of the absence of ^{31}P–^{13}C coupling. Unfortunately the resolution of this spectrum was insufficient to permit a reliable analysis to

be made. However, it is entirely consistent with the proposed formulation. Like **1**, **2** readily loses CO in solution and by briefly purging a solution of the latter in tetrahydrofuran or acetone with dinitrogen we can obtain the orange complex **4**. The analytical, infrared spectra, ^{13}C NMR spectra, and conductivity ($\Lambda_m(10^{-3}$ M acetone solution) = 83.5 Ω^{-1} cm^2 mol^{-1}) data for **4** clearly establish that it is [Rh$_2$(CO)$_2$(μ-Cl)(DAM)$_2$]B(C$_6$H$_5$)$_4$. As with **2**, **4** shows a "proximity shifted" band in its electronic spectrum at 430 nm which is similar to that observed for the neutral species [Rh(CO)-Cl(DAM)]$_2$[13] and which is absent from the spectrum of **2**. Since [Rh(CO)Cl(DAM)]$_2$ is known to have an Rh–Rh separation of 3.396 (1) Å,[16] these observations indicate that **4** does not have a metal–metal bond while **2** almost certainly does. Further evidence for the similarity of **4** and [Rh-(CO)Cl(DAM)]$_2$ comes from the ^{13}C {^{1}H} NMR spectra of the two species. That of **4** appears in Table III while the spectrum of the latter also shows a doublet at 183.9 ppm downfield from tetramethylsilane with $^1J_{Rh-C}$ = 62.5 Hz. Complex **4** can be reconverted to **2** by passing CO through a solution of it in tetrahydrofuran or acetone and both complexes show complete CO exchange analogous to that observed for **1** and **3**. This is demonstrated by the appearance of CO bands at 1954 (sh), 1941 (vs), and 1833 (w) cm^{-1} when a CH$_2$Cl$_2$ solution of either complex is treated briefly with ^{13}CO. This is further supported by variable-temperature ^{13}C {^{1}H} NMR studies of **2** in the presence of ^{13}CO. As observed for **1**, the CO resonances collapse on warming and by –27 °C have reappeared as a single peak at 190.0 ppm. The exchange presumably occurs by the same mechanism which is evidently more facile in **2** since coalescence occurs at ca. –50 °C as compared with ca. +5 °C for **1**.

In methanol the neutral dimer [Rh(CO)Cl(DPM)]$_2$ reacts readily with carbon monoxide to yield a bright yellow solution from which yellow crystals analyzing as [Rh$_2$(CO)$_3$Cl$_2$-(DPM)$_2$] (**5**) can be obtained. The infrared and ^{13}C {^{1}H} and ^{31}P {^{1}H} NMR spectra of **5** are essentially the same as those of **1** while the conductivity of a 10^{-3} M solution in methanol is 71.7 Ω^{-1} cm^2 mol^{-1}. For comparison a 1.13 × 10^{-3} M solution of sodium tetraphenylborate in methanol has a conductivity of 74.9 Ω^{-1} cm^2 mol^{-1} thus demonstrating that **5** behaves as a 1:1 electrolyte. On this basis we formulate **5** as [Rh$_2$(CO)$_2$(μ-CO)(μ-Cl)(DPM)$_2$]Cl. Unlike **1**, **5** shows a distinct tendency to lose CO in the solid state as evidenced by a slow reversion to the orange color of the neutral dimer over a period of months. This is presumably the result of the presence of the chloride ion which can coordinate to the metal. The ready formation of [Rh$_2$(CO)$_3$Cl(DPM)$_2$]$^+$ from *trans*-[Rh(CO)Cl(DPM)]$_2$ and CO in methanol and the ability to recover the latter following purging of the solution with dinitrogen provide a convenient route for preparing *trans*-[Rh(CO)Cl(DPM)]$_2$ which is ~80% enriched in ^{13}CO. The enriched complex shows $\nu_{C\equiv O}$ at 1924 cm^{-1}. Despite this success at enrichment, solubility problems prevented us from obtaining a satisfactory ^{13}C NMR spectrum of [Rh(CO)-Cl(DPM)]$_2$ even after accumulating 30 000 scans under the conditions given in the Experimental Section. We also attempted to prepare [Rh$_2$(CO)$_3$Cl(DAM)$_2$]Cl by the procedure outlined above but could only isolate the starting complex. This failure is perhaps not surprising in light of the considerably lower barrier to CO exchange in the arsine system which is evident from the NMR studies discussed earlier. Nevertheless, the tricarbonyl cation must be formed to some extent since it did prove possible to achieve ca. 50% enrichment of [Rh(CO)Cl(DAM)]$_2$ ($\nu_{^{13}C\equiv O}$ = 1922 cm^{-1}) by treatment of a methanol suspension with ^{13}CO.

As mentioned earlier the crystallographic study[4,9] of **1** does not give any indication that the bridging carbonyl ligand has
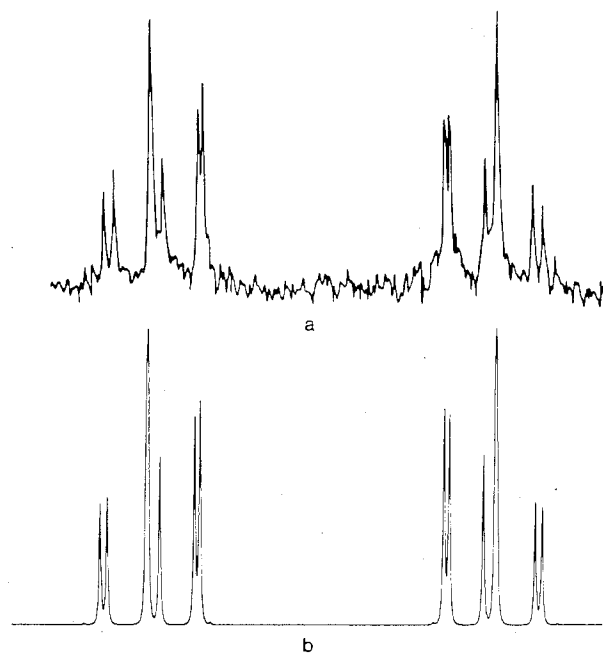

Figure 4. The ^{31}P {^{1}H} NMR spectrum of [Ir$_2$(CO)$_2$(μ-CO)$_2$Cl-(DPM)$_2$][Ir(CO)$_2$Cl$_2$] at –50 °C (a) and the computer simulation using calculated parameters (b).

any unusual structural feature even though it resides in the postulated "active site" of the "A-frame" complex. In keeping with this, we have been unable to detect any reaction of this ligand with either dihydrogen or dioxygen, at least under ambient conditions. In each case CO was displaced and **3** was recovered. The same results were obtained by using the arsine complex **2** and only **4** was recovered. Although these experiments indicate that no stable adducts of O$_2$ or H$_2$ are formed with **3** or **4** under these conditions, we have found that both complexes catalyze the hydrogenation of olefins and acetylenes under mild conditions.[23,24] Thus **3** and **4** are capable of activating H$_2$.

We have also attempted to synthesize iridium analogues of various of the above complexes of rhodium. The reaction of an acetone solution of [Ir$_2$Cl$_2$(COD$_2$)] (COD = 1,5 cyclo-octadiene) with DPM and CO was slower than the reaction of the rhodium complex. Initially a dark red solution was formed which, over a period of hours, became paler. Reduction of the volume of the solution under a stream of CO gave an unstable pale precipitate which dried over several days under vacuum to a pale brown powder. The product analyzed as [Ir$_2$(CO)$_3$Cl(DPM)$_2$][IrCl$_2$(CO)$_2$] (**8**) and showed infrared bands appropriate to the anion ($\nu_{C\equiv O}$ = 2048, 1975 cm^{-1}; ν_{Ir-Cl} = 333, 292 cm^{-1}) and other carbonyl bands at 1989 (sh), 1966 (vs), and 1816 (s) cm^{-1}. The brown powder redissolved in dichloromethane to form an orange-red solution which reacted with CO to form a pale yellow solution. Treatment of this solution with an ethanolic solution of NaB(C$_6$H$_5$)$_4$ and subsequent slow evaporation of dichloromethane under a stream of CO gave pale yellow crystals which analyzed as [Ir$_2$(CO)$_4$Cl(DPM)$_2$]B(C$_6$H$_5$)$_4$ (**9**). The solution was unstable except under an atmosphere of CO, and the crystals of **9** were unstable in vacuo, losing 1 mol of CO within a few days. The analytical results reported herein therefore apply to samples dried only between sheets of absorbent paper and stored in sealed glass vials under an inert atmosphere. The ^{31}P NMR spectrum of **9** was recorded for a solution in a sealed tube under an atmosphere of CO. The spectrum (Figure 4; CD$_2$Cl$_2$ solution, –50 °C) was successfully analyzed as an AA'BB' system with a difference of 8.9 ppm between the chemical shifts of the nonequivalent pairs of phosphorus atoms. The

positions of the lines in the calculated spectrum were relatively insensitive to variation in the values of $^2J_{P-Ir-P}$ and $^2J_{P'-Ir-P'}$; a value of 30.0 Hz was found to give satisfactory values for the relative intensities of the lines. The simulated spectrum using the calculated parameters (Table III) is also shown in Figure 4. The infrared and ^{31}P NMR data are consistent with an asymmetric structure for the cation of **9**. Thus **9** is not a direct analogue of **1** but, on the basis of the analytical and spectroscopic data, is $[Ir_2(CO)_2(\mu\text{-}CO)_2Cl(DPM)_2]B(C_6H_5)_4$. The low energy of the band assigned to the bridging carbonyl group is unusual but appears to be a feature of these highly carbonylated iridium dimers.[24] Even lower bridging carbonyl bands have been observed in the related complexes $[Pd_2(\mu\text{-}CO)Cl_2(L_2)_2]$ (L_2 = DPM, DAM)[11] and $[Pt_2(\mu\text{-}CO)Cl_2(DPM)_2]^{25}$ which have been explained in terms of a formaldehyde derivative or a $\sigma + \pi$ bonded carbonyl group. Until structural data are available for **9**, we prefer to say only that the low carbonyl stretching frequency implies considerable electron density has been transferred to this ligand. The upfield shift of the ^{31}P resonances of **9** as compared with that for **10**[26,27] is consistent with this.

When a solution of **9** in dichloromethane was not maintained under an atmosphere of CO, the AA'BB' pattern of the ^{31}P NMR spectrum slowly decreased in intensity to be replaced by a singlet. Slow evaporation of the now orange-red solution in a stream of dinitrogen gave orange crystals (**10**). The infrared spectrum of **10** showed carbonyl bands at 1984 (m, sh) 1968 (vs), and 1816 (s) cm^{-1}, indicating the continued presence of both terminal and bridging CO ligands. The ^{31}P $\{^1H\}$ NMR spectrum showed only a singlet (+2.0 ppm vs. H_3PO_4) and demonstrated the equivalence of all phosphorus atoms. These spectral data are consistent with a structure analogous to **1**. Treatment of a solution of the above complex with CO regenerated a solution of **9** (IR, ^{31}P NMR). In order
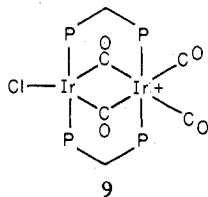
9

to fully determine the structure of **9** and **10** we are attempting to obtain crystals suitable for X-ray analysis. Results of these studies and reactions of **9** and **10** with dihydrogen and unsaturated organic species will be reported separately.

We have also investigated the capability of **3**, **4**, and **10** to bind molecules other than CO. Brief treatment of a tetrahydrofuran solution of **3** with gaseous sulfur dioxide gives a red-orange solution from which orange crystals analyzing as $[Rh_2(CO)_2(SO_2)Cl(DPM)_2]B(C_6H_5)_4$ (**6**) can be obtained. This complex,[5a] and related complexes of, e.g., NO or $C_6H_5N_2^+$,[5b] have also been independently prepared. The infrared spectrum of **6** shows two CO bands and the ^{31}P $\{^1H\}$ NMR spectrum shows a single second-order pattern which is similar to that observed for **1**. Besides indicating a symmetric phosphorus environment, the separation of the two major peaks ($|^1J_{Rh-P} + {^xJ_{Rh-P}}|$) of 98.0 Hz and the complexity of the remaining lines are indicative of a strong metal-metal interaction. The ^{13}C $\{^1H\}$ NMR spectrum of a 90% ^{13}CO-enriched sample shows a single second-order pattern which is quite similar to that of **3**; however, there is a noticeable difference in the relative intensities of the inner lines and the separation of the major peaks is about 7 Hz larger. The implied equivalence of the CO groups again confirms that the molecule is symmetric and on this basis we formulate **6** as $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}SO_2)(DPM)_2]B(C_6H_5)_4$. This is further supported by the values of the SO stretching frequencies (Table II) which are in the range previously observed for an SO_2

ligand bridging a metal-metal bond.[17,18] Reaction of **4** with SO_2 gives red crystals which analyze as $[Rh_2(CO)_2(SO_2)\text{-}Cl(DAM)_2]B(C_6H_5)_4$ (**7**) and exhibit values of $\nu_{C\equiv O}$ and ν_{S-O} which are virtually identical with those of **6** and imply an analogous structure with significant Rh–Rh interaction. Since a substantial $^1J_{Rh-Rh}$ is evident in the similar complexes **1**, **2**, and **6**, it is surprising that the ^{13}C $\{^1H\}$ NMR spectrum of **7** (Table II) does not also show the second-order effects (AA'XX' spectrum) that would be expected for the proposed structure. The spectrum is clearly that of **7** and not **4** since it is unchanged at -63 °C in the presence of excess SO_2 and the doublet splitting is ca. 7 Hz larger than in **4**. One explanation is that SO_2 exchange is rapid even at -63 °C. This is possible since the barrier to CO exchange in **2** is significantly lower than in **1**. It might be noted that in $[(\eta^5\text{-}C_5H_5)_2Rh_2\text{-}(CO)_3]$ where an Rh–Rh bond of 2.68 Å exists,[20] $^1J_{Rh-Rh}$ is negligible[21] so that the absence of significant Rh–Rh coupling is not inconsistent with the presence of a metal-metal bond as we propose although it is then puzzling why only **7** should show this.

The SO_2 ligand in both **6** and **7** is labile and can be replaced by CO to yield **1** and **2**, respectively. Purging a solution with nitrogen regenerates the starting complexes **3** and **4**. This lability is also evident from the ^{13}C NMR spectra of the two complexes which show incipient collapse at room temperature indicating the onset of SO_2 dissociation and exchange. In contrast to the reaction of **3** and **4** with CO, we find no evidence for species which would suggest initial attack of SO_2 on one metal. The only species detectable by infrared or ^{31}P NMR spectroscopy even at -63 °C is the symmetrically bridged complex which is the final product. Although this does not rule out such a species, if formed it must have only transient existence. Support for a different mode of attack by SO_2 on **3** and **4** from that for CO comes from the observation that the former reaction is noticeably slower.[5b]

Although the SO_2 ligand is labile and has ν_{SO} near 1200 and 1050 cm^{-1}, there does not appear to be any tendency to form sulfate complexes on reaction with dioxygen as has been suggested should occur for monomeric complexes with these characteristics.[19] Thus passage of O_2 through a CH_2Cl_2 solution of **6** leads only to removal of SO_2 and recovery of **2**.

The cationic complex of iridium(I), $[Ir_2(CO)_2Cl(SO_2)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2][Ir(CO)_2Cl_2]$ (**11**), analogous to **6**, was also prepared by the reaction of **8** with SO_2. Attempts to obtain crystals suitable for X-ray crystallographic analysis have so far proved unsuccessful but are continuing.[5b]

Treatment of a dichloromethane solution of **3** with SO_2 for long periods of time (>3 h) gave the neutral complex $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$, **12**, and a yellow solution containing an as yet unidentified ionic complex. The reaction proceeds through initial formation of **6** and appears to require the presence of traces of chloride since reaction of highly purified **6** with SO_2 proceeds very slowly if at all.[5a,b] The crystal structure of **12** has recently been described in a preliminary communication and consequently only some salient points will be briefly mentioned here. The crystal structure of **12** clearly demonstrates the presence of a metal-metal bond (Rh–Rh = 2.784 Å), and the SO_2 ligand symmetrically bridges the rhodium atoms (Rh(1)–S = Rh(2)–S = 2.169 Å) with an acute angle Rh(1)–S–Rh(2) (79.85 (7)°). The SO_2 bands in the infrared spectrum (1190, 1060 cm^{-1}) are consistent with tetrahedral coordination about sulfur. The ^{31}P NMR spectrum shows a single environment for phosphorus atoms, and the second-order spectrum has now been successfully analyzed as an AA'A"A'''XX' system. The principal parameters of the observed spectrum are δ_P = 19.6 and $(|^1J_{Rh-P} + {^xJ_{Rh-P}}|)$ = 115.0 Hz. Calculated coupling constants are given in Table III.

A solution of **12** in dichloromethane reacts readily with CO to yield a yellow solution from which a yellow crystalline material originally formulated as the neutral species *cis*-[Rh$_2$(CO)$_2$(μ-CO)Cl$_2$(DPM)$_2$][5a] can be isolated. Subsequent work[5b] has shown, however, that this complex has a conductivity of 48 Ω^{-1} cm^2 mol^{-1} in dichloromethane. The infrared spectrum of this solution ($\nu_{C\equiv O}$ = 1991 (vs), 1875 (m) cm^{-1}) is essentially the same as observed for **5** but the ^{31}P NMR spectrum (δ_P = 19.6 ($|^1J_{Rh-P} + {}^xJ_{Rh-P}|$ = 113.5 Hz)) although very similar in appearance differs somewhat in the chemical shift and separation of the major peaks from that observed for **5**. Purging of the above solution with dinitrogen yields an orange solution showing $\nu_{C\equiv O}$ at 1991 (vs) and 1978 (vs) cm^{-1} which was originally reported to contain the metal complex *cis*-[Rh(CO)Cl(DPM)]$_2$.[5a] We now find that a dichloromethane solution of **5** purged with dinitrogen showed $\nu_{C\equiv O}$ at 2002 (sh), 1991 (vs), and 1976 (vs) cm^{-1}. Evaporation of this solution to dryness or precipitation of the complex with diethyl ether yields orange crystals showing a single CO band at 1969 cm^{-1} indicating the product to be *trans*-[Rh(CO)Cl(DPM)]$_2$. Since the intensity of the 1976-cm^{-1} band grows relative to that of the 1991-cm^{-1} band as the purging of the solution continues, it appears that this solution may contain a mixture of [Rh(CO)$_2$(μ-Cl)(DPM)$_2$]Cl and *trans*-[Rh(CO)Cl(DPM)]$_2$ with conversion to the latter being relatively slow and completed only by formation of the solid complex. These observations together with the conductance observed for the product obtained from the reaction of CO with **12** suggest that this species is **5** although the differences in the ^{31}P NMR spectra of the two solutions remains unexplained. Possibly this could result from the different solvents used since the ^{31}P NMR parameters of **3** in acetone solution (δ_P = 19.4 ($|^1J_{Rh-P} + {}^xJ_{Rh-P}|$ = 112.3 Hz)) differ noticeably from those of **3** in noncoordinating solvents (Table III). Work is continuing to resolve this question.

In noncomplexing solvents a 1:1 complex with diphenylacetylene is formed (δ_P = 18.9 ($|^1J_{Rh-P} + {}^xJ_{Rh-P}|$ = 113.5 Hz)).[23] Under an atmosphere of hydrogen, acetylenes and alkenes are hydrogenated. The catalytic activity of these systems will be described in detail elsewhere.

Registry No. **1**, 67235-83-0; **2**, 70561-95-4; **3**, 67202-35-1; **4**, 70561-97-6; **5**, 70561-98-7; **6**, 68080-76-2; **7**, 68080-78-4; **8**, 70562-00-4; **9**, 70562-02-6; **10**, 70562-03-7; **11**, 70561-92-1; **12**, 69063-81-6; [Rh$_2$(CO)$_2$(μ-CO)(μ-Cl)(DPM)$_2$][Rh(CO)$_2$Cl$_2$], 70576-38-4; [Rh(CO)Cl(DPM)]$_2$, 22427-58-3; [Rh$_2$Cl$_2$(c-C$_8$H$_{12}$)$_2$], 12092-47-6; [Ir$_2$Cl$_2$(c-C$_8$H$_{12}$)$_2$], 12112-67-3.

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