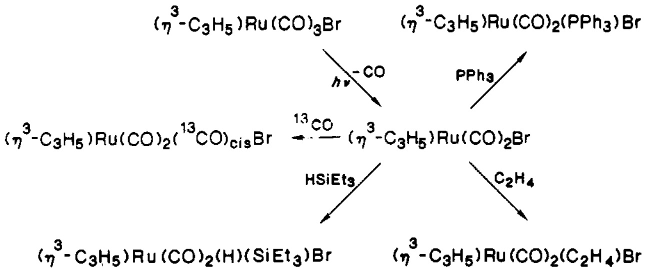
Scheme II. Photochemistry of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in Alkane Solution at 298 K Containing Reactive Molecules



exist in equilibrium in solution. *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ is more stable than *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ by about 2 kcal/mol. Photolysis shifts the equilibrium toward *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. The dibromo-bridged ruthenium dimer $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ is the dominant intermediate in the photoinduced endo–exo isomerization. Photolysis of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in the presence of CO does not yield significant endo → exo isomerization. Without detailed structural information, it is difficult to speculate why $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ and CO yield *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ rather than *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. However, we note that the two allyl ligands of $[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2$ are both in exo positions even though the precursor $(\eta^3\text{-}C_3H_5)Fe(CO)_3X$ (X = Br, I) has the endo structure.[6–7,11] Further attempts to isolate and structurally characterize of $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ are underway.

Interestingly, the allyl group remains π-coordinated to ruthenium in all of the products obtained from photolysis of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. In contrast, thermal reactions of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Cl$ typically result in σ-allyl complexes.[18b] This difference might be due to the fact that CO loss is the primary photoprocess, while π-allyl conversion to σ-allyl is believed to be the primary thermal process.[18a] Photolysis provides a useful route to $(\eta^3\text{-}C_3H_5)Ru(CO)_2(L)Br$ complexes.

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Registry No. $[(\eta^3\text{-}C_3H_5)Ru(CO)_2Br]_2$, 114860-57-0; $(\eta^3\text{-}C_3H_5)Ru(CO)_2(PPh_3)Br$, 114925-32-5; $(\eta^3\text{-}C_3H_5Ru(CO)_2(C_2H_4Br$, 114860-58-1; $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$, 114925-33-6; PPh_3, 603-35-0; C_2H_4, 74-85-1; *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$, 114925-34-7; *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$, 114925-35-8; *endo*-$(\eta_3\text{-}H_5)Fe(CO)_3Br$, 61216-85-1; *exo*-$(\eta^3\text{-}C_3H_5)Fe(CO)_3Br$, 80797-22-4; $(\eta^3\text{-}C_3H_5)Ru(CO)_2$(2-MeTHF)Br, 114860-59-2; $(\eta_3\text{-}C_3H_5)Ru(CO)_2CH)(SiEt_3)Br$, 114860-60-5; $(\eta^3\text{-}C_3H_5)Ru(CO)_2(^{13}CO)_{cis}Br$, 114860-61-6; $(\eta^3\text{-}C_3H_5)Ru(CO)_2(^{13}CO)_{trans}Br$, 114925-36-9; $Ru(CO)_4(C_2H_4e$, 52621-15-5; $(\eta^3\text{-}C_3H_5)Ru(CO)_3Cl$, 114925-37-0; $(\eta^3\text{-}C_4H_7)Ru(CO)_3Br$, 114860-62-7; $(\eta^3\text{-}C_4H_7)Ru(CO)_3Cl$, 114925-38-1; $[(\eta^3\text{-}C_3H_5)Fe(CO)_2Br]_2$, 114860-63-8.

Binuclear Bis(dimethylphosphino)methane Complexes of Rhodium and Some Comparisons with the Bis(diphenylphosphino)methane Analogues of Rhodium and Iridium

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The reaction of bis(dimethylphosphino)methane (DMPM = $Me_2PCH_2PMe_2$) with $[RhCl(C_8H_{12})]_2$ under CO yields the binuclear complex *trans*-$[RhCl(CO)(DMPM)]_2$ (1), which upon reaction with either 1 equiv of $AgBF_4$ or an excess of $Na_2S{\cdot}9H_2O$ yields the A-frame complexes $[Rh_2(CO)_2(\mu\text{-}Cl)(DMPM)_2][BF_4]$ or $[Rh_2(CO)_2(\mu\text{-}S)(DMPM)_2]$, respectively. In solution under a CO atmosphere the cationic, chloride-bridged species was found to be in equilibrium with the symmetrical tricarbonyl compound $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(DMPM)_2][BF_4]$. The additional carbonyl ligand in this complex is found to be more labile than that in the analogous "$Rh_2(DPPM)_2$" and "$Ir_2(DPPM)_2$" systems (DPPM = bis(diphenylphosphino)methane). This has been confirmed for the rhodium species by NMR magnetization transfer experiments. Under higher concentrations of CO a labile species, believed to be the tetracarbonyl $[Rh_2Cl(CO)_3(\mu\text{-}CO)(DMPM)_2]^+$, is observed. The neutral A-frame $[Rh_2(CO)_2(\mu\text{-}S)(DMPM)_2]$ also reacts with CO to yield the labile tetracarbonyl species $[Rh_2(CO)_4(\mu\text{-}S)(DMPM)_2]$. Addition of 1 equiv of the activated alkynes dimethyl acetylenedicarboxylate (DMA) or hexafluorobutyne (HFB) to 1 in solution provides the cis-dimetalated olefin species $[Rh_2Cl_2(CO)_2(\mu\text{-}RC_2R)(DMPM)_2]$ (R = CO_2CH_3, CF_3). Subsequent reaction of these products with 1 equiv of $AgBF_4$ yields the cationic species $[Rh_2Cl(CO)_2(\mu\text{-}RC_2R)(DMPM)_2][BF_4]$, both of which are found to be fluxional on the NMR time scale. These latter two complexes are also synthesized by the addition of 1 equiv of DMA or HFB to $[Rh_2(CO)_2(\mu\text{-}Cl)(DMPM)_2][BF_4]$. Compound 1 reacts with CH_2Cl_2 over an extended period of time yielding the tetrachloride product $[RhCl_2(CO)(DMPM)]_2$ which can also be obtained by reaction of 1 with HCl or Cl_2. The structure of this Cl_2 adduct was determined by X-ray techniques. It crystallizes in the orthorhombic space group *Pbcn* with $a = 30.573$ (4) Å, $b = 13.469$ (2) Å, $c = 12.624$ (2) Å, $V = 5198.8$ Å^3, and $Z = 8$. The structure was refined to $R = 0.044$ and $R_w = 0.058$ based on 3985 unique observed reflections and 239 variables. The structure has a Rh–Rh separation of 2.7591 (5) Å corresponding to a normal single bond. Each rhodium atom exhibits octahedral coordination in which the ligands on each metal are staggered with regard to each other about the Rh–Rh bond with an average torsion angle of 22.0°. The two Rh–Cl bonds opposite the Rh–Rh bond (2.480 (1), 2.478 (1) Å) are significantly longer than those cis to this bond (2.385 (1), 2.393 (1) Å).

Introduction

Much of the interest in binuclear complexes arises from the possibility that the two adjacent metals may interact in a cooperative manner with substrate molecules and in so doing may result in reactivity modes that differ from those displayed by mononuclear complexes. In any system

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involving adjacent metals one primary concern is to maintain the integrity of the complex during reactions while some degree of flexibility within the molecule is still allowed. Although several bridging groups have been used to accomplish this, one of the most popular has been the diphosphine bis(diphenylphosphino)methane (DPPM or DPM).[1-21]

In spite of the rich chemistry demonstrated for DPPM-bridged complexes, the relatively large bulk of this ligand may inhibit the accessibility of substrate molecules to the metal centers. For this reason, several groups, including our own, have recently turned to the much less sterically demanding diphosphine bis(dimethylphosphino)methane (DMPM).[22-29] In addition to the smaller size, the presumed increased basicity[30] of this ligand should lead to an increased nucleophilicity of the metals, which we anticipate should lead to an even richer chemistry than that demonstrated for DPPM. In this paper we describe the preparation and characterization of a series of binuclear DMPM-bridged complexes of rhodium and compare some of the chemistry with that previously reported for the DPPM-bridged complexes of rhodium[31-36] and iridium.[5b,f,37]

Experimental Section

General Comments. All solvents were appropriately dried and degassed prior to use under an atmosphere of dinitrogen, and reactions were routinely carried out under Schlenk conditions by using a dinitrogen atmosphere. Bis(dimethylphosphino)methane (DMPM) and bis(diphenylphosphino)methane (DPPM) were purchased from Strem Chemicals, hydrated rhodium trichloride was obtained on loan from Johnson-Matthey, dimethyl acetylenedicarboxylate (DMA), 1,5-cyclooctadiene (C_8H_{12}), and silver tetrafluoroborate from Aldrich Chemical Co., and sodium sulfide hydrate from J.T. Baker Chemical Co. C.P. grade carbon monoxide and high purity chlorine were purchased from Matheson, ^{13}CO, 99%, was purchased from Isotec Inc., and hexafluorobutyne-2 (HFB) was purchased from SCM, PCR Incorp. These and all other reagent grade chemicals were used as received. $[RhCl(C_8H_{12})]_2$[38] and *trans*-$[RhCl(CO)(DPPM)]_2$[31] were prepared by the reported procedures. $[Rh_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$ was

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prepared as the $[BF_4]^-$ salt by the addition of 1 equiv of $AgBF_4$ to a tetrahydrofuran slurry of *trans*-[RhCl(CO)(DPPM)]$_2$. After reaction (1 h) the solvent was removed under partial vacuum, and the subsequent workup was carried out in dichloromethane solution.

Infrared spectra were recorded on a Nicolet 7199 spectrometer with the use of Nujol mulls on KBr plates or in solution (CH_2Cl_2) in NaCl cells. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker WH-200 and WH-400 instruments. The ^1H NMR spectra were recorded at 200 or 400 MHz, the $^{13}C\{^1H\}$ NMR spectra at 100 MHz, and the $^{31}P\{^1H\}$ NMR spectra at 161.93 MHz. Phosphorus chemical shifts were measured relative to 85% phosphoric acid. An internal deuterium lock (usually CD_2Cl_2 or $(CD_3)_2CO$) was used for all samples. For all nuclei, positive chemical shifts are downfield from the standards.

Elemental analyses were performed within the department. Conductivity measurements were made by using a Yellow Springs Instrument Model 31 conductivity bridge using approximately 1×10^{-3} M solutions in dichloromethane or nitromethane. All compounds which were isolated in solid form were found to react with air over a period of several hours, so appropriate precautions were taken for their storage and handling.

Preparation of Compounds. 1. *trans*-[RhCl(CO)(DMPM)]$_2$ (1). $[RhCl(C_8H_{12})]_2$ (100 mg, 0.203 mmol), dissolved in 12 mL of acetone to which approximately 0.05 mL of water had been added, was refluxed under an atmosphere of carbon monoxide for 15 min. A solution of DMPM (63 μL, 0.405 mmol) in 3 mL of acetone was added via syringe over a period of 5 min. Refluxing under a carbon monoxide atmosphere was continued for a total of 40 min. The solution was then cooled, the solvent removed, and the red-orange solid washed repeatedly with diethyl ether and dried in vacuo; yield 90%. Anal. Calcd for $C_{12}H_{28}Cl_2O_2P_4Rh_2$: C, 23.80; H, 4.63; Cl, 11.74. Found: C, 23.83; H, 4.66; Cl, 11.70.

2. [Rh$_2$(CO)$_2$(μ-Cl)(DMPM)$_2$][BF$_4$] (3). To a slurry of 1 (100 mg, 0.165 mmol) in tetrahydrofuran (15 mL) was added a solution of $AgBF_4$ (32.2 mg, 0.165 mmol) dissolved in tetrahydrofuran (10 mL). After the solution was stirred for 40 min, the solvent was removed under vacuum and the product redissolved in CH_2Cl_2 (8 mL). Silver chloride was removed by filtration of the solution through a pad of Celite. Further reactions with **3** were carried out on the amber-colored filtrate solution based on 100% conversion of **1**. Compound **3** could be obtained in solid form by reduction of the filtrate volume under a stream of N_2 followed by addition of diethyl ether, but it reacted quickly with any traces of air. Compound **3** was determined to be a 1:1 electrolyte in nitromethane solutions (Λ (10^{-3} M) = 75.0 Ω^{-1} cm^2 equiv^{-1}).

3. [Rh$_2$(CO)$_2$(μ-S)(DMPM)$_2$] (6). To a 100-mg sample of 1 (0.165 mmol) dissolved in CH_2Cl_2 (10 mL) was added $Na_2S{\cdot}9H_2O$ (80 mg, 0.331 mmol) and 98% ethanol (10 mL). After the solution was stirred for 3 h, the solvents were removed in vacuo and the product was redissolved in a minimum volume of CH_2Cl_2 (ca. 8 mL). Addition of diethyl ether (25 mL), cooling to 0 °C, and filtration through a pad of Celite yielded a red solution. The solvents were again removed in vacuo, and the residue was redissolved in the minimum volume of CH_2Cl_2 (ca. 8 mL). Hexane (30 mL) was added, and the solution was cooled to 0 °C and filtered through a pad of Celite to remove a small amount of brown precipitate. The solvents were removed in vacuo, yielding a red solid; 62% yield.

4. [Rh$_2$Cl$_2$(CO)$_2$(μ-DMA)(DMPM)$_2$] (8). Dimethyl acetylenedicarboxylate (DMA) (20 μL, 0.165 mmol) was added via syringe to a solution of 1 (100 mg, 0.165 mmol) dissolved in CH_2Cl_2 (10 mL). This resulted in an immediate color change from orange-red to yellow. Stirring was continued for 30 min after which the solvent volume was reduced (to ca. 5 mL) in vacuo, diethyl ether added (25 mL), and the solution cooled to 0 °C. The solvents were removed, and the light yellow solid was washed with diethyl ether and dried in vacuo; yield 85%. Anal. Calcd for $C_{18}H_{34}Cl_2O_6P_4Rh_2$: C, 28.92; H, 4.55; Cl, 9.50. Found: C, 28.64; H, 4.97; Cl, 9.12.

5. [Rh$_2$Cl$_2$(CO)$_2$(μ-HFB)(DMPM)$_2$] (9). A 100-mg sample of 1 (0.165 mmol) dissolved in CH_2Cl_2 (12 mL) was placed under an atmosphere of hexafluorobutyne (HFB). The solution underwent an immediate color change from red to yellow. Stirring was continued under a static atmosphere of HFB for 60 min after which the solvent volume was reduced to ca. 5 mL under dinitrogen, diethyl ether added, and the solution cooled to 0 °C. The solvents were removed, and the bright yellow solid was dried under dinitrogen; yield 85%. Anal. Calcd for $C_{16}H_{28}Cl_2O_2F_6P_4Rh_2$: C, 25.03; H, 3.65; Cl, 9.26. Found: C, 25.07; H, 3.69; Cl, 9.03.

6. [Rh$_2$Cl(CO)$_2$(μ-DMA)(DMPM)$_2$][BF$_4$] (10). Method A. A 100-mg sample of 8 (0.134 mmol) was suspended in tetrahydrofuran (20 mL), and a solution of $AgBF_4$ (26 mg, 0.134 mmol) in tetrahydrofuran (10 mL) was added by syringe. The reaction mixture was stirred for 60 min over which time a fine white precipitate of silver chloride formed. The solvent was removed under vacuum, the product redissolved in CH_2Cl_2 (15 mL), and the solution filtered through a pad of Celite. The volume of the orange-yellow solution was reduced to ca. 8 mL in vacuo, diethyl ether added (25 mL), and the solution cooled to 0 °C. Removal of the solvents, washing with diethyl ether, and drying under vacuum afforded a yellow solid; yield 90%. Compound **10** was determined to be a 1:1 electrolyte in nitromethane solutions (Λ (10^{-3} M) = 86.0 Ω^{-1} cm^2 equiv^{-1}). Anal. Calcd for $C_{18}H_{34}ClBF_4O_6P_4Rh_2$: C, 27.08; H, 4.29; Cl, 4.44. Found: C, 27.23; H, 4.28; Cl, 4.69.

Method B. Dimethyl acetylenedicarboxylate (10 μL, 0.083 mmol) was added to a solution of 3 (54 mg, 0.083 mmol based upon 100% conversion of 1) in CH_2Cl_2 (12 mL). After the solution was stirred for 40 min, the solvent volume was reduced to ca. 6 mL under partial vacuum, diethyl ether was added (25 mL), the solution was cooled to 0 °C and the solvents were removed. The yellow solid was dried in vacuo; yield 74%.

7. [Rh$_2$Cl(CO)$_2$(μ-HFB)(DMPM)$_2$][BF$_4$] (11). Method A. Compound **11** was prepared in a manner analogous to that of **10** but with 100 mg of **9** (0.130 mmol) in 15 mL of tetrahydrofuran and 25.4 mg of $AgBF_4$ (0.130 mmol) dissolved in 10 mL of tetrahydrofuran. The yellow-orange solid was dried under vacuum; yield 91%. Compound **11** was determined to be a 1:1 electrolyte in nitromethane solutions (Λ (10^{-3} M) = 63.3 Ω^{-1} cm^2 equiv^{-1}). Anal. Calcd for $C_{16}H_{28}ClBF_{10}O_2P_4Rh_2$: C, 23.46; H, 3.42; Cl, 4.34. Found: C, 23.22; H, 3.51; Cl, 4.56.

Method B. Compound **11** was prepared in a manner analogous to that of **10** but placing an atmosphere of hexafluorobutyne over a CH_2Cl_2 solution of 3 (54 mg, 0.082 mmol based on 100% conversion of 1); yield 71%.

Reaction of [Rh$_2$(CO)$_2$(μ-Cl)(DMPM)$_2$][BF$_4$] (3) with CO. A solution of 3 was prepared in the manner described above using 50 mg (0.083 mmol) of 1 and 16 mg (0.083 mmol) of $AgBF_4$. CO was then passed through a CH_2Cl_2 solution of 3 for 2 min. The resulting product was stored in solution under an atmosphere of CO.

$^{31}P\{^1H\}$ NMR Magnetization Transfer Experiments. The cationic dicarbonyl complexes [Rh$_2$(CO)$_2$(μ-Cl)(diphosphine)$_2$][BF$_4$] (diphosphine = DMPM, DPPM) were prepared from *trans*-[RhCl(CO)(diphosphine)]$_2$ by the removal of a chloride ligand using 1 equiv of $AgBF_4$ in tetrahydrofuran solution. After isolation, each compound was redissolved in CD_2Cl_2, the solution placed in a 5-mm NMR tube, and less than 1-equiv of CO added via a gas-tight syringe. The $^{31}P\{^1H\}$ NMR spectrum of each sample, taken at −58 °C, contained two second-order signals, one due to the dicarbonyl starting material and a lower field signal due to the tricarbonyl product. The soft pulse transfer experiments were performed on these samples by using a Bruker WP-400 spectrometer, and the rate of exchange results was calculated by using nonlinear least-squares analysis at the University of Alberta Computing Services. The inversion experiments and calculations were performed by using the method described by Alger and Prestegard.[39] The required frequencies for pulsing were derived by using a PTS 160 frequency synthesizer. Typical 180° pulse times were 92 μs. For each run a total of fifteen 90° observation pulses were taken at delays ranging from 5.0×10^{-5} s to 3.0 s.

The rate of CO loss from the tricarbonyl species at −58 °C, as shown in eq 1, was found to be $k_{21} = 3.6 \pm 0.4$ for diphosphine = DMPM and $k_{21} = 0.35 \pm 0.14$ for diphosphine = DPPM.

$$[\mathrm{Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(diphosphine)_2}]^+ \xrightarrow[-\mathrm{CO}]{k_{21}} [\mathrm{Rh_2(CO)_2(\mu\text{-}Cl)(diphosphine)_2}]^+ \quad (1)$$

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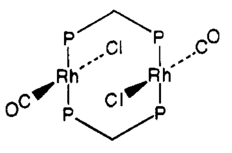
[39] Alger, J. R.; Prestegard, J. H. *J. Magn. Reson.* **1977**, *27*, 137.

X-ray Data Collection. Red crystals of $[Rh_2Cl_4(CO)_2(DMPM)_2]\cdot CH_2Cl_2$ (2) were obtained by serendipity upon attempts to obtain crystals of 1 via the diffusion of diethyl ether into a saturated CH_2Cl_2 solution of *trans*-$[RhCl(CO)(DMPM)]_2$. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22 °C using graphite-monochromated Mo Kα radiation. The automatic peak search and reflection indexing programs, in conjunction with a cell reduction program, established the orthorhombic crystal system, and the systematic absences unambiguously established the space group as *Pbcn*. Cell constants were obtained from a least-squares refinement of the setting angles (centered in both positive and negative θ) of 25 reflections having 2θ between 21.90° and 25.78°.

The intensity data were collected by using the $\theta/2\theta$ scan technique with variable scan speeds chosen to give $\sigma(I)/I \leq 0.03$ within a time limit of 50 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. The scan range was determined as a function of θ to compensate for the $\alpha_1 - \alpha_2$ wavelength dispersion, and backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range. Three reflections were chosen as standard reflections and were remeasured every 60 min of exposure time to check on crystal and electronic stability over the course of data collection. There was no noticeable decrease in the intensity of the standards, so no correction was applied. See Table III for crystal data and details of intensity collection. The data were corrected for Lorentz and polarization effects and for absorption by using the method of Walker and Stuart.[40] Data were reduced in the usual manner by using a value of $p = 0.04$ to downweight intense reflections.[41]

Discussion of Results

(a) Carbonyl Complexes. The reaction of $[RhCl(COD)]_2$ with carbon monoxide and 2 equiv of DMPM in refluxing acetone yields a red-orange product assigned as *trans*-$[RhCl(CO)(DMPM)]_2$ (1). On the basis of the spectroscopic parameters, it appears that 1 has a geometry in which the chloro ligands (and the carbonyls) have a mutually trans arrangement on adjacent metals, as shown.



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The $^{31}P\{^1H\}$ NMR spectrum of compound 1 appears as a symmetrical, second-order multiplet with a separation of 116 Hz between the two principal peaks. Such a second-order pattern, which is dominated by two major peaks, is typical of the $^{31}P\{^1H\}$ NMR spectra of symmetrical dirhodium complexes found in this work and previously for related "$Rh_2(DPPM)_2$" compounds.[32,33] In particular, the signal for 1 is very similar to that of the closely related compound $[Rh_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$.[32a,33a] (The exactly analogous DPPM species *trans*-$[RhCl(CO)(DPPM)]_2$ is highly insoluble in all common solvents, so its solution spectrum has not been obtained.)

The single carbonyl stretch in the infrared spectrum of 1, at 1956 cm^{-1}, is again consistent with the proposed trans geometry and is somewhat lower in frequency than that observed for the DPPM counterpart (ν(CO) = 1976 cm^{-1}, Nujol).[34] This frequency shift is accordant with the greater basicity of the DMPM ligand,[30] which gives rise to increased π back-donation to the carbonyl groups. Although the preparation of 1 succeeds equally well in a number of other solvents (dichloromethane, tetrahydrofuran, or toluene), the low solubility of the product in acetone provides an easy means for its isolation in high yield.

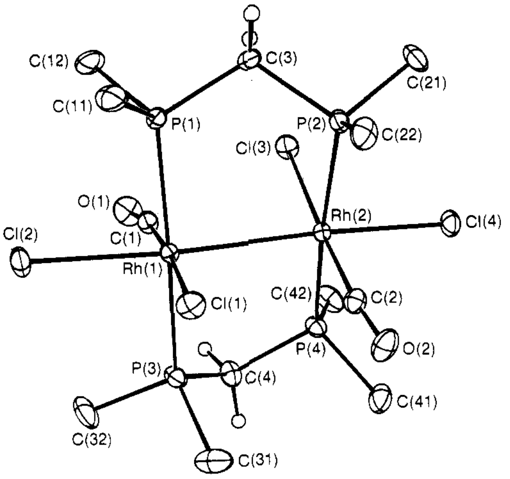

Figure 1. A perspective view of $[Rh_2Cl_4(CO)_2(DMPM)_2]$ showing the numbering scheme. Thermal parameters are shown at the 20% level except for methylene hydrogens which are drawn artificially small. Hydrogen atoms on the methyl groups are omitted for the sake of clarity.

The chemistry reported above, for the DMPM ligand, parallels that of rhodium involving the related DPPM group in which a similar dicarbonyl rhodium species was obtained[31] but contrasts to the DPPM-bridged iridium chemistry in which the species isolated under similar conditions was the tetracarbonyl complex $[Ir_2Cl(CO)_4(DPPM)_2][Cl]$.[5f] This diiridium tetracarbonyl species did ultimately yield the analogous dicarbonyl product *trans*-$[IrCl(CO)(DPPM)]_2$ through stepwise CO loss, but forcing conditions were required to eliminate the extra carbonyl groups. We had originally anticipated that with the more basic DMPM ligand higher carbonyl complexes of rhodium might be obtained, possibly analogous to those involving the "$Ir_2(DPPM)_2$" system; however, this was not the case, at least under these conditions.

In an attempt to obtain suitable crystals of 1 for an X-ray study, a sample of the material was set aside for several weeks to crystallize from CH_2Cl_2/ether. In addition to unsuitable orange-red crystals of 1, well-formed, red, single crystals of an additional product were obtained. This species analyzed as the tetrachloride $[RhCl_2(CO)(DMPM)]_2$ (2) and had a carbonyl stretch at 2039 cm^{-1}, consistent with the proposed Rh(II) formulation. An X-ray structure determination of this species indicates that it has the structure shown in Figure 1, resulting from the apparent oxidative addition of Cl_2 to complex 1. Bond lengths and angles are given in Tables IV and V. Compound 2 had been observed on previous occasions when 1 had been exposed to chlorinated solvents (CH_2Cl_2, $CHCl_3$) for extended periods of time and could also be prepared directly as the major species by the reaction of 1 with HCl or Cl_2 (the other minor products in these reactions were not identified). By contrast the analogous compound *trans*-$[RhCl(CO)(DPPM)]_2$ was not observed to form the oxidative addition product by chlorine abstraction from solvent. Such a difference is consistent with the more basic DMPM-bridged complex 1 favoring oxidative addition.

Compound 2 has the expected trans arrangement of diphosphine groups bridging the two pseudooctahedral metal centers. The Rh(1)–Rh(2) separation of 2.7591 (5) Å corresponds to a normal single bond as expected for two adjacent Rh(II) centers. There is no obvious difference between the Rh–P distances (range 2.333 (1)–2.352 (1) Å)

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[40] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 1581.

[41] Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

Table I. Infrared Spectroscopic Data

		Nujol, cm^{-1}		CH_2Cl_2 solution, cm^{-1}	
no.	compd	ν(CO)	others	ν(CO)	others
1	*trans*-$[RhCl(CO)(DMPM)]_2$	1956 (vs)[a]		1965 (s)	
2	$[RhCl_2(CO)(DMPM)]_2$	2039 (vs)			
3	$[Rh_2(CO)_2(\mu\text{-}Cl)(DMPM)_2][BF_4]$	1986 (vs)		1997 (s)	
		1958 (vs)		1980 (s)	
4	$[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(DMPM)_2][BF_4]$			2057 (w)	
				1997 (s), 1990 (w)	
				1860 (w), 1710 (w)	
				1603 (w)	
6	$[Rh_2(CO)_2(\mu\text{-}S)(DMPM)_2]$	1932 (s)		1925 (s)	
		1916 (s)		1941 (s)	
8	$[Rh_2Cl_2(CO)_2(\mu\text{-}DMA)(DMPM)_2]$	2028 (vs)	1712 (m),[b] 1665 (s)[b]	2035 (s)	1702 (m),[b] 1679 (m)[b]
		2005 (vs)	1562 (m)[c]	2025 (s)	1571 (w)[c]
		1980 (vs),[d] 1958 (vs)[d]			
9	$[Rh_2Cl_2(CO)_2(\mu\text{-}HFB)(DMPM)_2]$	2030 (vs)	1590 (m)[c]	2039 (s)	1590 (w)[c]
10	$[Rh_2Cl(CO)_2(\mu\text{-}DMA)(DMPM)_2][BF_4]$	2036 (s)	1687 (br)[b]	2048 (s)	1690 (br)[b]
		2023 (s)	1561 (m)[c]	2020 (sh)	1567 (br)[c]
11	$[Rh_2Cl(CO)_2(\mu\text{-}HFB)(DMPM)_2][BF_4]$	2045 (vs)	1597 (m)[c]	2059 (s)	1602 (m)[c]

[a] Abbreviations used: vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder. [b] ν(C=O) of CO_2CH_3. [c] ν(C=C). [d] $\nu(^{13}CO)$.

Table II. NMR Spectroscopic Data

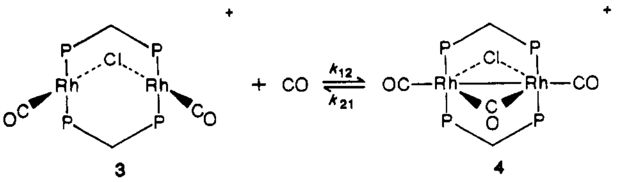
	^1H,[a] δ			
compd	P-CH_3	-CH_2-	others	$^{31}P\{^1H\}$,[a,b] δ
1	1.71 (t, 12 H, J = 3 Hz)[c]	2.46 (q, J = 4.6 Hz)		−3.56 (d, 116 Hz)
	1.66 (dt, 12 H, J = 1.2, 3.2 Hz)			
3[d]	1.73 (m, 12 H)	2.87 (dq), 2.26 (dq)[e]		−4.74 (d, 106 Hz)
	1.69 (m, 12 H)			
4[f]				0.18 (d, 96 Hz)[g]
6[h]	1.74 (t, 12 H)	3.57 (dq), 1.90 (dq)[e]		−10.74 (120.8 Hz)
	1.59 (s, 12 H)			
8	1.54 (t, 6 H, J = 3 Hz)	2.64 (m), 2.81 (m)[e]	3.65 (s, -OCH_3)	−8.55 (dt, 97, 27 Hz)
	1.70 (t, 6 H, J = 4 Hz)			−6.25 (dt, 90, 26 Hz)
	1.76 (t, 6 H, J = 3.5 Hz)			
	1.82 (t, 6 H, J = 3.5 Hz)			
9	1.61 (t, 6 H, J = 3 Hz)	2.77 (m), 2.88 (m)[e]		−8.07 (dt, 96, 28 Hz)
	1.63 (t, 6 H, J = 3 Hz)			−6.11 (dt, 92, 29 Hz)
	1.79 (t, 6 H, J = 3 Hz)			
	1.85 (t, 6 H, J = 3 Hz)			
10	1.84 (s, 12 H)	2.75 (m), 2.50 (m)[e]	3.68 (s, -OCH_3)	−6.47 (d, 91 Hz)
	1.66 (s, 12 H)			−5.77 (dt, 85, 25 Hz)[i]
				−9.96 (dt, 86, 25 Hz)[i]
11	1.68 (s, 12 H)	2.55 (q)		−5.82 (d, 89 Hz)
	1.88 (s, 12 H)			−5.10 (dt, 83, 26 Hz)[i]
				−7.45 (dt, 103, 25 Hz)[i]

[a] Ambient temperature. [b] Vs 85% H_3PO_4, numbers in parentheses represent the separation in hertz between the two major peaks in the second-order spectrum of the complex. [c] Abbreviations used: s, singlet; d, doublet; t, triplet; q, quintet; dt, doublet of triplets; dq, doublet of quintets; m, multiplet. [d] $^{13}C\{^1H\}$ NMR of 3 (CD_2Cl_2, −60 °C): δ 185.6 (dt, $J_{C\text{-}Rh}$ = 82.6 Hz, $J_{C\text{-}P}$ = 17.2 Hz). [e] Two halves of an AB quartet. [f] $^{13}C\{^1H\}$ NMR of 4 (CD_2Cl_2, −60 °C): δ 192.8 (m), 188.7 (m). [g] −60 °C. [h] $^{13}C\{^1H\}$ NMR of 6 (CD_2Cl_2): δ 185.2 (s) at ambient temperature, δ 183.8 (dt, $J_{C\text{-}Rh}$ = 69.2 Hz, $J_{C\text{-}P}$ = 15.2 Hz) at −93 °C. [i] −40 °C.

in this DMPM-bridged complex and those of analogous DPPM species.[5c,d,33b,35,36] The two Rh–Cl bonds opposite the Rh–Rh bond (2.480 (1), 2.478 (1) Å) are longer than those cis to it (2.385 (1), 2.393 (1) Å), consistent with a high trans influence of metal–metal bonds.[5b] Other bond lengths and angles within the complex are essentially as expected. The ligands on each metal are staggered with regard to each other about the Rh–Rh bond with an average torsion angle of 22.0°, in order to minimize nonbonded contacts.

The cationic A-frame complex $[Rh_2(CO)_2(\mu\text{-}Cl)(DMPM)_2][BF_4]$ (3) is readily prepared from *trans*-$[RhCl(CO)(DMPM)]_2$ (1) by removal of a chloride ion using 1 equiv of $AgBF_4$. The conductivity (75.0 Ω^{-1} cm^2 $equiv^{-1}$ in nitromethane) and spectroscopic data (Tables I and II) for 3 are consistent with the chloride-bridged, A-frame structure as has previously been reported for the corresponding rhodium and iridium DPPM compounds.[5f,32a,33a,35] Once again the effect of a more basic diphosphine ligand (DMPM) on the rhodium atoms is realized in lower carbonyl stretching frequencies for 3 (1986, 1958 cm^{-1}) compared to those of the DPPM analogue $[Rh_2(CO)_2(\mu\text{-}Cl)(DPPM)_2][BF_4]$ (1995 (s), 1978 (vs) cm^{-1}).[35]

Like the corresponding "$Rh_2(DPPM)_2$" complex,[32a,33a] 3 reacts reversibly with CO in solution to yield the tricarbonyl species $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(DMPM)_2][BF_4]$ (4). This reaction is presumed to follow the pathway



3 4

established[32a] for the DPPM adduct in which the incoming CO molecule binds terminally to one rhodium atom, followed by the movement of a terminal carbonyl ligand into the bridged position to give a symmetrical final product

Table III. Crystal Data and Details of Intensity Collection

compd	$[Rh_2Cl_4(CO)_2(DMPM)_2]\cdot CH_2Cl_2$
fw	760.81
mol formula	$C_{13}H_{30}Cl_6P_4Rh_2O_2$
cryst shape	irregular
cryst size, mm	0.36 × 0.37 × 0.47
systematic absences	*0kl*, *k* odd; *h0l*, *l* odd; *hk0*, *h* + *k* odd
space group	*Pbcn* (No. 60)
temp, °C	22
radiatn (λ, Å)	Mo Kα (0.71073), graphite monochromated
unit cell parameters	
a, Å	30.573 (4)
b, Å	13.469 (2)
c, Å	12.624 (2)
V, Å^3	5198.8
Z	8
ρ_{calcd}, g cm^{-3}	1.944
linear absorp coeff, μ, cm^{-1}	21.28
max 2θ, deg	52.00
takeoff angle, deg	3.00
detector aperture, mm	3.00 + (tan θ) wide × 4.00 high
cryst to detector distance, mm	173
scan type	θ/2θ
scan rate, deg min^{-1}	variable between 1.00 and 6.67
scan width, deg	(0.50 + 0.347 tan θ)
total no. of reflctns collected	5674 (+*h*,+*k*,+*l*)
no. of independent observns (NO) ($I > 3\sigma(I)$)	3985
no. of variables (NV)	239
R[a]	0.044
R_w[a]	0.058
GOF[a]	1.629

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

Table IV. Positional Parameters and Isotropic *B*'s for Individual Atoms[a]

atom	*x*	*y*	*z*	*B*, Å^3
Rh(1)	0.16210 (2)	0.19977 (4)	0.08078 (4)	1.980 (9)
Rh(2)	0.10726 (2)	0.30283 (4)	0.21506 (4)	1.958 (9)
Cl(1)	0.10442 (6)	0.1236 (1)	−0.0170 (1)	3.23 (4)
Cl(2)	0.21570 (6)	0.1185 (1)	−0.0385 (2)	3.92 (4)
Cl(3)	0.16261 (6)	0.4237 (1)	0.2514 (2)	3.26 (4)
Cl(4)	0.05757 (6)	0.3864 (1)	0.3419 (1)	3.37 (4)
Cl(5)[b]	−0.0325 (3)	0.2317 (6)	−0.1917 (6)	11.4 (2)
Cl(6)[b]	−0.0026 (3)	0.0838 (8)	−0.176 (1)	17.8 (4)
P(1)	0.16400 (5)	0.3315 (1)	−0.0414 (1)	2.28 (3)
P(2)	0.08555 (6)	0.4077 (1)	0.0777 (1)	2.56 (3)
P(3)	0.16371 (6)	0.0667 (1)	0.2004 (2)	2.88 (4)
P(4)	0.12698 (6)	0.2078 (1)	0.3637 (1)	2.72 (4)
O(1)	0.2416 (2)	0.2704 (4)	0.1930 (5)	4.6 (1)
O(2)	0.0330 (2)	0.1678 (4)	0.1658 (5)	4.3 (1)
C(1)	0.2096 (2)	0.2508 (5)	0.1530 (6)	2.9 (1)
C(2)	0.0627 (2)	0.2155 (5)	0.1821 (5)	2.8 (1)
C(3)	0.1315 (2)	0.4405 (5)	−0.0047 (6)	2.8 (1)
C(4)	0.1670 (2)	0.1098 (6)	0.3373 (6)	3.2 (2)
C(5)[b]	0.016 (1)	0.186 (2)	−0.224 (5)	22 (1)*
C(11)	0.1472 (3)	0.2985 (6)	−0.1755 (6)	4.1 (2)
C(12)	0.2173 (2)	0.3843 (6)	−0.612 (8)	4.7 (2)
C(21)	0.0642 (3)	0.5250 (5)	0.1217 (6)	3.9 (2)
C(22)	0.0442 (2)	0.3635 (6)	−0.0121 (6)	3.7 (2)
C(31)	0.1186 (3)	−0.0200 (6)	0.2013 (7)	5.3 (2)
C(32)	0.2111 (3)	−0.0134 (6)	0.1879 (8)	5.4 (2)
C(41)	0.0816 (3)	0.1441 (7)	0.4239 (7)	5.1 (2)
C(42)	0.1513 (3)	0.275 (6)	0.4728 (6)	4.5 (2)

[a] Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3\,[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. [b] Disordered CH_2Cl_2.

Table V. Bond Distances[a] (Å) for Compound 5

Rh(1)–Rh(2)	2.759 (5)	P(1)–C(11)	1.824 (6)
Rh(1)–Cl(1)	2.385 (1)	P(1)–C(12)	1.795 (6)
Rh(1)–Cl(2)	2.480 (1)	P(2)–C(3)	1.804 (5)
Rh(1)–P(1)	2.352 (1)	P(2)–C(21)	1.797 (6)
Rh(1)–P(3)	2.344 (1)	P(2)–C(22)	1.800 (6)
Rh(1)–C(1)	1.847 (6)	P(3)–C(4)	1.826 (6)
Rh(2)–Cl(3)	2.393 (1)	P(3)–C(31)	1.806 (7)
Rh(2)–Cl(4)	2.478 (1)	P(3)–C(32)	1.814 (6)
Rh(2)–P(2)	2.333 (1)	P(4)–C(4)	1.829 (6)
Rh(2)–P(4)	2.351 (1)	P(4)–C(41)	1.799 (7)
Rh(2)–C(2)	1.846 (6)	P(4)–C(42)	1.809 (6)
Cl(5)[b]–C(5)	1.67 (4)	O(1)–C(1)	1.132 (6)
Cl(6)–C(5)	1.61 (4)	O(2)–C(2)	1.132 (6)
P(1)–C(3)	1.831 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Atoms Cl(5), Cl(6), and C(5) are from CH_2Cl_2 of crystallization.

containing a bridging chloride and carbonyl ligand.

Monitoring the CO addition by $^{31}P\{^1H\}$ NMR spectroscopy at room temperature reveals the presence of a broad apparent doublet at δ −4.47, which upon cooling to −60 °C appears as two well-defined signals (δ 0.18, −5.67). Both are second order in nature with two principal peaks, characteristic of symmetrical species. The higher field signal is identical in every respect with the starting material and has been assigned as such. The remaining signal at δ 0.18 (*J* = 96 Hz) is attributed to the tricarbonyl species **4** and bears a strong resemblance to the resonance for the DPPM analogue.[32a,33a] In addition, the spectra over the above temperature range are very similar to those observed for the DPPM species.[33a] At −60 °C the resonance due to the carbonyl groups in ^{13}CO-enriched **3** appears in the $^{13}C\{^1H\}$ NMR spectrum as a doublet of triplets (J_{Rh-C} = 82.6 Hz, J_{P-C} = 17.2 Hz) at δ 185.6. The addition of ^{13}CO at this temperature results in the appearance of two new unresolved peaks at δ 192.8 and 188.7, integrating in the ratio 1:2, respectively. These resonances are consistent with a tricarbonyl species, with the bridging carbonyl ligand appearing at lower field.

Of some surprise to us, the tricarbonyl species **4** loses CO more readily than does its DPPM analogue. Although $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(DPPM)_2]^+$ could be isolated as a solid and was stable to CO loss as such, compound **4** could not be isolated pure owing to facile CO loss; in solution under an atmosphere of CO both **3** and **4** were observed together. We had expected that the more basic DMPM group would favor binding of strong π acids.

Our inability to separate **3** and **4** in solution or in the solid made identification of the carbonyl stretches due to **4** difficult. Careful monitoring of the solution-infrared spectrum of **3** upon stepwise CO addition showed that the strong sharp bands at 1997 and 1980 cm^{-1} coalesced to give a broad band at 1997 cm^{-1} with a shoulder at 1990 cm^{-1}. The terminal carbonyl stretches due to both **3** and **4** are apparently overlapping within this broad envelope. In addition, weak new bands at 2057, 1860, 1710, and 1603 cm^{-1} also appeared. On the basis of analogies with the DPPM-bridged tricarbonyl species, we assign the 1860 cm^{-1} band to the bridging carbonyl of the static structure **4** and propose that the other bands are due to species involved in some fluxional processes entailing rearrangement of the carbonyl ligands over both metal centers, not unlike that proposed for the DPPM species. That **4** should be more fluxional than the DPPM analogue is not surprising since this process should be facilitated by the less bulky methyl substituents on DMPM. Such facile CO migration around the binuclear framework may be responsible for the increased lability of **4** compared to the DPPM species. These arguments are consistent with the rates of CO loss from **4** and the DPPM analogue $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(DPPM)_2][BF_4]$, which have been determined by selective

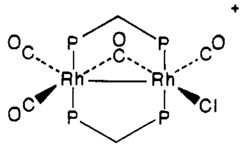
Table VI. Bond Angles[a] (deg) in Compound 5

Rh(2)–Rh(1)–Cl(1)	94.89 (4)	Cl(3)–Rh(2)–Cl(4)	90.04 (5)	C(3)–P(2)–C(21)	104.3 (3)
Rh(2)–Rh(1)–Cl(2)	175.33 (4)	Cl(3)–Rh(2)–P(2)	86.09 (5)	C(3)–P(2)–C(22)	105.4 (3)
Rh(2)–Rh(1)–P(1)	92.18 (4)	Cl(3)–Rh(2)–P(4)	92.06 (5)	C(21)–P(2)–C(22)	103.4 (3)
Rh(2)–Rh(1)–P(3)	90.09 (4)	Cl(3)–Rh(2)–C(2)	176.5 (2)	Rh(1)–P(3)–C(4)	111.6 (2)
Rh(2)–Rh(1)–C(1)	89.2 (2)	Cl(4)–Rh(2)–P(2)	91.96 (5)	Rh(1)–P(3)–C(31)	118.8 (2)
Cl(1)–Rh(1)–Cl(2)	89.10 (5)	Cl(4)–Rh(2)–P(4)	83.62 (5)	Rh(1)–P(3)–C(32)	114.5 (3)
Cl(1)–Rh(1)–P(1)	90.20 (5)	Cl(4)–Rh(2)–C(2)	89.0 (2)	C(4)–P(3)–C(31)	104.0 (3)
Cl(1)–Rh(1)–P(3)	91.14 (5)	P(2)–Rh(2)–P(4)	175.03 (5)	C(4)–P(3)–C(32)	103.2 (3)
Cl(1)–Rh(1)–C(1)	175.5 (2)	P(2)–Rh(2)–C(2)	90.5 (2)	C(31)–P(3)–C(32)	103.1 (4)
Cl(2)–Rh(1)–P(1)	85.35 (5)	P(4)–Rh(2)–C(2)	91.3 (2)	Rh(2)–P(4)–C(4)	114.7 (2)
Cl(2)–Rh(1)–P(3)	92.27 (5)	C(16)–C(15)–C(5)	47 (1)	Rh(2)–P(4)–C(41)	113.5 (2)
Cl(2)–Rh(1)–C(1)	86.8 (2)	C(15)–C(16)–C(5)	49 (1)	Rh(2)–P(4)–C(42)	116.1 (2)
P(1)–Rh(1)–P(3)	177.25 (5)	Rh(1)–P(1)–C(3)	115.2 (2)	C(4)–P(4)–C(41)	104.5 (3)
P(1)–Rh(1)–C(1)	91.4 (2)	Rh(1)–P(1)–C(11)	114.7 (2)	C(4)–P(4)–C(42)	103.1 (3)
P(3)–Rh(1)–C(1)	87.1 (2)	Rh(1)–P(1)–C(12)	114.3 (2)	C(41)–P(4)–C(42)	103.6 (3)
Rh(1)–Rh(2)–C(12)	91.74 (4)	C(3)–P(1)–C(11)	106.1 (3)	Rh(1)–C(1)–O(1)	170.4 (5)
Rh(1)–Rh(2)–C(13)	176.65 (4)	C(3)–P(1)–C(12)	102.1 (3)	Rh(2)–C(2)–O(2)	174.1 (5)
Rh(1)–Rh(2)–P(2)	91.20 (4)	C(11)–P(1)–C(12)	102.9 (3)	P(1)–C(3)–P(2)	111.8 (3)
Rh(1)–Rh(2)–P(4)	93.47 (4)	Rh(2)–P(2)–C(3)	110.8 (2)	P(3)–C(4)P(4)	111.5 (3)
Rh(1)–Rh(2)–C(2)	89.4 (2)	Rh(2)–P(2)–C(21)	113.9 (2)	Cl(5)–C(5)–Cl(6)	84 (2)
		Rh(2)–P(2)–C(22)	117.9 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

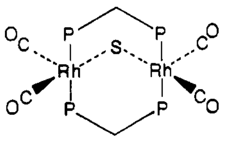
inversion magnetization transfer experiments (see Experimental Section). It has been determined that CO loss from 4 occurred at a rate of ca. 10 times faster (k_{21}(DMPM)/k_{21}(DPPM) = 3.6/0.35) than that from the DPPM species.

The nature of the complex formed under CO is highly sensitive to slight changes in the CO pressure. When CO is flushed through the system at atmospheric pressure such that the reaction vessel atmosphere is completely replaced by CO, a new unsymmetrical species (**5**) appears in the $^{31}P\{^1H\}$ NMR spectrum while a new broad undefined peak appears in the $^{13}C\{^1H\}$ NMR spectrum (δ 184.6; CD_2Cl_2 at -60 °C) when ^{13}CO is used. Replacing the static CO atmosphere above the reaction solution by N_2 apparently lowers the concentration of CO in solution enough to cause the resonance of **5** to immediately be replaced by those of **3** and **4**. This extreme lability of **5** made it impossible to obtain an IR spectrum of **5** without the presence of major amounts of **3** and **4**. The only obvious change in the spectra upon addition or removal of CO was the appearance or disappearance of a new weak band at 1807 cm^{-1}. On the basis of analogies with the well-studied "$Ir_2(DPPM)_2$" system,[5f] we propose that the labile, unsymmetrical species **5** is the tetracarbonyl species shown. In this case the more basic DMPM ligand would appear to impart enough basicity to the Rh centers to cause some resemblence to the "$Ir_2(DPPM)_2$" system; no analogous species was observed upon reaction of $[Rh_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$ with CO.



5

The neutral "A-frame" $[Rh_2(CO)_2(\mu\text{-}S)(DMPM)_2]$ (**6**) is obtained in much the same manner as its "$Rh_2(DPPM)_2$" analogue,[31] by reaction of the *trans*-dichloro dicarbonyl complex **1** with $Na_2S\cdot9H_2O$. The yield of the red solid is somewhat less (~62%) than that reported for the DPPM counterpart (85–95%) due to significant decomposition of this species. Compound **6** undergoes complete decomposition over a period of several days even under a dinitrogen atmosphere to an unidentified brown solid and is extremely sensitive to oxygen in solution. The $^{31}P\{^1H\}$ NMR spectrum of **6** again appears very similar to that of **3**, and the IR spectrum shows two carbonyl stretches at 1932 and 1916 cm^{-1}, reminiscent of $[Rh_2(CO)_2(\mu\text{-}S)(DPPM)_2]$ (ν(CO) = 1933, 1920 cm^{-1}, Nujol).[31] The $^{13}C\{^1H\}$ NMR spectrum of **6** at room temperature shows a broad singlet at δ 185.2 that resolves into the expected doublet of triplets (δ 183.8 (J_{Rh-C} = 69.2 Hz, J_{P-C} = 15.2 Hz); CD_2Cl_2 solution) at -93 °C. Compound **6** also reacts with CO to give a second-order doublet in the $^{31}P\{^1H\}$ NMR spectrum at ambient temperature (δ -21.68; CD_2Cl_2) together with the resonance for the starting material. At the same time the infrared spectrum shows a strong, new carbonyl stretch at 1994 cm^{-1} together with the bands due to **6**. There is no indication of a bridging carbonyl band other than a very weak band at 1720 cm^{-1}. The $^{13}C\{^1H\}$ NMR spectrum at -93 °C shows a new broad resonance at δ 183.9 (CD_2Cl_2). On the basis of this information, the new species appears to be the tetracarbonyl complex **7**. The additional carbonyl bands expected for a tetracarbonyl species are not observed, presumably being obscured by the broad intense bands of the starting material **6**. Unlike the chloro analogue **5**, this species retains the bridging sulfido group presumably because movement of this *dianionic* bridging group to a terminal position would result in an unfavorable dipolar species. The appearance of two separate signals in the $^{31}P\{^1H\}$ NMR spectrum at room temperature indicates that no rapid CO exchange takes place between **6** and **7** as was observed between **3** and **4**. The formation of the tetracarbonyl complex **7** is in contrast to the chemistry of both the rhodium and iridium DPPM analogues $[Rh_2(CO)_2(\mu\text{-}S)(DPPM)_2]$[31] and $[Ir_2(CO)_2(\mu\text{-}S)(DPPM)_2]$;[37] whereas the rhodium complex did not react with CO, the iridium one did, but to yield a tricarbonyl complex like **4**. We see no obvious reason for the differences observed in our DMPM-bridged species, except to note that the more basic DMPM ligand would favor CO addition and that this smaller group would tend to allow a higher metal coordination than would DPPM.



7

(b) Reactions with Alkynes. *trans*-$[RhCl(CO)(DMPM)]_2$ (**1**) reacts with 1 equiv of the activated alkynes

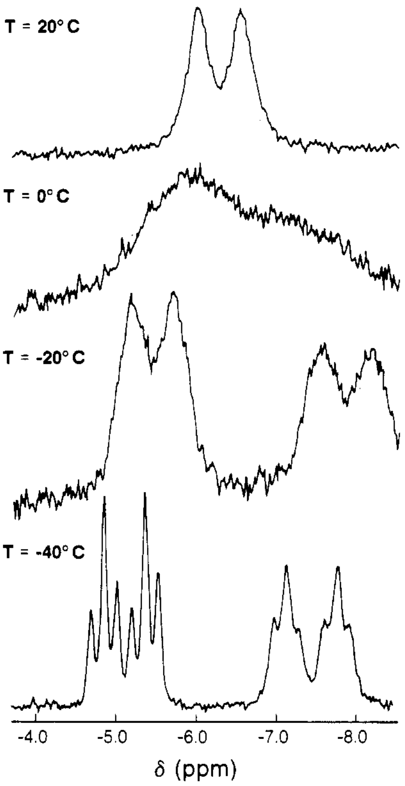
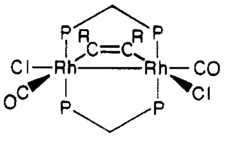


Figure 2. The $^{31}P\{^1H\}$ NMR spectrum, at 161.93 MHz, of $[Rh_2Cl(CO)_2(\mu\text{-HFB})(DMPM)_2][BF_4]$ (11) between −40 and 20 °C.

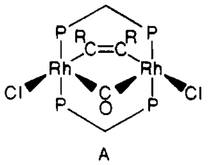
dimethyl acetylenedicarboxylate (DMA) and hexafluorobutyne (HFB) to yield 1:1 adducts of the form $[Rh_2Cl_2(CO)_2(\mu\text{-alkyne})(DMPM)_2]$ (8, alkyne = DMA; 9, alkyne = HFB). No reaction is observed with the unactivated alkynes phenylacetylene, diphenylacetylene, and 2-butyne. Both compounds 8 and 9 are assigned the structure shown, based on analogies with the alkyne adducts of *trans*-$[IrCl(CO)(DPPM)]_2$[5b] in which the alkyne group bridges the two metals essentially parallel to the metal–metal axis.



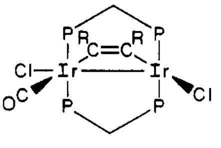
8, R=CO_2CH_3
9, R=CF_3

The $^{31}P\{^1H\}$ NMR spectra of both 8 and 9 exhibit complex second-order patterns consisting of two pseudodoublets of triplets (Table II). This pattern is typical for an unsymmetrical complex having an AA′BB′XY spin system by virtue of the chemically inequivalent rhodium atoms. The infrared spectrum of 8 (Nujol) displays the carbonyl ligand stretches at 2028 and 2005 cm^{-1} with additional stretches at 1712 and 1665 cm^{-1} for the carbonyl groups of the coordinated DMA group. The infrared spectrum of 9, on the other hand, displays only one carbonyl stretch at 2030 cm^{-1}. However, on the basis of similarities in the other spectral parameters (IR, NMR) with compound 8, we assume that 9 is a dicarbonyl species in which the stretches due to both carbonyls appear to be coincident. It is noteworthy that this was exactly the situation observed for $[Ir_2Cl_2(CO)_2(\mu\text{-HFB})(DPPM)_2]$.[5b]

The chemistry of 1 with alkynes more closely resembles that of *trans*-$[IrCl(CO)(DPPM)]_2$[5b] than of *trans*-$[RhCl(CO)(DPPM)]_2$.[36] For the rhodium DPPM complex one carbonyl ligand was very labile and the only complex isolated was the unusual species $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-alkyne})(DPPM)_2]$, containing a bridging carbonyl ligand but no accompanying Rh–Rh bond (see structure A). The more basic DMPM ligand apparently imparts enough basicity to the Rh atoms to decrease the lability of this carbonyl group via π back-donation, much as was the case for the "$Ir_2(DPPM)_2$" complexes. Upon heating, the iridium species $[Ir_2Cl_2(CO)_2(\mu\text{-alkyne})(DPPM)_2]$ did lose one carbonyl ligand; however, the resulting products had the remaining carbonyl ligand terminally bound with an Ir–Ir bond (structure B).[5b] We were interested in labilizing one of the carbonyl ligands in 8 or 9 to discover which structural type would be adopted by the "$Rh_2(DMPM)_2$" system. Unfortunately attempts to obtain the monocarbonyl products failed; trimethylamine oxide did not remove a carbonyl group and heating under reflux in various solvents resulted in decomposition to a number of unidentified products.

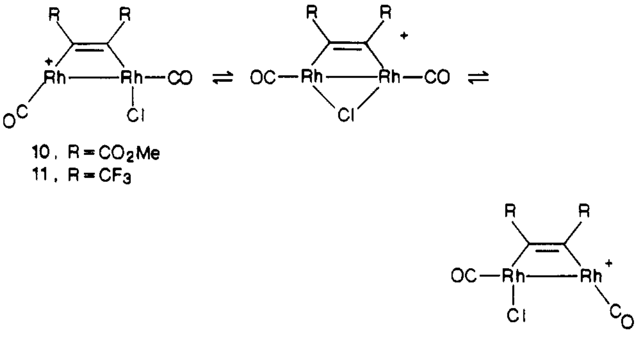


A



B

The cationic alkyne-bridged complexes $[Rh_2Cl(CO)_2(\mu\text{-}RC_2R)(DMPM)_2][BF_4]$ (10, R = CO_2CH_3; 11, R = CF_3) can be prepared by either chloride ion removal from compounds 8 and 9, respectively, or by the direct reaction of the cationic A-frame (3) with the alkyne molecules. These cationic species are assigned the geometry shown above (DMPM groups perpendicular to the plane of the paper are omitted). At room temperature both complexes 10 and 11 display broad resonances in the $^{31}P\{^1H\}$ NMR spectrum, suggestive of symmetrical species; however, lowering the temperature to −40 °C results in the appearance of patterns typical for unsymmetrical species (see Figure 2). This temperature dependence suggests a fluxionality, as was observed for the analogous "$Ir_2(DPPM)_2$" systems, in which chloride ligand transfer from one metal to the other occurs. Such processes appear to be common in these systems.[5b,i,7,42]



10, R=CO_2Me
11, R=CF_3

In the infrared spectra of 10 two bands appear for the terminal carbonyl ligands at 2036 and 2023 cm^{-1} and a broad band for the DMA carbonyl groups is also present at 1687 cm^{-1}. For compound 11 only one terminal carbonyl band is observed at 2045 cm^{-1}, as was the case for the parent compound 9. However, the fluxionality of this system and the similarity of its spectroscopic properties to 10 make it clear that it is also a dicarbonyl complex. For all alkyne-bridged complexes the C=C stretches for the cis-dimetalated olefinic moiety are observed near 1560 cm^{-1} (see Table I), and the ^1H NMR parameters (see Table II)

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(42) Cowie, M.; Vaartstra, B., manuscript in preparation.

are consistent with the species proposed.

In the analogous "$Ir_2(DPPM)_2$" chemistry chloride removal from $[Ir_2Cl_2(CO)_2(\mu\text{-alkyne})(DPPM)_2]$ and alkyne addition to $[Ir_2(CO)_2(\mu\text{-Cl})(DPPM)_2]^+$ resulted in different isomers, the latter of which slowly rearranged to the more stable one.[5b] In the "$Rh_2(DMPM)_2$" chemistry only one isomer is observed in these cationic alkyne adducts, that corresponding to the thermodynamically more stable diiridium species. While it may be that only this isomer is formed, it may also be that alkyne attack at $[Rh_2(CO)_2(\mu\text{-Cl})(DMPM)_2]^+$ yields the unstable isomer, analogous to the iridium system, but that rearrangement to the more stable one is extremely facile. This presumed more rapid isomerization is consistent with the greater lability of the second-row metals over their third-row counterparts and with the smaller DMPM ligand facilitating such a process, although it must be stressed that our presumption of another isomer being involved is based solely on analogies with the $Ir_2(DPPM)_2$ chemistry.

Conclusions

The series of "$Rh_2(DMPM)_2$" complexes reported is quite analogous, although not identical, to those of rhodium and iridium containing the larger and less basic DPPM ligand. Both differences in ligand properties (bulk and basicity) are evident in the observed chemical differences for these complexes. Not surprisingly, the more basic $Me_2PCH_2PMe_2$ ligand results in better π donation to carbonyl ligands from the metals such that the chemistry of the "$Rh_2(DMPM)_2$" complexes more closely resemble the DPPM analogues of iridium than of rhodium. This is seen most clearly in the alkyne adducts where the dicarbonyl complexes $[M_2Cl_2(CO)_2(\mu\text{-alkyne})(\text{diphosphine})_2]$ and $[M_2Cl(CO)_2(\mu\text{-alkyne})(\text{diphosphine})_2]^+$ (M = Rh, diphosphine = DMPM; M = Ir, diphosphine = DPPM) are in contrast with the only observed "$Rh_2(DPPM)_2$" species, $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-alkyne})(DPPM)_2]$. Similarly the tetracarbonyl species $[Rh_2Cl(CO)_3(\mu\text{-CO})(DMPM)_2]^+$ and $[Rh_2(CO)_4(\mu\text{-S})(DMPM)_2]$ were obtained with the DMPM group whereas with DPPM only the tricarbonyl $[Rh_2(CO)_2(\mu\text{-Cl})(\mu\text{-CO})(DPPM)_2]^+$ and the dicarbonyl $[Rh_2(CO)_2(\mu\text{-S})(DPPM)_2]$ were obtained.

The smaller steric bulk of the DMPM group appears to allow more facile ligand rearrangements over the two metals, so the observation of only one isomer of $[Rh_2Cl(CO)_2(\mu\text{-alkyne})(DMPM)_2]^+$ rather than the two observed with the "$Ir_2(DPPM)_2$" system[5b] may be due to facile isomerization. In addition it may be that the greater lability of $[Rh_2(CO)_2(\mu\text{-Cl})(\mu\text{-CO})(DMPM)_2]^+$ compared with its DPPM analogue is due to more facile rearrangement within the complex.

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Registry No. **1**, 114445-93-1; **2**, 114445-95-3; **3**, 114446-02-5; **4**, 114446-09-2; **5**, 114445-97-5; **6**, 114446-03-6; **7**, 114445-98-6; **8**, 114445-99-7; **9**, 114446-00-3; **10**, 114446-05-8; **11**, 114446-07-0; $[RhCl(C_8H_{12})]^2$, 12092-47-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen parameters (2 pages); a listing of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

Synthesis and Structural Characterization of Heterocyclic Thiocarbene, Selenocarbene, Thione, and Selone Complexes of Tungsten Pentacarbonyl or Chromium Pentacarbonyl

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Received December 15, 1987

Various pentacarbonyl complexes of W and Cr containing heterocyclic ligands were prepared from the synthon formed by the addition of PhC≡CXLi (X = S or Se) to carbene complexes $[M(CO)_5\{C(OEt)Ph\}]$ (M = Cr, W). The nature of the electrophile (S or Se) that was added, as well as the temperature at which the reaction was carried out, determined whether the synthon acted mainly as an anionic thio- or selenocarbene complex to give rise to carbene complexes $[W(CO)_5L]$ (L = $\mathrm{CC(Ph){=}C(Ph)SeS}$, $\mathrm{CC(Ph){=}C(Ph)SSe}$, $\mathrm{CC(Ph){=}C(Ph)SeSe}$) or as a thio- or selenoacyl anion to form thione or selone complexes $[Cr(CO)_5\{S{=}CC(Ph){=}C(Ph)SS\}]$ and $[W(CO)_5L]$ (L = $\mathrm{S{=}CC(Ph){=}C(Ph)SS}$, $\mathrm{Se{=}CC(Ph){=}C(Ph)SS}$, $\mathrm{Se{=}CC(Ph){=}C(Ph)SeSe}$).

Introduction

In our study of the insertion of the anionic species $PhC{\equiv}CS^-$ and $PhC{\equiv}CSe^-$ into the carbene bond in $[W(CO)_5\{C(OEt)Ph\}]$,[1] we found that the anionic adduct resulting from the addition of $PhC{\equiv}CX^-$ (X = S, Se) to the carbene complex could be used to prepare various novel

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(1) Raubenheimer, H. G.; Kruger, G. J.; Marais, C. F. *J. Chem. Soc., Chem. Commun.* **1984**, 634.

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