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Binuclear Cationic Complexes of Rhodium(I) and Iridium(I) Containing both Carbonyl and Isocyanide Ligands

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The reactions of *tert*-butyl isocyanide with the A-frame complexes $[Rh_2(CO)_2Cl(L_2)_2]X$ and $[Ir_2(CO)_3Cl(L_2)_2]X$ (L_2 = bis(diphenylphosphino)methane (DPM), bis(diphenylarsino)methane (DAM); X = $B(C_6H_5)_4^-$, BF_4^-, PF_6^-) are described. With rhodium, the complexes $[Rh_2(CO)_2(t\text{-}C_4H_9NC)Cl(DAM)_2]PF_6$, $[Rh_2(CO)(t\text{-}C_4H_9NC)_2Cl(DAM)_2]B(C_6H_5)_4$, $[Rh_2(CO)_2(t\text{-}C_4H_9NC)Cl(DPM)_2]B(C_6H_5)_4$, and $[Rh_2(CO)(t\text{-}C_4H_9NC)_2Cl(DPM)_2]B(C_6H_5)_4$ result when 1 or 2 equiv of isocyanide are used. The last two contain bridging carbonyl and chloride ligands while in the first two all the ligands are terminal. The use of excess isocyanide and $NaB(C_6H_5)_4$ yields $[Rh_2(t\text{-}C_4H_9NC)_4(L_2)_2](B(C_6H_5)_4)_2$ which reacts further with CO and SO_2 to yield $[Rh_2(\mu\text{-}L)(t\text{-}C_4H_9NC)_4(L_2)_2](B(C_6H_5)_4)_2$ (L = CO, SO_2). With iridium, the complexes $[Ir_2(CO)_3(t\text{-}C_4H_9NC)Cl(L_2)_2]X$, $[Ir_2(CO)_2(t\text{-}C_4H_9NC)_2Cl(L_2)_2]X$ (L_2 = DPM, X = $B(C_6H_5)_4^-$; L_2 = DAM, X = BF_4^-), and $[Ir_2(CO)(t\text{-}C_4H_9NC)_4(L_2)_2](B(C_6H_5)_4)_2$ are obtained. The infrared, ^{13}C and ^{31}P NMR, and the electronic spectra of the complexes are discussed.

Introduction

Considerable interest has recently been shown in binuclear complexes of rhodium,[1-5] iridium,[1] palladium,[6,7] and platinum[8-10] containing the ligands bis(diphenylphosphino)methane (DPM) and bis(diphenylarsino)methane (DAM). Of particular importance are those having the A-frame geometry of which $[Pd_2(CNCH_3)_2(\mu\text{-}CNCH_3)(DPM)_2](PF_6)_2$[6] was the first completely characterized example. Subsequently we have described the preparation of the related cationic species $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]A$ (L_2 = DPM, DAM; A = $B(C_6H_5)_4^-$, PF_6^-), the ability of both complexes to *reversibly* coordinate CO and SO_2 in the postulated[2] active site, and the structure of one of these adducts ($[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$).[1,11,12] The preparation and structure of the SO_2-bridged A-frame $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$ has also been described.[13] In light of the current interest in multicentered, homogeneous catalysts[14,15] and the demonstrated ability of our A-frame complexes to catalyze the hydrogenation of simple and functionalized olefins and acetylenes under mild conditions,[16,17] we have undertaken an extensive study of these systems. We report here on some further aspects of their chemistry.

Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under nitrogen. A nitrogen atmosphere and standard Schlenk techniques were used in all preparative operations. Hydrated iridium(III) chloride was purchased from Alfa Inorganics and the ligands bis(diphenylphosphino)methane (DPM) and bis(diphenylarsino)methane (DAM) were obtained from Strem Chemicals. Published procedures were used to prepare $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]B(C_6H_5)_4$ (L_2 = DPM, DAM),[11] $[Ir_2(CO)_3Cl(DPM)_2]B(C_6H_5)_4$,[11] *tert*-butyl isocyanide[18] and $[IrCl(C_8H_{14})_2]_2$.[19] 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 spectrophotometers. Proton NMR spectra were obtained on a JEOL MH-100 spectrometer with chemical shifts referred to internal tetramethylsilane. Carbon-13 and phosphorus-31 NMR spectra were obtained on a JEOL FX-60 spectrometer operating in the Fourier transform mode at 15.03 (flip angle 30°, pulse repetition rate 5 s) and 24.15 MHz (flip angle 45°, pulse repetition rate 4.5 s), respectively. Carbon chemical shifts are referred to external tetramethylsilane and phosphorus chemical shifts to external H_3PO_4. In both cases, chemical shifts are increasing to low field. Temperatures were measured with a thermometer inserted directly into the probe. Analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Conductivities were measured with a Thomas-Serfass Model RCM 15B1 conductance bridge and a cell containing platinized electrodes which was calibrated with 0.01 M aqueous potassium chloride. Melting points were determined on a Mel-Temp apparatus in open capillaries and are uncorrected.

$[Rh_2(CO)_2Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]PF_6$. Carbon monoxide was bubbled through a refluxing solution of 0.20 g (0.76 mmol) of hydrated rhodium(III) chloride in aqueous ethanol until it had become pale yellow. Successive addition of 0.360 g (0.76 mmol) of $(C_6H_5)_2AsCH_2As(C_6H_5)_2$ in 5 mL of tetrahydrofuran and 0.17 g (0.76 mmol) of NH_4PF_6 in ethanol to the cooled solution under CO yielded the product as a yellow powder. This was filtered, washed with successive portions of ethanol, water, ethanol, and diethyl ether, and recrystallized from acetone–diethyl ether to yield yellow-orange crystals.

$[Rh_2(CO)_2(t\text{-}C_4H_9NC)Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]PF_6\cdot 0.5(CH_3)_2CO$. To an acetone solution (5 mL) of $[Rh_2(CO)_2Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]PF_6$ (0.208 g, 0.158 mmol) was added 0.013 g (0.158 mmol) of *tert*-butyl isocyanide dropwise with stirring. Addition of diethyl ether to the resulting dark red solution precipitated the product as fine orange needles which were filtered off, washed with diethyl ether, and dried in vacuo.

$[Rh_2(CO)(t\text{-}C_4H_9NC)_2Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$. To a solution of 0.136 g (0.087 mmol) of $[Rh_2(CO)_2Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$ in 5 mL of tetrahydrofuran was added 0.014 g (0.174 mmol) of *tert*-butyl isocyanide dropwise with stirring. Addition of petroleum ether precipitated a flocculent orange solid. This was dissolved in tetrahydrofuran and filtered to give a dark red-violet solution. Addition of diethyl ether and petroleum ether

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followed by allowing the solution to stand at room temperature afforded the product as dark red-violet crystals. These were filtered off, washed with diethyl ether, and dried in vacuo.

$[Rh_2(t\text{-}C_4H_9NC)_4((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2](B(C_6H_5)_4)_2$. To a tetrahydrofuran solution (5 mL) of $[Rh_2(CO)_2Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$ (0.136 g, 0.087 mmol) was added 0.028 g (0.348 mmol) of *tert*-butyl isocyanide dropwise with stirring followed by 0.030 g (0.087 mmol) of $NaB(C_6H_5)_4$. Diethyl ether was added to the intense blue-violet solution to precipitate a purple solid. Recrystallization from acetone–diethyl ether yielded the product as intense purple crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

$[Rh_2(CO)_2(t\text{-}C_4H_9NC)Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$. To an acetone solution (5 mL) of $[Rh_2(CO)_2Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$ (0.200 g, 0.152 mmol) was added 0.013 g (0.152 mmol) of *tert*-butyl isocyanide dropwise with stirring. Addition of diethyl ether and petroleum ether to the resulting orange solution precipitated the product as fluffy yellow microcrystals which were filtered off, washed with diethyl ether, and dried in a stream of carbon monoxide.

$[Rh_2(CO)(t\text{-}C_4H_9NC)_2Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$. To an acetone solution (5 mL) of $[Rh_2(CO)_2Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$ (0.200 g, 0.152 mmol) was added 0.025 g (0.303 mmol) of *tert*-butyl isocyanide dropwise with stirring. Addition of diethyl ether and petroleum ether to the resulting red orange solution precipitated the product as fluffy orange-yellow microcrystals which were filtered off, washed with diethyl ether, and dried in vacuo.

$[Rh_2(CO)(t\text{-}C_4H_9NC)_4((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](B(C_6H_5)_4)_2\cdot(CH_3)_2CO$. Carbon monoxide was bubbled through an acetone solution (5 mL) of $[Rh_2(t\text{-}C_4H_9NC)_4((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](B(C_6H_5)_4)_2$ (0.150 g, 0.077 mmol) whereupon the color changed from magenta to orange. Addition of petroleum ether while the CO flow was maintained precipitated the product as bright yellow crystals which were filtered off, washed with petroleum ether, and dried in a stream of carbon monoxide.

$[Rh_2(SO_2)(t\text{-}C_4H_9NC)_4((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](B(C_6H_5)_4)_2$. An acetone solution (5 mL) containing 0.150 g (0.077 mmol) of $[Rh_2(t\text{-}C_4H_9NC)_4((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](B(C_6H_5)_4)_2$ was stirred under an atmosphere of sulfur dioxide for 5 min during which time the color rapidly changed from magenta to yellow-orange. Addition of diethyl ether precipitated a voluminous yellow solid which became orange when filtered and washed with diethyl ether. The orange crystals so obtained appeared stable to the atmosphere.

$[Rh_2(SO_2)(t\text{-}C_4H_9NC)_4((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2](B(C_6H_5)_4)_2$. This was prepared in an analogous fashion to the previous complex from $[Rh_2(t\text{-}C_4H_9NC)_4((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2](B(C_6H_5)_4)_2$ and SO_2 in tetrahydrofuran. Addition of diethyl ether produced a voluminous yellow solid which was collected and recrystallized from dichloromethane to give the product as orange crystals.

$[Ir_2(CO)_2Cl_2((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]$. To a solution of 0.210 g (0.446 mmol) of bis(diphenylarsino)methane in 25 mL of acetone under an atmosphere of CO was added 0.200 g (0.223 mmol) of $[IrCl(c\text{-}C_8H_{14})_2]_2$ in small increments. The resulting yellow solution was concentrated to ca. 3 mL under reduced pressure during which time it became dark red and magenta crystals formed. These were filtered off, washed with diethyl ether, and dried in vacuo. The complex can also be prepared by refluxing $[Ir_2(CO)_4Cl(DAM)_2]PF_6$ in acetone under nitrogen. It is stable under nitrogen but decomposes to a grey material on contact with air.

$[Ir_2(CO)_4Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$. A solution of hydrated Ir(III) chloride (0.200 g, 0.670 mmol) in 15 mL of 2-methoxyethanol containing 0.5 mL of water was refluxed under an atmosphere of CO until it had become lemon yellow (4–6 h). After it was cooled to room temperature, the resulting pale yellow solution was transferred via a stainless steel cannula into a solution of 0.331 g (0.700 mmol) of bis(diphenylarsino)methane and 0.121 g (0.340 mmol) of $NaB(C_6H_5)_4$ in 20 mL of tetrahydrofuran under pressure of CO. Following concentration of the reaction mixture under CO to the appearance of crystals, water was added to complete the precipitation. The yellowish solid was filtered, washed with water and ethanol, redissolved in dichloromethane, and filtered through a pad of diatomaceous earth under CO pressure. Addition of diethyl ether and hexane to this solution under CO precipitated the product as pale yellow microcrystals which were filtered off, washed with CO-saturated diethyl ether, and dried in a CO stream. The complex is stable under CO but turns orange if CO is not present.

$[Ir_2(CO)_3Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4\cdot 0.5CH_2Cl_2$. Dinitrogen was bubbled through a dichloromethane solution of $[Ir_2(CO)_4Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$ for 6 h. Addition of diethyl ether to the resulting red-orange solution precipitated the product as orange crystals which were filtered off, washed with diethyl ether, and dried in vacuo. The complex can also be prepared by heating solid $[Ir_2(CO)_4Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$ at 60 °C in vacuo for 36 h.

$[Ir_2(CO)_3(t\text{-}C_4H_9NC)Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$. To a suspension of 0.200 g (0.125 mmol) of $[Ir_2(CO)_3Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$ in 10 mL of tetrahydrofuran was added 0.011 g (0.125 mmol) of *tert*-butyl isocyanide dissolved in a few drops of tetrahydrofuran. The yellow suspension rapidly lightened and slowly (ca. 2 h) dissolved to give a pale yellow solution. Addition of diethyl ether precipitated the product as white crystals which were filtered off, washed with diethyl ether, and dried in a stream of dinitrogen.

$[Ir_2(CO)_2(t\text{-}C_4H_9NC)_2Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$. This was prepared in an analogous fashion to the previous compound with the addition of 0.022 g (0.250 mmol) of *tert*-butyl isocyanide. After it was stirred for 4 h, the cloudy solution was filtered through a pad of diatomaceous earth. Addition of diethyl ether and hexane precipitated the product as pale pink crystals which were filtered off, washed with diethyl ether, and dried in a stream of dinitrogen.

$[Ir_2(CO)(t\text{-}C_4H_9NC)_4((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](B(C_6H_5)_4)_2$. To a suspension of 0.2 g (0.125 mmol) of $[Ir_2(CO)_3Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$ in 10 mL of tetrahydrofuran was added 0.055 g (0.625 mmol) of *tert*-butyl isocyanide dissolved in a few drops of hexane. The solid dissolved to give a yellow solution to which was added 0.077 g (0.223 mmol) of sodium tetraphenylborate. Filtration of the cloudy solution through a pad of diatomaceous earth followed by reduction of the volume under reduced pressure and dilution with diethyl ether afforded the product as very pale yellow crystals. These were recrystallized from tetrahydrofuran–diethyl ether and dried in vacuo.

$[Ir_2(CO)_3(t\text{-}C_4H_9NC)Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]BF_4$. To a suspension of 0.2 g (0.128 mmol) of $[Ir_2(CO)_4Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]BF_4$ (prepared as for the tetraphenylborate salt but by using $NaBF_4$ in place of $NaB(C_6H_5)_4$ and identified by its infrared spectrum) in 10 mL of dichloromethane was added 0.011 g (0.128 mmol) of *tert*-butyl isocyanide dissolved in a few drops of hexane. The mixture was stirred for 1 h by which time the solid had dissolved to give a yellow solution. Addition of diethyl ether precipitated a pale pink solid which was filtered off, washed with diethyl ether, and dried with a stream of carbon monoxide.

$[Ir_2(CO)_2(t\text{-}C_4H_9NC)_2Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]BF_4$. This was prepared analogously to the previous complex but with the addition of 0.022 g (0.256 mmol) of *tert*-butyl isocyanide. After it was stirred for 1 h, the cloudy mixture was filtered through a pad of diatomaceous earth to give a yellow-orange solution. Addition of diethyl ether yielded the product as off-white crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

$[Ir_2(CO)(t\text{-}C_4H_9NC)_4((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2](B(C_6H_5)_4)_2$. To a suspension of 0.2 g (0.111 mmol) of $[Ir_2(CO)_4Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$ in 10 mL of tetrahydrofuran was added 0.046 g (0.555 mmol) of *tert*-butyl isocyanide dissolved in tetrahydrofuran. Upon stirring under reduced pressure the solid dissolved to give a pale yellow solution. To this solution was added 0.0395 g (0.111 mmol) of $NaB(C_6H_5)_4$ dissolved in tetrahydrofuran followed by filtration through a pad of diatomaceous earth. Addition of diethyl ether precipitated the product as pale yellow crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

Results and Discussion

Analytical, infrared, and NMR spectroscopic data for the complexes are presented in Tables I–V, respectively, while Table VII lists their electronic spectra. Conductivity data are given in Table VI and confirm the proposed formulations of the complexes as either 1:1 or 1:2 electrolytes.

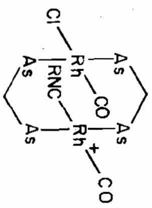
Rhodium Complexes. Treatment of an ethanolic solution of $[Rh(CO)_2Cl_2]^-$ with equimolar quantities of bis(diphenylarsino)methane (DAM) and ammonium hexafluorophosphate in a carbon monoxide atmosphere yielded yellow crystals. The original sample showed only terminal carbonyl absorptions (Table II) which are essentially identical with those observed for $[Rh_2(CO)_2(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$[11], and on

Table I. Analytical Data

no.	complex	% found				% calcd				mp, °C	yield, %
		C	H	Cl	N	C	H	Cl	N		
1	$[Rh_2(CO)_2Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]PF_6$	46.4	3.85	2.9		45.03	3.20	2.56		265 dec	90
2	$[Rh_2(CO)_2(CNC(CH_3)_3)Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]PF_6\cdot 0.5(CH_3)_2CO$	46.8	3.9	2.9	0.8	47.89	3.86	2.42	0.95	165 dec	71
3	$[Rh_2(CO)(CNC(CH_3)_3)_2Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$	58.9	5.0	2.2	1.4	60.07	4.87	2.09	1.65	156	82
4	$[Rh_2(CNC(CH_3)_3)_4((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2](B(C_6H_5)_4)_2$	68.2	5.9		2.5	66.93	5.53		2.65	180 dec	85
5	$[Rh_2(CO)_2(CNC(CH_3)_3)Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$	64.7	5.1	2.95	0.95	66.24	5.02	2.41	0.95	139 dec	83
6	$[Rh_2(CO)(CNC(CH_3)_3)_2Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$	66.35	5.5	2.35	1.8	67.00	5.44	2.33	1.84	211 dec	88
7	$[Rh_2(CO)(CNC(CH_3)_3)_4((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](B(C_6H_5)_4)_2\cdot(CH_3)_2CO$	71.3	6.5		2.5	72.66	6.08		2.76	167	92
8	$[Rh_2(SO_2)(CNC(CH_3)_3)_4((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](B(C_6H_5)_4)_2$	68.35	6.2		2.7	70.66	5.83		2.79	183 dec	76
10	$[Rh_2(SO_2)(CNC(CH_3)_3)_4((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2](B(C_6H_5)_4)_2$	64.1	5.7		2.4	64.96	5.36		2.57	189 dec	82
11	$[Ir_2(CO)_2Cl_2((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]$	42.0	3.2	4.75		42.89	3.05	4.87		252 dec	68
12	$[Ir_2(CO)_4Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4$	51.7	3.4	2.5		52.16	3.60	1.97		166 dec	75
13	$[Ir_2(CO)_3Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]B(C_6H_5)_4\cdot 0.5CH_2Cl_2$	51.4	3.9	4.25		51.42	3.57	3.92		184 dec	60
14	$[Ir_2(CO)_3(CNC(CH_3)_3)Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$	58.0	4.4	2.3	0.8	58.79	4.40	2.12	0.84	178 dec	88
15	$[Ir_2(CO)_2(CNC(CH_3)_3)_2Cl((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$	61.6	5.5	2.1	1.6	59.69	4.79	2.05	1.62	165 dec	68
16	$[Ir_2(CO)(CNC(CH_3)_3)_4((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](B(C_6H_5)_4)_2$	66.7	5.85		2.7	66.40	5.63		2.60	190 dec	92
17	$[Ir_2(CO)_3(CNC(CH_3)_3)Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]BF_4$	41.0	3.6	2.4	0.9	43.04	3.31	2.19	0.87	170 dec	73
18	$[Ir_2(CO)_2(CNC(CH_3)_3)_2Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2]BF_4$	42.7	3.9	2.1	1.75	44.49	3.74	2.12	1.67	164 dec	78
19	$[Ir_2(CO)(CNC(CH_3)_3)_4((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2](B(C_6H_5)_4)_2$	61.1	5.3		2.3	61.50	5.03		2.41	183 dec	90

the basis of this and the analytical data the product is formulated as $[Rh_2(CO)_2(\mu\text{-}Cl)(DAM)_2]PF_6$ (**1**). In subsequent preparations, the isolated yellow crystals sometimes showed an additional carbonyl band at 1864 cm^{-1} indicative of the presence of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DAM)_2]PF_6$; however, on standing overnight this band disappeared, indicating that CO loss occurs readily even in the solid state. This behavior contrasts with that observed for $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(L_2)_2]B(C_6H_5)_4$ (L_2 = DPM, DAM)[11] and $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]PF_6$ (prepared as for **1**; ν_{CO} = 2001 (sh), 1978 (vs), 1876 (m) cm^{-1} (Nujol mull)) which are all stable to CO loss in the solid state. In solution **1** is readily converted to the tricarbonyl (ν_{CO} = 2000 (sh), 1986 (vs), 1876 (w) cm^{-1} (CH_2Cl_2 solution)). A possible explanation may be that, because of the larger size of DAM as compared with DPM, attachment of a carbonyl ligand in the bridging position is rather weak and that packing considerations in the solid may dictate a more stable structure for the dicarbonyl cation when it is combined with the more compact hexafluorophosphate ion. We have previously demonstrated that CO exchange in $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DAM)_2]^+$ is considerably more facile than in the DPM analogue which together with the bridge–terminal exchange mechanism for the process[11] is consistent with this proposal.

This difference in the lability of the bridging carbonyl ligand between the A-frame complexes of DPM and DAM is also evident in the reactions of $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]^+$ (L_2 = DPM, DAM) with *tert*-butyl isocyanide where a bridging carbonyl is found in the phosphine complexes but not in those with the arsine ligand. The reaction of **1** with 1 equiv of *t*-BuNC yields orange crystals analyzing as $[Rh_2(CO)_2(t\text{-}BuNC)Cl(DAM)_2]PF_6\cdot 0.5(CH_3)_2CO$ (**2**). The spectroscopic data in Table II show that only terminal carbonyl and isocyanide ligands are present, and this is confirmed by preparation of the ^{13}CO-labeled derivative ($\nu_{^{13}C\equiv O}$ = 1959 (vs), 1910 (vs) cm^{-1}; $\nu_{C\equiv N}$ = 2209 cm^{-1}). The large separation between the carbonyl absorptions indicates that they are bound to different metals and that they are *trans* to different ligands. This is also evident from the $^{13}C\{^1H\}$ NMR spectrum of a 90% ^{13}CO-enriched sample. The lower energy CO band is comparable to that observed in a wide variety of complexes of the type *trans*-$[Rh(CO)Cl(L)_2]$ (L = tertiary phosphine or arsine)[20] and in particular to that for $[Rh(CO)Cl(DAM)]_2$ ($\nu_{C\equiv O}$ = 1965 cm^{-1}).[21] The high energy of the other CO absorption together with the high energy of C≡N stretching vibration is consistent with the presence of a trans *t*-BuNC–Rh–CO unit in which the metal carries a formal positive charge although there do not appear to be any data available for direct comparison. From these considerations we propose that **2** be formulated as



R = *t*-Bu

2

Unfortunately interference from ligand absorptions prevented identification of ν_{Rh-Cl}, but since only terminal carbonyl and isocyanide ligands are present, it is more reasonable to propose a terminal chloride since each metal then attains a 16-electron configuration whereas retention of a bridging chloride would

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(20) L. M. Vallarino, *J. Chem. Soc.*, 2287 (1957); J. Chatt and B. L. Shaw, *J. Chem. Soc. A*, 1437 (1966); A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. M. Stainbank, *ibid.*, 1826 (1971); B. E. Mann, C. Masters, and B. L. Shaw, *ibid.*, 1104 (1971).

(21) J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, **8**, 119 (1969).

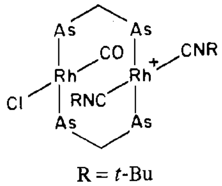
Table II. Infrared Spectral Data

complex[a]	infrared abs maxima, cm^{-1} [b]	assignt
$[Rh_2(CO)_2Cl(DAM)_2]PF_6$	1983 (s), 1968 (vs)	ν_{CO}
$[Rh_2(CO)_2(L)Cl(DAM)_2]PF_6$	2007 (s), 1955 (vs)	ν_{CO}
	2210 (m)	ν_{CN}
$[Rh_2(CO)(L)_2Cl(DAM)_2]B(C_6H_5)_4$	1974 (sh), 1957 (vs) [1984 (sh), 1967 (vs)][c]	ν_{CO}
	2186 (w), 2140 (s) [2179 (w), 2139 (s)][c]	ν_{CN}
$[Rh_2L_4(DAM)_2](B(C_6H_5)_4)_2$	2174 (sh), 2126 (vs)	ν_{CN}
$[Rh_2(CO)_2(L)Cl(DPM)_2]B(C_6H_5)_4$	1970 (vs), 1855 (m), 1820 (sh) [1984 (s), 1854 (w)][c]	ν_{CO}
	2152 (m) [2142 (m)][c]	ν_{CN}
$[Rh_2(CO)(L)_2Cl(DPM)_2]B(C_6H_5)_4$	1827 (m) [1826 (m)][c]	ν_{CO}
	2155 (s) [2125 (s)][c]	ν_{CN}
$[Rh_2(CO)(L)_4(DPM)_2](B(C_6H_5)_4)_2$	1759 (m) [1765 (m)]	ν_{CO}
	2150 (sh), 2135 (s) [2146 (s)]	ν_{CN}
$[Rh_2(SO_2)(L)_4(DPM)_2](B(C_6H_5)_4)_2$	2200 (sh), 2171 (vs) [2184 (s), 2172 (vs)]	ν_{CN}
	1161 (m), 1033 (m)	ν_{SO}
$[Rh_2(CO)(L)_4(DAM)_2](B(C_6H_5)_4)_2$	[1825 (w)]	ν_{CO}
	[2166 (m)]	ν_{CN}
$[Rh_2(SO_2)(L)_4(DAM)_2](B(C_6H_5)_4)_2$	2178 (sh), 2166 (s) [2194 (s), 2182 (sh)]	ν_{CN}
	1168 (m), 1040 (m)	ν_{SO}
$[Ir_2(CO)_2Cl_2(DAM)_2]$	1940 (vs) [1960 (s)]	ν_{CO}
$[Ir_2(CO)_4Cl(DAM)_2]B(C_6H_5)_4$	2042 (m), 1992 (s), 1975 (vs), 1790 (m) [2040 (w), 1997 (sh), 1987 (s), 1765 (m)][c]	ν_{CO}
$[Ir_2(CO)_3Cl(DAM)_2]B(C_6H_5)_4$	1974 (sh), 1950 (s), 1816 (m) [1987 (sh), 1967 (s), 1822 (m)]	ν_{CO}
$[Ir_2(CO)_3(L)Cl(DPM)_2]B(C_6H_5)_4$	1980 (s), 1966 (s), 1728 (m) [1998 (sh), 1985 (vs), 1747 (m)]	ν_{CO}
	2180 (m) [2184 (m)]	ν_{CN}
$[Ir_2(CO)_2(L)_2Cl(DPM)_2]B(C_6H_5)_4$	1978 (s), 1717 (m) [1974 (s), 1720 (m)]	ν_{CO}
	2179 (m), 2126 (s) [2169 (m), 2136 (s)]	ν_{CN}
$[Ir_2(CO)(L)_4(DPM)_2](B(C_6H_5)_4)_2$	1706 (m) [1703 (m)]	ν_{CO}
	2175 (sh), 2132 (vs) [2152 (sh), 2140 (vs)]	ν_{CN}
$[Ir_2(CO)_3(L)Cl(DAM)_2]BF_4$	1966 (sh), 1958 (vs), 1733 (m) [1992 (sh), 1978 (vs), 1741 (m)]	ν_{CO}
	2182 (m) [2180 (m)]	ν_{CN}
$[Ir_2(CO)_2(L)_2Cl(DAM)_2]BF_4$	1954 (vs), 1709 (s) [1972 (vs), 1722 (m)]	ν_{CO}
	2174 (m), 2134 (vs) [2168 (m), 2130 (s)]	ν_{CN}
$[Ir_2(CO)(L)_4(DAM)_2](B(C_6H_5)_4)_2$	1704 (s) [1702 (s)]	ν_{CO}
	2149 (sh), 2133 (vs) [2146 (sh), 2132 (vs)]	ν_{CN}

[a] DAM = $(C_6H_5)_2AsCH_2As(C_6H_5)_2$; DPM = $(C_6H_5)_2PCH_2P(C_6H_5)_2$; L = $(CH_3)_3CNC$. [b] Unbracketed values in Nujol mulls, bracketed values in CH_2Cl_2 solution unless otherwise noted. Key: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [c] Tetrahydrofuran solution.

lead to 16- and 18-electron counts, respectively, which seems less likely. Finally, although the data do not unequivocally establish the cis arrangement of the carbonyl groups, this is probable since it requires the minimum of molecular motion to produce from the A-frame precursor.

The addition of 2 equiv of *t*-BuNC to $[Rh_2(CO)_2(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$ yields burgundy crystals analyzing as $[Rh_2(CO)(t\text{-}BuNC)_2Cl(DAM)_2]B(C_6H_5)_4$ (**3**). Again, only terminal carbonyl and isocyanide ligands are present as confirmed by ^{13}CO labeling ($\nu_{^{13}C{\equiv}O}$ = 1913 (s) cm^{-1}; $\nu_{C{\equiv}N}$ = 2138 (s) cm^{-1}). Of particular note is the observation that $\nu_{C{\equiv}O}$ and δ_{CO} for **3** are each very similar to one of the values found for **2** which suggests that the environment about one metal is the same in **3** as in **2**. Following our previous argument, the low energy of $\nu_{C{\equiv}O}$ suggests the presence of a trans Cl–Rh–CO moiety and we propose the structure



R = *t*-Bu
3

Consistent with this is the much lower value of $\nu_{C{\equiv}N}$ as compared with that in **2**, but a value which is comparable to that observed in $[Rh_2(t\text{-}BuNC)_4(DPM)_2](PF_6)_2$[3] where the trans $RNC\text{-}Rh^+\text{-}CNR$ moiety is present. Again, it was not possible to identify ν_{Rh-Cl}, but as for **2** the presence of a terminal chloride ligand is more reasonable as it gives both metals the same electron count.

In all preparations of **3** the infrared spectrum showed weak bands attributable to $\nu_{C{\equiv}O}$ and $\nu_{C{\equiv}N}$ at somewhat higher energies than the main absorptions (Table II). While these may be due to a small proportion of the isomer resulting from isocyanide substitution trans to chloride, there is no evidence from the ^{13}C NMR spectra to indicate its presence. Thus the origin of these bands is uncertain.

Attempts to prepare a tris(isocyanide) derivative of the $[Rh_2(CO)_2(\mu\text{-}Cl)(DAM)_2]^+$ cation by adding 3 equiv of *t*-BuNC were unsuccessful as only $[Rh_2(CO)(t\text{-}BuNC)_2Cl(DAM)_2]^+$ was obtained according to infrared spectral evidence. However, if 4 equiv or more of the isocyanide are added to $[Rh_2(CO)_2(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$ in the presence of 1 equiv of $NaB(C_6H_5)_4$, the intensely blue-violet complex $[Rh_2(t\text{-}BuNC)_4(DAM)_2](B(C_6H_5)_4)_2$ (**4**) can be obtained. From the data in Tables II and III, this is clearly the arsine analogue of $[Rh_2(t\text{-}BuNC)_4(DPM)_2](B(C_6H_5)_4)_2$ which has previously been extensively studied.[3] Unlike the latter complex however, **4** cannot be prepared from $[Rh(t\text{-}BuNC)_4]B(C_6H_5)_4$ as the DAM ligand appears incapable of replacing isocyanide ligands even in refluxing tetrahydrofuran. While this work was in progress a similar preparation of this complex was reported.[22]

The course of the reaction of *t*-BuNC with the phosphine complex $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$ is different from that described above. Upon addition of 1 equiv of the isocyanide, the yellow complex analyzing as $[Rh_2(CO)_2(t\text{-}BuNC)Cl(DPM)_2]B(C_6H_5)_2$ (**5**) is obtained whose infrared and $^{13}C\{^1H\}$ NMR spectra show the presence of both terminal and bridging carbonyl ligands. The infrared spectrum of the ^{13}CO-labeled derivative confirms this and also confirms that the isocyanide is a terminal ligand ($\nu_{^{13}CO}$ = 1922 (vs), 1812

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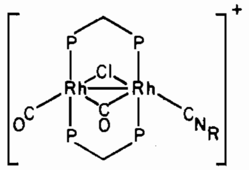
[22] A. L. Balch, J. W. Labadie, and G. Delker, *Inorg. Chem.*, **18**, 1224 (1979).

Table III. ^{1}H NMR Chemical Shifts[a]

complex[b]	τ[c]	assignt
$[Rh_2(CO)_2(L)Cl(DAM)_2]PF_6$	9.48 (s, 9 H)	$C(CH_3)_3$
	6.58 (br, 4 H)	CH_2
$[Rh_2(CO)(L)_2Cl(DAM)_2]B(C_6H_5)_4$	9.38 (s, 18 H)	$C(CH_3)_3$
	6.38 (s, 4 H)	CH_2
$[Rh_2(L)_4(DAM)_2](B(C_6H_5)_4)_2$	9.25 (s, 36 H)	$C(CH_3)_3$
	6.64 (s, 4 H)	CH_2
$[Rh_2(CO)_2(L)Cl(DPM)_2]B(C_6H_5)_4$	9.49 (s, 9 H)	$C(CH_3)_3$
	6.40 (br, 4 H)	CH_2
$[Rh_2(CO)(L)_2Cl(DPM)_2]B(C_6H_5)_4$	9.46 (s, 18 H)	$C(CH_3)_3$
	6.48 (br, 4 H)	CH_2
$[Rh_2(CO)(L)_4(DPM)_2](B(C_6H_5)_4)_2$	9.20 (s, 18 H), 8.88 (s, 18 H)	$C(CH_3)_3$
	6.38 (br, 4 H)	CH_2
$[Rh_2(SO_2)(L)_4(DPM)_2](B(C_6H_5)_4)_2$	9.16 (s, 18 H), 9.24 (s, 18 H)	$C(CH_3)_3$
	5.88 (br, 4 H)	CH_2
$[Rh_2(SO_2)(L)_4(DAM)_2](B(C_6H_5)_4)_2$	9.27 (s, 18 H), 9.14 (s, 18 H)	$C(CH_3)_3$
	6.48 (AB, 4 H)	CH_2
$[Ir_2(CO)_3(L)Cl(DPM)_2]B(C_6H_5)_4$	8.92 (s, 9 H)	$C(CH_3)_3$
	5.42 (br, 4 H)	CH_2
$[Ir_2(CO)_2(L)_2Cl(DPM)_2]B(C_6H_5)_4$	8.90 (s, 9 H), 8.96 (s, 9 H)	$C(CH_3)_3$
	5.60 (br, 4 H)	
$[Ir_2(CO)(L)_4(DPM)_2](B(C_6H_5)_4)_2$	8.84 (s, 18 H), 9.25 (s, 18 H)	$C(CH_3)_3$
	6.48 (br, 4 H)	CH_2
$[Ir_2(CO)_3(L)Cl(DAM)_2]BF_4$	9.02 (s, 9 H)	$C(CH_3)_3$
	5.50 (AB, 4 H)	CH_2
$[Ir_2(CO)_2(L)_2Cl(DAM)_2]BF_4$	9.01 (s, 18 H)	$C(CH_3)_3$
	5.24 (AB)	CH_2
$[Ir_2(CO)(L)_4(DAM)_2](B(C_6H_5)_4)_2$	8.91 (s, 18 H), 9.26 (s, 18 H)	$C(CH_3)_3$
	6.16 (AB, 4 H)	CH_2

[a] Recorded in CD_2Cl_2 solution. Key: s, singlet; br, broad; AB, second-order AB pattern. [b] DPM = $(C_6H_5)_2PCH_2P(C_6H_5)_2$; DAM = $(C_6H_5)_2AsCH_2As(C_6H_5)_2$; L = $(CH_3)_3CNC$. [c] Referred to tetramethylsilane (internal, τ = 10.0). Number in parentheses indicates number of protons.

(m) cm^{-1}; $\nu_{C\equiv N}$ = 2152 (m) cm^{-1} (Nujol mull)). The ^{13}C NMR spectrum (90% ^{13}CO enriched) in the carbonyl region is exceedingly complex. The resonance for the terminal carbonyl shows a major splitting due primarily to $^1J_{Rh-C}$ which is of the expected magnitude. That for the bridging carbonyl contains 25 identifiable lines but without the clearly defined triplet pattern ($^1J_{Rh-C}$) that is observed for the bridging carbonyl ligand in symmetrical systems such as $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$.[11] Because of the large number of spins and coupling constants in this system it is difficult to predict what the appearance of this resonance should be, but clearly the complex is not symmetrical. This is further supported by the $^{31}P\{^1H\}$ NMR spectrum which is an extremely complex second-order pattern with no apparent symmetry, centered at approximately 27 ppm downfield from H_3PO_4. This is in contrast to the highly symmetric spectra observed for the other rhodium DPM complexes studied here (vide infra) and previously.[11] Because of its complexity and modest resolution we have not attempted an analysis. From these data the most reasonable structure for **5** is



R = *t*-Bu

5

This is also the structure which would be anticipated on the basis of the proposed mechanism[11] for the formation of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$ from $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$ and in fact provides further support for this mechanism. Thus attack by the isocyanide adjacent to one terminal carbonyl causes the latter to assume a bridging role.

Like $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$, **5** loses CO in solution. Thus on flushing of a tetrahydrofuran solution with nitrogen, the pale orange solution darkens considerably and the infrared spectrum now shows only two strong bands at 2132 (ν_{CN}) and 1983 (ν_{CO}) cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of this species (centered at 29.3 ppm) more closely resembles the AA'A''A'''XX' spectra discussed below but is still noticeably asymmetric. On the basis of the spectroscopic data and by analogy with $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$ we suggest that this species is $[Rh_2(CO)(CNC(CH_3)_3)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$.

The bis(isocyanide) complex $[Rh_2(CO)(t\text{-}BuNC)_2Cl(DPM)_2]B(C_6H_5)_4$ (**6**) results from reaction of $[Rh_2(CO)_2$-

Table IV. ^{13}C NMR Chemical Shifts[a]

complex[b]	$\delta(^{13}C)$[c]	assignt	T, °C
$[Rh_2(CO)_2(L)Cl(DAM)_2]PF_6$	193.3 (d, $^1J_{Rh-C}$ = 60.5 Hz)	CO(terminal)	−39.5
	186.3 (d, $^1J_{Rh-C}$ = 70.3 Hz)	CO(terminal)	
$[Rh_2(CO)(L)_2Cl(DAM)_2]B(C_6H_5)_4$	187.2 (d, $^1J_{Rh-C}$ = 67.4 Hz)	CO(terminal)	−39.5
$[Rh_2(CO)_2(L)Cl(DPM)_2]B(C_6H_5)_4$	204.5 (m)	CO(bridge)	−68
	187.1 (m)	CO(terminal)	
$[Rh_2(CO)(L)_2Cl(DPM)_2]B(C_6H_5)_4$	212.1 (m)	CO(bridge)	30
$[Rh_2(CO)(L)_4(DPM)_2](B(C_6H_5)_4)_2$	242.9 (tq, $^1J_{Rh-C}$ = 38.1, $^2J_{P-C}$ = 8.8 Hz)	CO(bridge)	−37.5
$[Rh_2(CO)(L)_4(DAM)_2](B(C_6H_5)_4)_2$	231.7 (br)	CO(bridge)	−75
$[Ir_2(CO)_2Cl_2(DAM)_2]$	168.8 (s)	CO(terminal)	−30
$[Ir_2(CO)_4Cl(DAM)_2]B(C_6H_5)_4$	198.4 (m)	CO(bridge)	−57
	170.6 (m), 168.5 (m), 166.8 (m)	CO(terminal)	
$[Ir_2(CO)_3Cl(DAM)_2]B(C_6H_5)_4$	180.8 (t, $^2J_{C_b-C_t}$ = 12.2 Hz)	CO(bridge)	−57
	170.4 (d, $^2J_{C_b-C_t}$ = 12.2 Hz)	CO(terminal)	
$[Ir_2(CO)_3(L)Cl(DPM)_2]B(C_6H_5)_4$	204.7 (m)	CO(bridge)	−30
	171.5 (m)	CO(terminal)	
$[Ir_2(CO)_2(L)_2Cl(DPM)_2]B(C_6H_5)_4$	212.7 (m)	CO(bridge)	−33
	171.5 (m)	CO(terminal)	
$[Ir_2(CO)(L)_4(DPM)_2](B(C_6H_5)_4)_2$	230.4 (q, $^2J_{P-C}$ = 6.2 Hz)	CO(bridge)	25
$[Ir_2(CO)_3(L)Cl(DAM)_2]BF_4$	202.8 (s)	CO(bridge)	−61
	169.7 (s), 169.2 (s)	CO(terminal)	
$[Ir_2(CO)(L)_4(DAM)_2](B(C_6H_5)_4)_2$	230.2 (s)	CO(bridge)	30

[a] Recorded in CD_2Cl_2 solution. [b] DPM = $(C_6H_5)_2PCH_2P(C_6H_5)_2$; DAM = $(C_6H_5)_2AsCH_2As(C_6H_5)_2$; L = $(CH_3)_3CNC$. [c] Referred to tetramethylsilane (external, δ 0.0) and positive downfield. Key: s, singlet; d, doublet; t, triplet; q, quintet; tq, triplet of quintets; br, broad; m, multiplet.

Table V. ^{31}P NMR Chemical Shifts[a]

complex[b]	$\delta(^{31}P)$[c]	$^1J_{Rh-P}$	$^2J_{P-Rh-P}$	$^2J_{P-C-P}$	$^4J_{P-P}$	$^xJ_{Rh-P}$[d]	$^1J_{Rh-Rh}$	T, °C
$[Rh_2(CO)(L)_2Cl(DPM)_2]B(C_6H_5)_4$	31.3	106.9	390	82.4	21.9	0.8	0.0	−60
$[Rh_2(CO)(L)_4(DPM)_2](B(C_6H_5)_4)_2$	21.1	88.9	327	78.2	21.9	−1.6	0.0	−12
$[Rh_2(SO_2)(L)_4(DPM)_2](B(C_6H_5)_4)_2$	18.5	91.0	329	58.6	27.2	−1.2	0.0	−28
$[Ir_2(CO)_3(L)Cl(DPM)_2]B(C_6H_5)_4$	−11.6, −17.7 (AA′BB′ pattern)							−30
$[Ir_2(CO)_2(L)_2Cl(DPM)_2]B(C_6H_5)_4$	−11.4, −19.0 (AA′BB′ pattern)							−30
$[Ir_2(CO)(L)_4(DPM)_2](B(C_6H_5)_4)_2$	11.4 (d, $^2J_{P-C}$ = 6.2 Hz)							30

[a] Recorded in CD_2Cl_2 solution. [b] DPM = $(C_6H_5)_2PCH_2P(C_6H_5)_2$, L = $(CH_3)_3CNC$. [c] Referred to 85% H_3PO_4 (external, δ 0.0) and positive downfield. Key: d, doublet. All coupling constants in Hz. [d] Corresponds to $J_{AX'}$ of the AA′A″A‴XX′ spin system.

Table VI. Conductivity Data on Complexes

complex	concn × 10^3, M[a]	Λ_m, Ω^{-1} cm^2 mol^{-1}
1	1.32	127
2	1.00	128
3	1.42	82
4	1.13	171
5	1.16	73
6	1.10	66
7	0.25	185
8	1.05	169
10	0.79	156
14	1.12	84
15	1.02	98
16	1.04	174
17	0.75	125
18	0.99	135
19	0.85	174

[a] Acetone solution.

Table VII. Electronic Absorption Spectra[a]

complex	λ_{max}[c] (ε)
$[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$	373 (7980), 290 sh (17 600), 275 sh (23 300)
$[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$	360 (5560)
$[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$	443 (6050), 313 sh (8830), 278 sh (18 600), 261 sh (27 400)
$[Rh_2(CO)_2(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$	430 (6890), 303 sh (13 500)
2	503 sh (3420), 437 (4810), 385 (3620), 302 (10 800)
3	513 (7810), 450 sh (5970), 380 (4590), 306 (17 900)
4	515 (15 700), 385 (6670), 328 (21 800) 315 (18 800)
5	363 (10 800)
6	366 (9040), 300 sh (13 750)
7	382 (7460), 328 sh (9710), 308 (17 100)
8	456 sh (4850), 410 (8010)
9	384 (8940), 309 (26 400), 288 sh (27 000)
10	466 sh (2640), 408 (4940)
11[b]	530 (5360), 384 (2360)
$[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$	335 (9000)
13[b]	348 (4980)
16	319 (5500)
19	335 (5180)

[a] Dichloromethane solution unless otherwise noted. [b] Tetrahydrofuran solution. [c] nm.

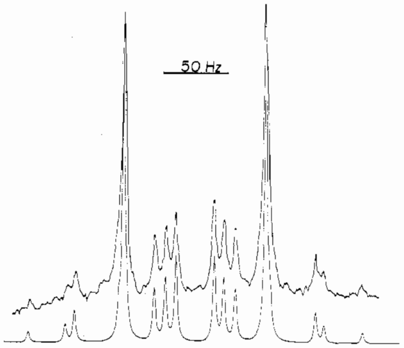
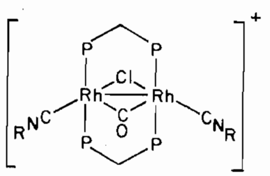


Figure 1. Observed (−60 °C) and calculated $^{31}P\{^1H\}$ NMR spectrum of $[Rh_2(t\text{-}C_4H_9NC)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$ (**5**).

$(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$ with 2 equiv of t-BuNC. The infrared and ^{13}C NMR spectra indicate that the remaining carbonyl ligand is bridging, and this is confirmed by the infrared spectrum of the ^{13}CO-labeled derivative ($\nu_{^{13}CO}$ = 1787 (s) cm^{-1}; $\nu_{C{\equiv}N}$ = 2129 cm^{-1} (Nujol mull)). These latter data also confirm that the isocyanide ligands are terminal. In contrast to that for **5**, the $^{31}P\{^1H\}$ NMR spectrum of **6** (Figure 1) is a symmetrical second-order pattern quite similar to the spectrum of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$.[11] This spectrum has been successfully analyzed as an AA′A″A‴XX′ system and the derived coupling constants are presented in Table V. Because of the large value of $^2J_{P-Rh-P}$, the appearance of the spectrum is relatively insensitive to the magnitude of this parameter, and hence it cannot be accurately determined. Nevertheless, it is in the range previously observed for such coupling constants.[35] The $^{13}CO\{^1H\}$ NMR spectrum (90% ^{13}CO enriched) appears as a triplet of multiplets, indicating equivalent coupling to two rhodium atoms. All these data are consistent with the symmetrical structure



R = t-Bu
6

A particularly interesting feature of the analysis of the ^{31}P

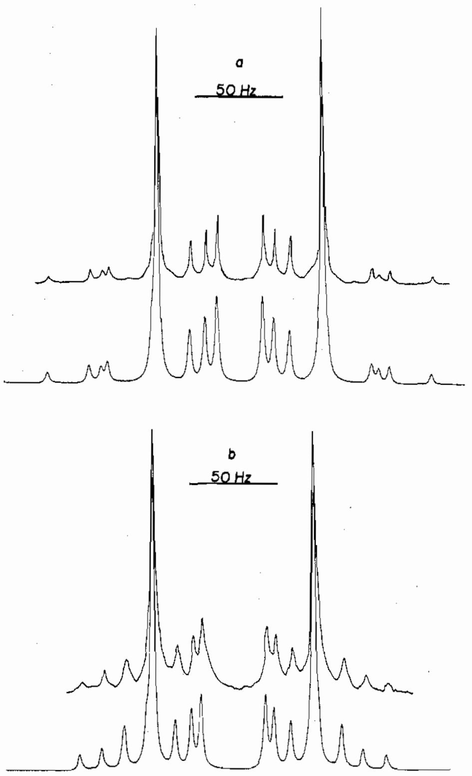
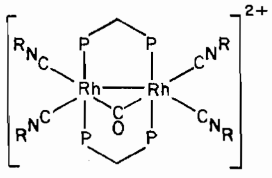


Figure 2. Observed (−24 °C) and calculated $^{31}P\{^1H\}$ NMR spectra of (a) $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$ and (b) $[Rh_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$.

NMR spectrum of **5** is the absence of any direct rhodium–rhodium coupling. This result was at first surprising in light of our previous analysis of the ^{31}P NMR spectra of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$ and $[Rh_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-}Cl)(DPM)_2]^+$ where substantial values were obtained for $^1J_{Rh-Rh}$.[11] We therefore undertook a reanalysis of the spectra of these complexes and present the observed and calculated spectra in Figure 2. The relevant parameters are δ(P) = 25.5 ($^1J_{Rh-P}$ = 93.4, $^2J_{P-Rh-P}$ = 355, $^2J_{P-C-P}$ = 68.4, $^4J_{P-P}$ = 21.5, $^xJ_{Rh-P}$ = 0.8, $^1J_{Rh-Rh}$ = 0.1 Hz) and δ(P) = 23.6 ($^1J_{Rh-P}$ = 91.2, $^2J_{P-Rh-P}$ = 312, $^2J_{P-C-P}$ = 46.6, $^4J_{P-P}$ = 17.1, $^xJ_{Rh-P}$ = 0.5, $^1J_{Rh-Rh}$ = 0 Hz), respectively. Again, $^2J_{P-Rh-P}$ is not accurately determined, but the values obtained are consistent with previous results.[35] Also we find that both $^1J_{Rh-Rh}$ and $^xJ_{Rh-P}$ are negligible. We surmise that the errors in our original interpretation arose primarily because, in the original spectrum, the resolution was not sufficient to fully separate the three sets of inner lines or to allow the weak outer lines to be properly assigned. Without the latter, it is not possible to accurately determine $^2J_{P-C-P}$ and $^4J_{P-P}$, and since there are actually eight lines in each half of the inner portion of the spectrum whose positions depend on $^2J_{P-C-P}$, $^4J_{P-P}$, and $^1J_{Rh-Rh}$, the uncertainty in the former evidently led to difficulty in determining the latter as well.

The reaction of $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$ with 3 equiv of *tert*-butyl isocyanide initially yielded an unstable orange solid which on workup provided a purple material showing only C≡N absorptions as the only isolable material. This was shown to contain the $[Rh_2(t\text{-}BuNC)_4(DPM)_2]^{2+}$ cation. Because of its instability the initial product could not be characterized but presumably was $[Rh_2(CO)(t\text{-}BuNC)_3(DPM)_2]^{2+}$, $[Rh_2(CO)(t\text{-}BuNC)_3Cl(DPM)_2]^+$, $[Rh_2(t\text{-}BuNC)_3Cl(DPM)_2]^+$, or some mixture of these species. Evidently reaction of one or more of these possible species occurred to give $[Rh_2(t\text{-}BuNC)_4(DPM)_2]^{2+}$ with the other product(s) possibly being **5** or **6**, but this could not be confirmed.

The presence of four *tert*-butyl groups in the complexes $[Rh_2(t\text{-}BuNC)_4(L_2)_2](B(C_6H_5)_4)_2$ (L_2 = DPM, DAM) might be thought to severely restrict access to the metal atoms by additional ligands. Despite this, both complexes readily add carbon monoxide and sulfur dioxide. Thus treatment of $[Rh_2(t\text{-}BuNC)_4(DPM)_2](B(C_6H_5)_4)_2$ with CO under ambient conditions causes a rapid color change from purple to light yellow, and from the solution bright yellow crystals of $[Rh_2(CO)(t\text{-}BuNC)_4(DPM)_2](B(C_6H_5)_4)_2\cdot(CH_3)_2CO$ (**7**) can be obtained. The infrared and $^{13}C\{^1H\}$ NMR spectra of **7** clearly indicate the presence of terminal isocyanide ligands and a bridging carbonyl ligand. This is confirmed by preparation from ^{13}CO where only the 1765-cm^{-1} band has shifted ($\nu_{^{13}CO}$ = 1725 (m) cm^{-1}, $\nu_{C\equiv N}$ = 2150 (sh), 2142 (vs) cm^{-1} (CH_2Cl_2 solution)). The ^{13}C resonance for the carbonyl ligand appears as a well-resolved first-order triplet of quintets as expected for coupling to two equivalent rhodium and four equivalent phosphorus atoms. The symmetrical CO-bridged structure is further confirmed by the $^{31}P\{^1H\}$ NMR spectrum which appears as a symmetrical AA′A″A‴XX′ pattern (Figure 3a). The ^{31}P NMR spectrum of the parent complex, $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](B(C_6H_5)_4)_2$, which appears not to have been previously analyzed, is presented in Figure 3b for comparison (δ(P) 18.3; $^1J_{Rh-P}$ = 121.4, $^2J_{P-Rh-P}$ = 305, $^2J_{P-C-P}$ = 57.5, $^4J_{P-P}$ = 6.5, $^xJ_{Rh-P}$ = 1.2, $^1J_{Rh-Rh}$ = 0.0 Hz). On the basis of the spectroscopic data, **7** is formulated as



R = *t*-Bu

7

Two points of interest are the low energy of ν_{CO} and the large chemical shift of the carbonyl carbon. It has been suggested that in $[M_2Cl_2(\mu\text{-}CO)(DAM)_2]$ (M = Pd,[23,24a] Pt[24b]) the bridging ligand should be considered as a dimetallated ketone rather than as a normal bridging carbonyl in light of the low value of ν_{CO} (1720 (M = Pd), 1635 (M = Pt) cm^{-1}). There does not appear to be any reason to consider this possibility for **7** despite its very low ν_{CO} as compared with the other complexes discussed here. First, there is only a very slight change in $\nu_{C\equiv N}$ on addition of CO to $[Rh_2(t\text{-}BuNC)_4(DPM)_2](B(C_6H_5)_4)_2$ whereas an increase of 30–50 cm^{-1} would have been expected[22] were the CO to behave as a dimetallated ketone since the latter formulation would imply a formal oxidation Rh(I) → Rh(II). Second, although δ(CO) is larger than for most bridging carbonyl ligands reported,[25] recent studies on $[Rh_4(CO)_{11}(P(CH_3)(C_6H_5)_2)]$[26] and $[Rh_{17}(S)_2(CO)_{32}]^{3-}$[27] show even greater chemical shifts for the μ-CO ligands. We conclude, therefore, that these parameters simply reflect the fact that the complex is electron rich and that only the carbonyl ligand functions as a significant π acid.

The bright orange sulfur dioxide adduct $[Rh_2(SO_2)(t\text{-}BuNC)_4(DPM)_2](B(C_6H_5)_4)_2$ (**8**) results from brief treatment

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(23) R. Colton, M. J. McCormick, and C. D. Pannan, *J. Chem. Soc., Chem. Commun.*, 823 (1977).

(24) (a) S. D. Robinson, *Inorg. Chim. Acta*, **27**, L108 (1978); (b) M. P. Brown, A. N. Keith, L. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt, and K. R. Seddon, *Inorg. Chim. Acta*, **34**, L223 (1979).

(25) L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **77**, 1 (1974).

(26) J. Evans, B. F. G. Johnson, T. Lewis, T. W. Matheson, and J. R. Norton, *J. Chem. Soc., Dalton Trans.*, 626 (1978).

(27) J. L. Vidal, R. C. Schoenig, R. L. Pruett, and R. A. Fisto, *Inorg. Chem.*, **18**, 1821 (1979).

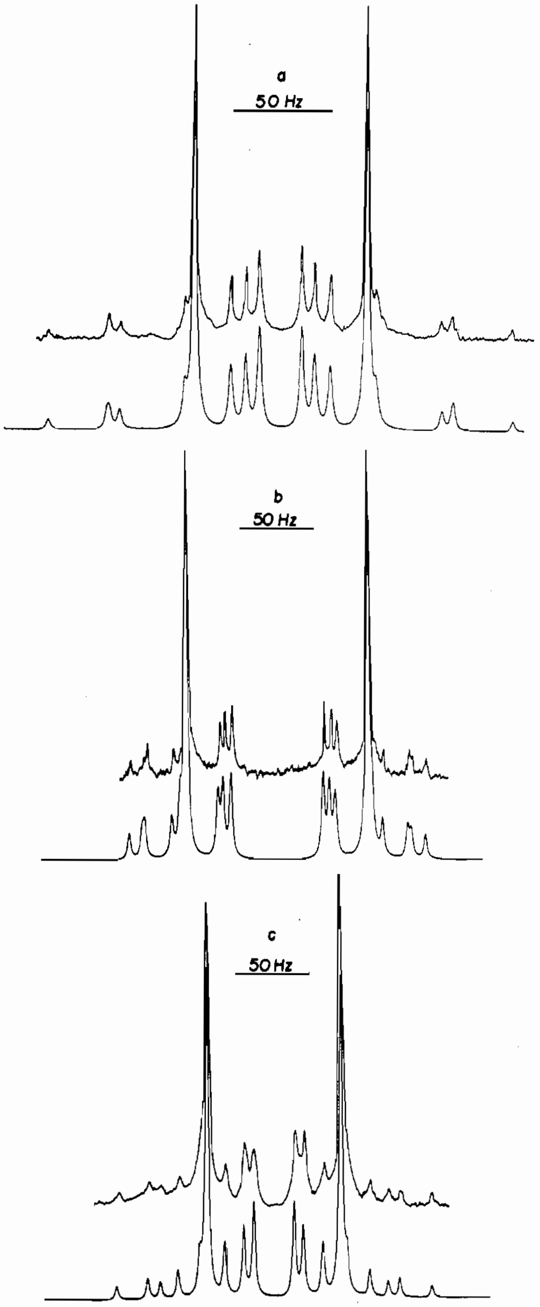

Figure 3. Observed and calculated $^{31}P\{^1H\}$ NMR spectra of (a) $[Rh_2(t\text{-}C_4H_9NC)_4(\mu\text{-}CO)(DPM)_2](B(C_6H_5)_4)_2$ (**7**, −12 °C), (b) $[Rh_2(t\text{-}C_4H_9NC)_4(DPM)_2](B(C_6H_5)_4)_2$ (−24 °C), and (c) $[Rh_2(t\text{-}C_4H_9NC)_4(\mu\text{-}SO_2)(DPM)_2](B(C_6H_5)_4)_2$ (**8**, −28 °C).

of $[Rh_2(t\text{-}BuNC)_4(DPM)_2](B(C_6H_5)_4)_2$ with SO_2. Although there is a definite color change of the isolated solid from yellow for the initial precipitate to orange for the crystals obtained after filtration which appears to be accompanied by a diminution in the intensity of the infrared absorptions assigned to ν_{S-O}, the elemental analysis indicates a stoichiometric complex. Possibly the initial precipitate also contains additional weakly bound or "solvent" SO_2[28] which is lost on filtration. The $^{31}P\{^1H\}$ NMR spectrum (Figure 3c) clearly indicates the equivalence of all four phosphorus atoms, and the analysis again shows negligible Rh–Rh coupling. The S–O absorptions are in the range associated with bridging SO_2. On this basis we formulate **8** as $[Rh_2(\mu\text{-}SO_2)(t\text{-}BuNC)_4(DPM)_2](B(C_6H_5)_4)_2$ with a structure analogous to **7**.

For $[Rh_2(t\text{-}BuNC)_4(DAM)_2](B(C_6H_5)_4)_2$ only the adduct with SO_2 (**10**) could be isolated. This is formulated as $[Rh_2(\mu\text{-}SO_2)(t\text{-}BuNC)_4(DAM)_2](B(C_6H_5)_4)_2$ from the infrared spectrum which closely resembles that of **8**. The ^1H NMR spectrum which shows two inequivalent sets of *tert*-butyl groups is also consistent with this formulation. Neither of these data unequivocally establish the proposed formulation since both would also be consistent with SO_2 bound to only one metal. However the similarity between the various DAM- and DPM-bridged binuclear complexes reported here and previously[11] in their reactions with CO and SO_2 suggests that the presence of bridging SO_2 in **10** is more likely.

The adduct of **4** with carbon monoxide (**9**) proved to be too unstable to be isolated in solid form at room temperature. However, both the infrared and $^{13}C\{^1H\}$ NMR spectra establish the presence of a bridging carbonyl ligand in solution under a CO atmosphere. As with $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$ instrumental limitations prevented us from obtaining a low-temperature limiting ^{13}C NMR spectrum. Even at −75 °C, CO exchange appeared to be occurring at a measurable rate as evidenced by the broad, featureless appearance of the resonance. At these temperatures, the solution was light yellow, and a yellow solid, presumed to be $[Rh_2(\mu\text{-}CO)(t\text{-}BuNC)_4(DAM)_2](B(C_6H_5)_4)_2$ could be obtained. However on warming of the solution to room temperature, the solid rapidly became purple, and only **4** could be finally isolated.

In the reactions leading to **7** and **9**, no evidence was obtained to indicate the presence of species containing either terminal carbonyl or bridging isocyanide ligands. Thus in contrast to $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]B(C_6H_5)_4$, the carbonyl ligand appears to enter the bridging site directly. The reasons for the difference in the presumed modes of formation between **7**–**10** and **2**, **3**, **5**, **6**, and $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(L_2)_2]^+$ are not obvious. However since attack of CO at the open square-planar face of $[Rh_2(CNC(CH_3)_3)_4(L_2)_2]^{2+}$ might initially be expected to induce an isocyanide ligand to bridge the metal atoms by analogy with the process proposed for the reaction of CO with $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]^+$, the apparent reluctance of the isocyanide ligand to form a bridge in the systems studied here may indicate that this pathway is not feasible.

Iridium Complexes. The preparation of neutral and cationic binuclear carbonyl complexes of iridium(I) containing DPM has been reported previously.[11,29] We have now extended these studies to include related complexes of DAM and mixed carbonyl–isocyanide derivatives of both series of complexes. The reaction of $[IrCl(cyclooctene)_2]_2$ with a CO-saturated acetone solution of DAM rapidly yields a yellow solid and an orange solution. Upon purging of the solution with dinitrogen followed by a brief period of reflux or upon concentration of the solution under reduced pressure, the color darkens to red-brown, and magenta crystals analyzing as $[Ir(CO)Cl(DAM)]$ (**11**) are produced. From the spectroscopic data (Tables II and IV) and the similarity of the preparative method to that used for $[Rh(CO)Cl(DAM)]_2$ and $[Ir(CO)Cl(DPM)]_2$ it is reasonable to formulate **11** as the neutral dimer $[Ir(CO)Cl(DAM)]_2$. Of the four complexes of formula $[M(CO)Cl(L_2)]_2$ (M = Rh, Ir; L_2 = DPM, DAM), **11** is the most sensitive to dioxygen. Thus while the other three appear to be unaffected by dioxygen both in the solid state and in solution for extended periods, **11** turns to a grayish powder in 2 to 3 days on contact with air, and tetrahydrofuran solutions rapidly turn from magenta to yellowish upon exposure. Like $[Rh(CO)Cl(DPM)]_2$, **11** reacts with CO over a period of several minutes in methanol–dichloromethane. The resulting pale

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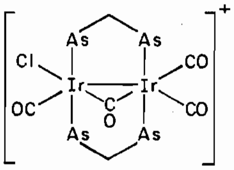
(28) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 224 (1973).

(29) A. R. Sanger, *J. Chem. Soc., Dalton Trans.*, 1971 (1978).

yellow solution shows four bands in the carbonyl region at 2055 (m), 1992 (s), 1971 (s), and 1766 (w) cm^{-1}. The similarity of this spectrum to that observed for $[Ir_2(CO)_4Cl(DAM)_2]B(C_6H_5)_4$ (vide infra) indicates that the same cation is present in this solution. Regeneration of **11** can be accomplished by removing the solvent under reduced pressure followed by refluxing the residue in acetone under an inert atmosphere. This carbonylation–decarbonylation cycle provides a convenient means for preparing **11** enriched (~50%) in ^{13}CO ($\nu_{C≡O}$ = 1896 cm^{-1}).

If the mixture obtained initially from the reaction of $[IrCl(cyclooctene)_2]_2$ with DAM and CO is further treated with $NaB(C_6H_5)_4$, pale yellow crystals analyzing as $[Ir_2(CO)_4Cl(DAM)_2]B(C_6H_5)_4$ (**12**) are obtained. The reaction is considerably faster than that reported for the DPM analogue $[Ir_2(CO)_4Cl(DPM)_2]B(C_6H_5)_4$,[11] presumably because the monodentate olefin cyclooctene is more readily displaced from $[IrCl(cyclooctene)_2]$ than is the chelating cyclooctadiene from the $[IrCl(cyclooctadiene)]_2$ used to prepare the phosphine complex. Complex **12** is more conveniently prepared by adding a solution of $[Ir(CO)_2Cl_2]^-$ [30] to a solution of DAM and $NaB(C_6H_5)_4$ under carbon monoxide (see Experimental Section). The pattern of two rather closely spaced terminal carbonyl bands slightly below 2000 cm^{-1} and a single band in the bridging carbonyl region (Table II) is quite similar to that observed[11] for the rhodium complexes $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(L_2)_2]B(C_6H_5)_4$ (L_2 = DPM, DAM). However in **12** there is an additional band near 2040 cm^{-1}, indicating that the complex contains a fourth carbonyl group. That this band is not due to some residual $Ir(CO)_2Cl_2^-$ as a counterion is indicated by the absence of any NMR signal due to this species in a ^{13}CO-labelled sample of the complex. The presence of three terminal carbonyl bands is in contrast to the two observed previously for $[Ir_2(CO)_4Cl(DPM)_2]B(C_6H_5)_4$.[11] A plausible structure which is consistent with these data and which gives each metal an 18-electron configuration is



12

This structure, as opposed to one with two bridging carbonyl groups as proposed for $[Ir_2(CO)_4Cl(DPM)_2]B(C_6H_5)_4$,[11] is also consistent with the $^{13}C\{^1H\}$ NMR spectrum of a 90% enriched sample obtained at −57 °C in the presence of ^{13}CO which shows three resonances attributable to terminal carbonyls and one in the region expected for a bridging carbonyl (Figure 4). Attempts to analyze the spectrum were only partially successful due to the overlap of many of the lines associated with the terminal carbonyl resonance centered at δ 168.5. Nevertheless it does appear that the spectrum can best be described as ABCX which is what would be anticipated for the proposed structure. When the sample is warmed to room temperature, the three high-field carbonyl resonances coalesce to a broad, featureless signal while the bridging resonance although still distinct has also lost all fine structure. Clearly exchange with free CO is now beginning to occur.

Purging a solution of **12** in dichloromethane with dinitrogen for several hours causes the color to change from yellow to a dark red-orange, and from this solution can be isolated orange crystals analyzing as $[Ir_2(CO)_3Cl(DAM)_2]B(C_6H_5)_4 \cdot 0.5CH_2Cl_2$ (**13**). The infrared spectrum in the carbonyl region closely resembles that of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$,[11] and an analogous structure is proposed. This is supported by $^{13}C\{^1H\}$ NMR spectrum of a partially ^{13}CO-labelled sample. The terminal carbonyl resonance consists of a strong line flanked by two weaker ones. The strong line is due to molecules containing ^{13}CO in either or both terminal positions while the weaker lines constitute the doublet (due to $^2J_{C_b-Ir-C_t}$) expected for molecules containing ^{13}CO in the bridging position as well as in one or both terminal positions. The resonance for the bridging carbonyl appears as a five-line pattern which is interpreted as superimposed singlet, doublet, and triplet signals from molecules containing ^{13}CO in the bridging, bridging plus one terminal, and bridging plus both terminal positions, respectively. In contrast to the facile decarbonylation of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$ to $[Rh_2(CO)_2(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$,[11] the conversion of **12** to **13** is relatively difficult, and in most samples of **13** prepared in this work, traces of **12** remained. This greater resistance to interconversion notwithstanding, it still proved possible to demonstrate exchange of all carbonyl groups in mixtures of **12** and **13** under ambient conditions. Thus when **12** is dissolved in dichloromethane, an orange color develops, and the infrared spectrum shows the presence of both **12** and **13**. Treatment of this solution with ^{13}CO regenerates the yellow color of **12**, and the infrared spectrum shows the slow growth of absorptions due to incorporation of ^{13}CO at all positions. After about 10 min the only bands present are at 1996 (m), 1959 (sh), 1951 (vs), and 1728 (m) cm^{-1}, indicative of completely ^{13}CO-labelled **12**. The same spectrum results if preformed **13** is treated with ^{13}CO. The mechanism of the exchange process is presumably similar to that proposed for the rhodium A-frame complexes[11] but would necessarily be more complex because of the greater number of carbonyl groups in the present system.

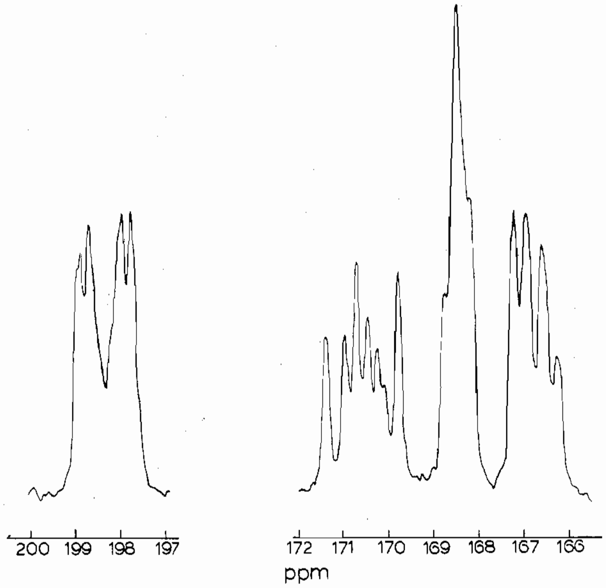


Figure 4. $^{13}C\{^1H\}$ NMR spectrum of a 90% enriched sample of $[Ir_2(CO)_4Cl(DAM)_2]B(C_6H_5)_4$ (**12**) under ^{13}CO at −57 °C.

Complex **12** can also be substantially converted to **13** by heating at 60 °C in vacuo for several days; however, this route also appears to occasion further CO loss as suggested by the presence of bands in the infrared spectrum not attributable to either of the above complexes. Attempts to convert **12** to **13** more rapidly by refluxing in acetone with a dinitrogen purge led to the recovery of small amounts of **11**. The yield of **11** by this method is considerably higher if one starts with $[Ir_2(CO)_4Cl(DAM)_2]PF_6$. Evidently chloride abstraction from one iridium species by another is relatively facile, but we were

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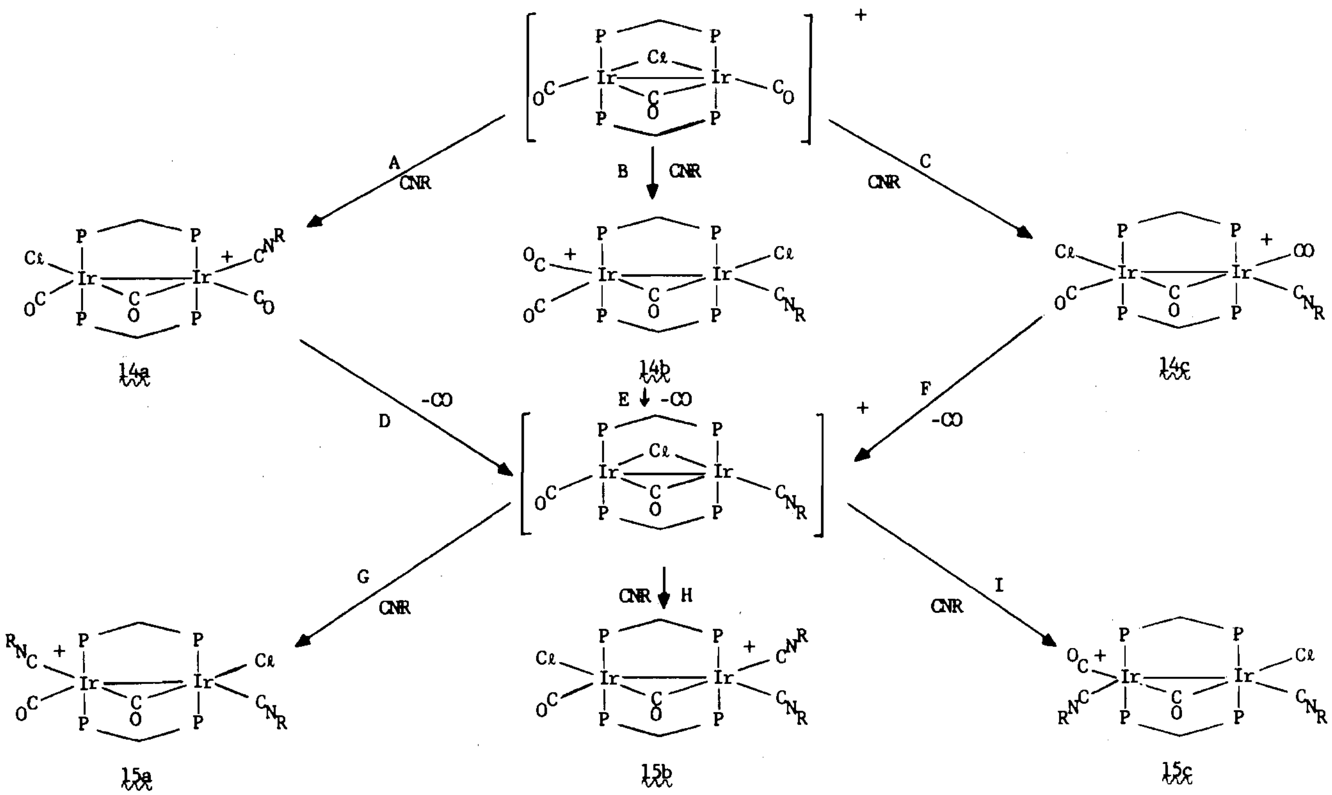
(30) D. Forster, *Inorg. Nucl. Chem. Lett.*, **5**, 433 (1969).

Scheme I



unable to characterize the other products of these reactions.

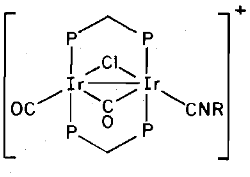
The reactions of **12** or **13** and their DPM analogues with *tert*-butyl isocyanide bear a number of resemblances to the rhodium systems described earlier in that species containing one, two, and four isocyanide ligands are produced. In contrast to the rhodium complexes however, both the DPM and DAM complexes appear to have the same or very similar structures and to be more susceptible to loss of carbon monoxide.

The reactions of $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$ with 1 and 2 equiv of *tert*-butyl isocyanide yield white and pale pink crystals, respectively, which from the analytical and spectroscopic data in Tables I–III are formulated as $[Ir_2(CO)_3(t\text{-}BuNC)Cl(DPM)_2]B(C_6H_5)_4$ (**14**) and $[Ir_2(CO)_2(t\text{-}BuNC)_2Cl(DPM)_2]B(C_6H_5)_4$ (**15**). The $^{31}P\{^1H\}$ NMR spectra of **14** and **15** are second-order patterns which closely resemble that observed for $[Ir_2(CO)_4Cl(DPM)_2]^+$. As the latter has been successfully analyzed as an AA′BB′ spin system,[11] those of **14** and **15** are probably best described as AA′BB′ also despite our inability to completely analyze them. We are uncertain of the reason for this, but it may be the result of the near degeneracy of some of the lines which made unequivocal assignments impossible. Nevertheless it did prove possible to obtain the phosphorus chemical shifts. The $^{13}C\{^1H\}$ NMR spectra of **14** and **15** (ca. 90% enriched) show resonances attributable to terminal and bridging carbonyl groups in 2:1 and 1:1 intensity ratios, respectively, thus confirming the proposed formulations. Because of the large numbers of spins (7 and 6, respectively) neither spectrum was clearly resolved. However the terminal carbonyl resonance in each case did show a pronounced triplet splitting of ca. 10 Hz which can reasonably be assigned to $^2J_{P-Ir-C}$. For **14** this resonance was also distinctly asymmetric, suggesting a slight difference in chemical shift between the two terminal carbonyl groups. While no structural information is provided by the ^1H NMR spectrum of **14**, that of **15** clearly shows two resonances for *tert*-butyl groups of the isocyanide ligands, indicating them to be in slightly different environments.

Possible structures for the mono- and bis(isocyanide) complexes are shown as **14a–c** and **15a–c** in Scheme I. A fourth possibility for the latter, **15d**, is that obtained by interchanging the chloride and isocyanide ligands in **15a**. The most reasonable site for attack of isocyanide on $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$ is that adjacent to the chloride (path A) since, on the assumption that this complex has the same structure as its rhodium analogue,[12] this site is more open than that between the bridging and terminal carbonyl groups (path C). The initial product should therefore be **14a**. Path B seems unlikely as a concerted process as it would require movement of two carbonyl groups across the face of the molecule. However since **14** contains a labile carbonyl group (probably terminal, vide infra), loss of CO to form a species such as $[Ir_2(CO)(CNC(CH_3)_3)(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$ followed by reentry of CO adjacent to chloride as before could lead to either **14b** or **14c** or perhaps both. The spectroscopic data do not permit a distinction to be made between **14a** and **14c** but do suggest that **14b** is not present in a significant quantity. Thus the spectrum in the terminal carbonyl region is quite similar to that observed for $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$[11] while **14b** would be expected to show terminal carbonyl bands at noticeably higher energies (cf. **12**) since it places the two carbonyl groups on a formally unipositive metal with a C–Ir–C angle which is likely to be considerably less than 180°. Furthermore the terminal carbonyl band at 1966 cm^{-1} is comparable to that found in neutral iridium(I) carbonyl complexes. Thus we prefer **14a** as the structure of this complex although we note that in some preparations the bridging carbonyl absorption appeared to be somewhat asymmetric, suggesting that a mixture of **14a** and **14c** was formed.

Since it appears that **14** is an intermediate in the formation of **15**, the lower portion of Scheme I shows a plausible route for this conversion. Since **14** is coordinatively saturated and rather sterically congested, we suggest that direct attack of isocyanide on this species is probably unlikely. A more feasible process would involve loss of carbon monoxide to form $[Ir_2(CO)(CNC(CH_3)_3)(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$ (path D, E, or F) followed by attack of isocyanide on this species (paths G–I). Since the spectroscopic data are insufficient to distinguish between **15a**, **15c**, and **15d**, we cannot rule out **15d**, but it does not appear that it could be formed readily except by direct attack on **14a** which we have suggested is less likely. We also argue that **15c** is not likely to result via path I for the same reasons that **14c** should be unlikely to be formed via path C although it could result from isomerization of **15a** by a route analogous to that discussed above for **14a** → **14c**. As with **14**, the bridging carbonyl band for **15** in some instances showed the possibility of a shoulder which suggests a mixture of **15a** and **15c**. The argument against **15b** can be made as follows. First the large difference in the two C≡N stretching frequencies is consistent with one isocyanide being on a formally positive metal and the other on a neutral center (cf. the similar difference in $\nu_{C≡O}$ in **2** where an analogous situation of formally positive and neutral centers is present). Second, the remaining terminal carbonyl band is at a relatively high energy which is consistent with its being assigned to a carbonyl on a formally positive center. On comparison of the infrared spectra of **14** and **15** in this region it can be noted that it is the lower energy CO band in **14** that disappears on conversion to **15**. Third, the chemical shifts of the pair of phosphorus atoms at low field are very similar in **14** and **15** while those at higher field differ to a greater extent. Since the low-field pair can reasonably be assigned to that on the formally positive metal, this means that this end of the molecule is the same in both **14** and **15**. Finally, if **15b** were correct, the formally positive end of the molecule would closely resemble one end of **16** (vide infra), and one would expect a similar chemical shift difference between the two *tert*-butyl groups. The near equivalence of these two groups observed for **15** is again more consistent with structure **15a**. While these spectroscopic arguments would equally well support **15c**, this isomer, as noted above, should not be as easily produced from **14** as would **15a**.

If a solution of **14** in tetrahydrofuran or dichloromethane is purged with dinitrogen or if solid **14** is dried in vacuo, the color changes to an intense blue-violet. The original pale yellow (solution) or white (solid) color can be restored by treatment of either the solution or the solid with carbon monoxide. This observation together with the fact that $\nu_{C≡N}$ is unaffected by these transformations indicates that the blue material is formed by CO loss from **14**. While the $^{13}C\{^1H\}$ NMR spectrum of the blue species is not very much different from that of **14**, the $^{31}P\{^1H\}$ NMR spectrum is considerably altered and shows the presence of at least two species. In particular, the well-defined AA′BB′ pattern of **14** is no longer evident although a poorly resolved pattern possibly of this type is observed. In addition, a signal is present which is suggestive of a species with four equivalent phosphorus atoms. The infrared spectrum of the blue material is also not markedly different from that of **14**, but a diminution in the intensity of the 1980-cm^{-1} carbonyl band relative to that for the 1966-cm^{-1} band is apparent. These observations suggest that, under the conditions employed (solid, in vacuo, 1 week at 25 °C), CO loss from **14** is not complete. Attempts to obtain a pure sample of the blue material led to decomposition. Since the apparent mixture of **14** and the blue material shows a weaker 1980-cm^{-1} band than for pure **14**, we suggest that the blue complex has only one terminal carbonyl band at ca. 1965 cm^{-1} which in turn suggests the structure



R = *t*-Bu

which is analogous to that proposed for **5**. Complex **15** also tends to lose carbon monoxide at reduced pressure as evidenced by a color change to greenish which can be reversed by treatment with CO. We were unable to satisfactorily characterize this complex, but on the basis of the behavior of **14**, CO loss from **15** would probably lead to a species with a structure analogous to **6**.

Reactions of either $[Ir_2(CO)_4Cl(DAM)_2]BF_4$ or $[Ir_2(CO)_3Cl(DAM)_2]BF_4$ with 1 and 2 equiv of *tert*-butyl isocyanide yield pale pink and off-white crystals, respectively, which from the analytical and spectroscopic data in Tables I–IV are formulated as $[Ir_2(CO)_3(t\text{-BuNC})Cl(DAM)_2]BF_4$ (**17**) and $[Ir_2(CO)_2(t\text{-BuNC})_2Cl(DAM)_2]BF_4$ (**18**). The reported $^{13}C\{^1H\}$ NMR spectrum is of a slightly enriched sample which is therefore not complicated by $^{13}C-^{13}C$ coupling. As for **14**, the two terminal carbonyl groups have slightly different chemical shifts, and an analogous structure is proposed. For **18**, considerable difficulty was encountered in obtaining a satisfactory $^{13}C\{^1H\}$ NMR spectrum as a variety of signals were observed in both the bridging and terminal carbonyl regions. Since no evidence of an isomer mixture was evident from infrared data, we suggest that over the time required to collect the spectrum (ca. 5 h) reaction with the dichloromethane solvent occurred. Although we did not encounter this problem with the other iridium complexes, we and others[31] have noted a tendency for various rhodium A-frame complexes to react with halogenated solvents, and it is not unreasonable to expect this for the iridium systems. Without satisfactory ^{13}C NMR data, the structure assignment for **18** must be tentative. Although the separation of the C≡N bands is very similar to that observed for **15**, the terminal CO band is very low for CO on a formally positive center. If the structure were analogous to **15b** rather than **15a**, this low $\nu_{C≡O}$ could be accommodated, but then the C≡N bands would be expected to be similar to those for **19** which they are not. Thus while **18** probably has a structure analogous to either **15a** or **15b**, it is not possible with the available data to decide between them. Like **14** and **15**, **17** and **18** turn purple on heating presumably as a result of CO loss. Similar structures to those proposed for the decarbonylation products of **14** and **15** are suggested for these species.

Reaction of either $[Ir_2(CO)_4Cl(L_2)_2]B(C_6H_5)_4$ or $[Ir_2(CO)_3Cl(L_2)_2]B(C_6H_5)_4$ (L_2 = DPM, DAM) with an excess of *tert*-butyl isocyanide (ca. 5 equiv) followed by 1 equiv of $NaB(C_6H_5)_4$ yields pale yellow crystals analyzing as $[Ir_2(CO)(t\text{-BuNC})_4(L_2)_2](B(C_6H_5)_4)_2$ (L_2 = DPM (**16**), DAM (**19**)). From the spectroscopic and conductivity data, **16** and **19** are clearly the iridium analogues of **7** and **9**, respectively. Again ν_{CO} is quite low, and the chemical shift of the carbonyl carbon is large. The ^{13}CO labeled derivatives used for the ^{13}C NMR measurements show ν_{CO} at 1667 (m) (**16**) and 1665 (m) (**19**) cm^{-1} (Nujol mull), respectively. Unlike the rhodium analogues, neither **16** nor **19** shows any tendency to lose CO.

Electronic Spectra. Balch has made an extensive study of the electronic spectra of $[Rh(CO)Cl(L_2)]_2$, $[Rh_2(CNR)_4(L_2)_2]^+$ (L_2 = DPM, DAM), and related complexes.[3–6,22] The lowest energy band observed for these "face-to-face" dimers has been considered to arise from a metal-to-ligand charge-transfer (MLCT) transition as shown in Figure 5. In these systems the HOMO is largely metal d_{z^2} in nature while the LUMO consists mainly of ligand orbitals having π symmetry. Since the structure of $[Rh_2(CO)_2(\mu\text{-Cl})(DPM)_2]BF_4$[32] shows that the coordination about each metal is very nearly square planar, this qualitative scheme should serve to describe the pertinent aspects of the electronic structure of $[Rh_2(CO)_2(\mu\text{-Cl})(L_2)_2]B(C_6H_5)_4$ (L_2 = DPM, DAM). As noted previ-

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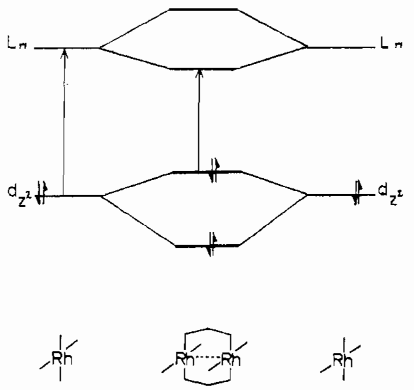

Figure 5. Molecular orbital diagram showing the interaction between metal d_{z^2} orbitals and ligand π orbitals which accounts for the low-energy absorption for the face-to-face and A-frame dimers.

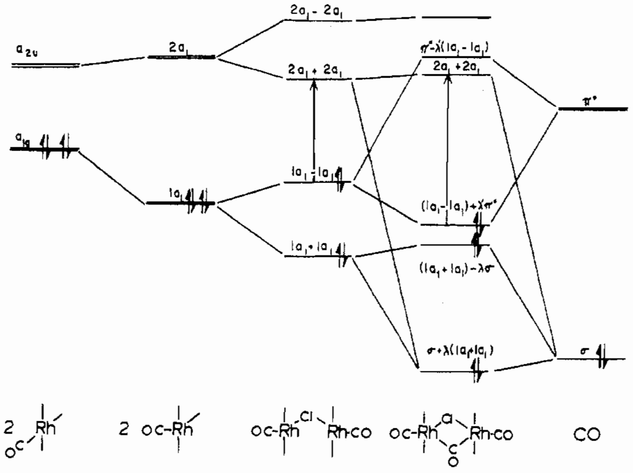

Figure 6. Molecular orbital diagram showing the effect of adding a bridging carbonyl ligand to the A-frame dimers.

ously,[11] these do indeed show a "proximity shifted" band in their electronic spectra (Table VII) which is comparable to those reported by Balch.[5] Similar low-energy bands are observed in the spectra of **2–4** and **11**, consistent with their formulations as face-to-face dimers, and the qualitative MO scheme of Figure 5 should also suffice to describe their electronic structures.

When carbon monoxide is added to $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]^+$ to produce $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(L_2)_2]^+$ (L_2 = DPM, DAM), the "proximity shifted" band disappears to be replaced by a similar band at ~355 nm. This change can be adequately explained by the molecular orbital scheme shown in Figure 6 which is based on the work of Elian and Hoffmann.[33] In the construction of this scheme we first consider the major structural changes which occur on going from $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]^+$ to $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(L_2)_2]^+$ as revealed in X-ray studies on the DPM complexes.[12,32] These are the binding of the bridging carbonyl ligand to both metals, a decrease of ~0.3 A in the Rh–Rh separation, and a decrease in the Cl–Rh–CO (terminal) angle from ~175 to ~140°. Starting with two square-planar fragments in which the HOMO is mainly metal d_{z^2} (a_{1g}) and the LUMO is largely ligand π (a_{2u}), we first decrease the Cl–Rh–CO (terminal) angle to ~140°. This has the result of significantly stabilizing the HOMO and modestly destabilizing the LUMO. In addition, with the descent in symmetry to C_{2v} (idealized) both of these orbitals now have a_1 symmetry.[33] When these two fragments together are brought together, both sets of orbitals interact as described previously for the face-to-face dimers. However because of the A-frame geometry the symmetric and antisymmetric combinations of the primarily metal d_{z^2} orbitals ($1a_1 + 1a_1$ and $1a_1 - 1a_1$, respectively) are directed toward the site where the bridging carbonyl is to be coordinated. Moreover they are of the proper symmetry to overlap with the σ and the equatorial π^* orbitals, respectively, of this ligand. As shown in Figure 6, the pertinent part of the former interaction corresponds to the $Rh_2(\mu\text{-}CO)$ σ^* combination and is expected to still be largely metal in character. It is also probable that it will be raised only slightly in energy as the result of this interaction. The major interaction is expected to be that between the Rh ($1a_1 - 1a_1$) combination and the equatorial π^* orbital of the bridging carbonyl groups which should markedly stabilize this combination. In the absence of quantitative calculations it is not possible to state with certainty what the ordering of these two levels is, but nevertheless it is clear that the addition of a bridging carbonyl to the A-frame complexes $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]^+$ results in a marked stabilization in the original HOMO via π back-bonding to this ligand. As little if any change would be expected in the energy of the LUMO, the result is an increase in the HOMO–LUMO separation consistent with the observed blue shift of the lowest energy transition in going from $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)]^+$ to $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(L_2)_2]^+$.

Qualitatively, this molecular orbital scheme should also serve to describe the electronic spectra of **5–7** and **9** as well as the iridium complexes $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$, **16**, and **19** since all have their lowest energy transition below 400 nm.[34] A possible exception is **13** which in addition to the band reported in Table VII shows a weaker band (ϵ = 2200) at 494 nm. Since we experienced considerable difficulty in obtaining pure samples of **13**, this band may be due to a small amount of an impurity, possibly $[Ir_2(CO)_2(\mu\text{-}Cl)(DAM)_2]^+$.

When solutions of **5** and **6** are purged with nitrogen, additional bands are observed at 448 and 455 nm, respectively, while those at ~365 nm are diminished in intensity. Passage of carbon monoxide through these solutions removes the low-energy bands and restores the original intensities of the others. The similarity of the low-energy absorptions to that observed for $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$ suggests a partial conversion of **5** and **6** into species not containing a bridging carbonyl. As discussed earlier for **5**, the species produced in the first instance may be $[Rh_2(CO)(CNC(CH_3)_3)(\mu\text{-}Cl)(DPM)_2]^+$, and these spectral changes are consistent with this. For **6** there appears to be relatively little difference in the infrared spectrum whether or not carbon monoxide is present, so it is difficult to determine the nature of the new species produced.

The lowest energy bands of the sulfur dioxide adducts **8** and **10** are significantly blue shifted from their tetrakis(isocyanide) precursors, but this shift is not so great as for the carbonyl adducts **7** and **9**. Possibly this indicates that the interaction of the $1a_1 - 1a_1$ metal combination with the bridging SO_2 is not as great as with a bridging carbonyl.

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Registry No. **1**, 74965-10-9; **2**, 74965-12-1; **3**, 74977-87-0; **4**, 69420-82-2; **5**, 74977-89-2; **6**, 74977-91-6; **7**, 74977-93-8; **8**, 74964-96-8; **9**, 74977-95-0; **10**, 74964-98-0; **11**, 74977-96-1; **12**,

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74977-98-3; **13**, 74978-00-0; **14**, 74978-02-2; **15**, 74978-04-4; **16**, 74987-45-4; **17**, 74977-75-6; **18**, 74977-77-8; **19**, 74977-79-0; $[Rh_2(CO)_2Cl(DAM)_2]B(C_6H_5)_4$, 70561-97-6; $[Rh_2(CO)_2Cl(DPM)_2]B(C_6H_5)_4$, 67202-35-1; $[Rh_2L_4(DPM)_2](B(C_6H_5)_4)_2$, 74977-80-3; $[IrCl(c\text{-}C_8H_{14})_2]_2$, 12112-67-3; $[Ir_2(CO)_4Cl(DAM)_2]BF_4$, 75023-45-9; $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$, 67235-83-0; $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$, 70561-95-4; $[Rh_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$, 68080-76-2; $[Ir_2(CO)_3Cl(DPM)_2]B(C_6H_5)_4$, 74977-82-5; $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]PF_6$, 74977-83-6; $[Rh_2(CO)(L)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$, 74977-85-8.

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Metallacyclic Complexes of Iridium

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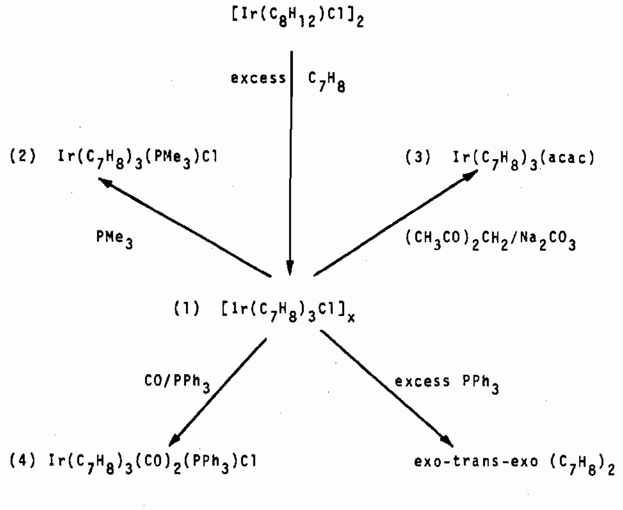
The reaction of norbornadiene with $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ or $[Ir(cyclooctene)_2Cl]_2$ yields a product containing three norbornadiene units, $[Ir(C_7H_8)_3Cl]_x$. Treatment of this product with PMe_3 or acetylacetone yields species containing two of these norbornadiene units half-linked together with exo-trans-exo stereochemistry in a five-membered metallacycle, as confirmed by a single-crystal X-ray diffraction study on the latter, $Ir(C_7H_8)_3(acac)$, space group $P\bar{1}$ (C_i^1, No. 2), $a = 9.239$ (2) Å, $b = 14.267$ (3) Å, $c = 9.638$ (2) Å, $\alpha = 111.95$ (1)°, $\beta = 65.77$ (1)°, $\gamma = 106.70$ (1)°, and $Z = 2$. Treatment of $[Ir(C_7H_8)_3Cl]_x$ with CO and then PPh_3 yields the compound $Ir(C_7H_8)_3(CO)_2(PPh_3)Cl$, believed to contain a six-membered metallacycle comprising two norbornadiene units, linked as in the five-membered case, and an inserted CO group. Degradation of $[Ir(C_7H_8)_3Cl]_x$ with excess PPh_3 leads to the reductive elimination of exo-trans-exo norbornadiene dimer. A compound $Ir(C_7H_8)_3(PPhMe_2)Cl$ is obtained on treatment of $[Ir(C_3H_8)_3]_x$ with $PPhMe_2$. This compound is converted, with excess CO in solution, to $Ir(C_7H_8)_3(CO)_2(PPhMe_2)Cl$, a white compound, which on standing in solution yields a yellow compound with the same empirical formula. This latter compound has been shown crystallographically to contain an eight-membered ring containing iridium linked to an acyl carbonyl group and three norbornadiene residues, the first two joined as in $Ir(C_7H_8)_3(acac)$ and the second joined to the third with exo-cis-endo stereochemistry. For $Ir(C_{22}H_{24}O)(CO)(PPhMe_2)Cl\cdot CH_2Cl_2$, space group $P2_1/c$ (C_{2h}^5, No. 14), $a = 9.610$ (7) Å, $b = 30.81$ (2) Å, $c = 10.248$ (7) Å, $\beta = 103.52$ (3)°, and $Z = 4$. The coordination at iridium is square pyramidal with the acyl CO group in the apical position and the CO group trans to Cl.

Introduction

Metallacycles have gained acceptance recently as probable intermediates in a variety of metal-catalyzed processes. In particular, they have been postulated in olefin reactions such as dimerization, cyclic ketone formation, and metathesis.[2-11] Separately, the isolation of metallacyclic compounds from reactions involving unsaturated precursors has been achieved in several cases, i.e., with Ni,[12] Pt,[13] Fe,[14] Co,[15] Ir,[16,17] and Rh.[18] Invariably the unsaturated organic precursor is strained, as in the case of cyclopropenes or norbornadienes,[8,12] or particularly reactive, as in the case of acetylenes,[13,14] allenes,[17,18] or butadienes.[12] Very recently, however, the formation of a metallacyclopentane derivative from simple olefins has been reported.[7,8] The synthesis of saturated metallacycles by other routes, with a view to investigating their reactivity as model intermediates, has also been the subject of several recent studies.[19,20]

Scheme I



We report here the coupling of norbornadiene on iridium(I) to form metallacyclic products containing two linked norbornadiene molecules. A further sequence of reactions leading to complexes containing three linked norbornadiene moieties is also described. The structure of these products including

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