the starting V:P ratio. As Preuss and Schug mentioned,[4] high temperature seems to promote the decomposition of the heteropolyvanadate anion.

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Acetylene Activation in Binuclear Rhodium Complexes and the Structure of [Rh₂Cl₂(μ-CO)(μ-CH₃O₂CC₂CO₂CH₃)(Ph₂PCH₂PPh₂)₂]: A Complex Containing a Bridging Acetylene and a Ketonic Carbonyl Ligand

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trans-[RhCl(CO)(DPM)]₂ and [Rh₂Cl₂(μ-CO)(DPM)₂] react with DMA and HFB (DMA = CH₃O₂CC₂CO₂CH₃; HFB = CF₃C₂CF₃; DPM = Ph₂PCH₂PPh₂), yielding the complexes [Rh₂Cl₂(μ-CO)(μ-acetylene)(DPM)₂]. The bromo and iodo derivatives have also been prepared from [Rh₂Br(CO)(μ-CO)(DPM)₂][Br], [Rh₂Br₂(μ-CO)(DPM)₂], [Rh₂I(CO)(μ-CO)(DPM)₂][I], and [Rh₂I₂(μ-CO)(DPM)₂]. One member of this series, [Rh₂Cl₂(μ-CO)(μ-DMA)(DPM)₂], has been structurally characterized by X-ray crystallography. This complex crystallizes in the space group $P4_12_12$ with a = 15.021 (2) Å, c = 25.738 (5) Å, and Z = 4. On the basis of 4566 unique observed reflections, the structure has been refined to R = 0.049 and R_w = 0.066. The molecule contains an acetylene ligand bound to both metals as a cis-dimetalated olefin, a bridging ketonic carbonyl ligand, and no metal–metal bond. All parameters about the acetylenic carbon atoms suggest sp^2 hybridization of these atoms. Similarly, the Rh–CO–Rh angle (116.0 (4)°) and the large metal–metal separation (3.3542 (9) Å) suggest that the carbonyl carbon atom is also sp^2 hybridized and bound to the metals by two localized electron-pair bonds. The ^{13}C NMR chemical shifts for these carbonyl carbons are at unusually high field compared to those for conventional carbonyl ligands, being more comparable to the values observed for organic carbonyl groups. The complex [Rh₂Cl₂(μ-CO)(DPM)₂] catalyzes the cyclotrimerization of DMA but not its hydrogenation. In contrast, [Rh₂Cl₂(μ-CO)(DPM)₂] catalyzes the hydrogenation of phenylacetylene to styrene but does not bring about its cyclotrimerization.

Introduction

As part of our continuing interest in binuclear complexes and their reactions with small molecules,[1-6] we undertook an investigation into the chemistry of several binuclear rhodium complexes with acetylene molecules. Of initial concern to us were the mode of acetylene binding and its relationship to the subsequent chemistry displayed by the acetylene molecule. In binuclear complexes, two acetylene bonding modes are most commonly observed: the tetrahedral μ_2-η^2 geometry (A) in
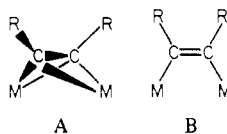
which the acetylene molecule sits perpendicular to the metal–metal axis[7-18] and the cis-dimetalated olefinic geometry (B)

in which the acetylene molecule lies parallel to the metal–metal axis.[19-22]

It is anticipated that these acetylene coordination modes will give rise to different reactivity patterns. Not only are the steric environments of these groups different, but their electronic environments also differ significantly. In mode A each acetylenic carbon atom is bound to both metals whereas in structure B each carbon is bound to only one metal. Therefore, the acetylene in A functions as a two-electron donor to each metal whereas in B it donates one electron to each metal. As a corollary of this, complexes having the same metal and ancillary ligands but differing in the acetylene coordination mode (A or B) will differ with respect to metal–metal interactions. For example, if there is no metal–metal bond in A, there will be one in B (and vice versa).

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Table I. Spectra Data

| | | infrared, cm^{-1} | | $^{31}P\{^{1}H\}$ NMR | |
| | | | | | $|^{1}J_{Rh-P} + {}^{x}J_{Rh-P}|^{a}$ |
no.	compound	ν(CO)	ν(C≡C)	δ, ppm	Hz
6	[Rh$_2$I$_2$(μ-CO)(DPM)$_2$]	1755 (m)^{b}		16.3	114.1
7	[Rh$_2$Cl$_2$(μ-CO)(μ-DMA)(DPM)$_2$]	1700 (m, b)		9.7	141.6
8	[Rh$_2$Br$_2$(μ-CO)(μ-DMA)(DPM)$_2$]	1700 (m, b)		9.9	140.3
9	[Rh$_2$I$_2$(μ-CO)(μ-DMA)(DPM)$_2$]	1700 (m, b)		10.8	137.9
10	[Rh$_2$Cl$_2$(μ-CO)(μ-HFB)(DPM)$_2$]	1705 (m)		8.9	131.8
11	[Rh$_2$Br$_2$(μ-CO)(μ-HFB)(DPM)$_2$]	1690 (m)		8.8	132.4
12	[Rh$_2$I$_2$(μ-CO)(μ-HFB)(DPM)$_2$]	1690 (m)		9.4	130.1
13	[Rh$_2$Cl$_2$(μ-HFB)(DPM)$_2$]		1638	7.5	111.8

^{a} This is the splitting between the two major peaks. ^{b} Spectra run in Nujol mulls. Abbreviations: m = medium; b = broad.

Furthermore, it is anticipated that binuclear acetylene complexes will show significantly enhanced reactivity over that of the free acetylenes. In structurally characterized binuclear acetylene complexes[7-22] the acetylenic bond is significantly lengthened with respect to that in free acetylenes[23] or even with respect to acetylenes bound to one metal.[24] This lengthening, which results from bond-order reduction, has been found to be necessary for activation of acetylenes for hydrogenation[25-27] and, in some cases, oligomerization reactions.[21,28] One aspect of this study was therefore to investigate the ability of our binuclear rhodium complexes to activate acetylenes toward hydrogenation and oligomerization reactions.

While this study was in its infancy it became obvious to us that a series of the acetylenic complexes that we formulated as [Rh$_2$X$_2$(μ-CO)(μ-acetylene)(DPM)$_2$] had bridging carbonyl ligands, which on the basis of spectroscopic studies appeared not to be accompanied by metal–metal bonds. At that time only two ketonic carbonyl[29] complexes had been structurally characterized,[30,31] and none had been reported with rhodium. Owing to the novelty of this unusual type of bridging carbonyl ligand and in order to unambiguously characterize the acetylene coordination mode, we undertook the structural determination of a representative member of this series, [Rh$_2$Cl$_2$-(μ-CO)(μ-DMA)(DPM)$_2$] (DMA = dimethyl acetylenedicarboxylate). A preliminary report of this structure has appeared.[32] In the present report we outline the preparations and spectral characterizations of a series of acetylene complexes and report the structure of the above representative member of this series. In addition, some preliminary acetylene hydrogenation and cyclotrimerization reactions are reported.

Experimental Section

All solvents were appropriately dried and degassed prior to use under an atmosphere of dinitrogen, and reactions were routinely carried out under Schlenk conditions with an atmosphere of either dinitrogen or the reactant gas. Bis(diphenylphosphino)methane (DPM) was purchased from Strem Chemicals, hydrated rhodium chloride from Research Organic/Inorganic Chemicals, dimethyl acetylenedicarboxylate (DMA) from Aldrich, and hexafluoro-2-butyne (HFB) from Pierce Chemical. These and all other reagent grade chemicals were used as received. *trans*-[RhCl(CO)(DPM)]$_2$[33] (1), [Rh$_2$Cl$_2$-

(μ-CO)(DPM)$_2$] (2), [Rh$_2$Br$_2$(μ-CO)(DPM)$_2$] (3), [Rh$_2$Br(CO)(μ-CO)(DPM)$_2$][Br] (4), and [Rh$_2$I(CO)(μ-CO)(DPM)$_2$][I] (5) were prepared by the reported procedures.[4] [Rh$_2$I$_2$(μ-CO)(DPM)$_2$] (6) was prepared by the addition of 300 mg (1.81 mmol) of KI dissolved in 10 mL of methanol to 200 mg (0.186 mmol) of [Rh$_2$Cl$_2$(μ-CO)(DPM)$_2$][4] in 10 mL of CH$_2$Cl$_2$. This mixture was stirred at room temperature for 36 h, after which time the solvents were removed under N$_2$. The solid was washed with degassed H$_2$O/methanol and was recrystallized from CH$_2$Cl$_2$ (yield ca. 75%). Spectral data are shown in Table I. The ^{13}CO-substituted complexes were prepared by analogous procedures but by using ^{13}CO. Infrared spectra were recorded on a Perkin-Elmer 467 spectrometer with use of Nujol mulls on KBr plates or in solution in KBr cells. $^{31}P\{^{1}H\}$ and $^{13}C\{^{31}P\{^{1}H\}\}$ NMR spectra were obtained at 36.4 and 22.6 MHz, respectively, on a Bruker HFX-90 spectrometer at 233 K, unless otherwise specified. The phosphorus chemical shifts were measured relative to external H$_3$PO$_4$ whereas those for carbon were measured relative to CD$_2$Cl$_2$ solvent and are reported relative to tetramethylsilane. An internal deuterium lock (CD$_2$Cl$_2$) was used for all samples. For both nuclei, positive shifts are downfield from the standards. Elemental analyses were performed within the department or by Canadian Microanalytical Service Ltd., Vancouver, Canada. Hydrogenation products were characterized on an Aerograph Autoprep Model A-700 GLC using a 5% Carbowax 20 on Chromosorb W column operating at a fixed column temperature of 85 °C, a detector temperature of 110 °C, an injector temperature of 140 °C, and a helium flow rate of 20 mL min⁻¹. The retention times for PhCCH, PhHCCH$_2$, and PhH$_2$CCH$_3$ were 15.7, 9.5, and 5.0 min, respectively.

Preparation of the Acetylene Complexes. (a) [Rh$_2$Cl$_2$(μ-CO)(μ-DMA)(DPM)$_2$][33] (7). **Method A.** To a suspension of 1 (200 mg, 0.182 mmol) in 20 mL of CH$_2$Cl$_2$ was added 50 μL (0.407 mmol) of degassed dimethyl acetylenedicarboxylate. The solid sample rapidly dissolved, giving a red-brown solution which after approximately 24 h gave a dark green solid essentially quantitatively. The spectral parameters (Table I) and the elemental analyses (C, H, Cl) were consistent with the formulation given.

Method B. To a solution of 200 mg (0.186 mmol) of 2 in 20 mL of CH$_2$Cl$_2$ was added 50 μL (0.407 mmol) of DMA. Precipitation with diethyl ether after approximately 15 min yielded a dark green solid having infrared and $^{31}P\{^{1}H\}$ NMR parameters identical with those of the product of method A.

(b) [Rh$_2$X$_2$(μ-CO)(μ-DMA)(DPM)$_2$] (X = Br, I; 8, 9). The bromo species was obtained from either 3 or 4 and the iodo species was obtained from 5 or 6 by reacting CH$_2$Cl$_2$ solutions of these complexes with DMA as described above.

(c) [Rh$_2$X$_2$(μ-CO)(μ-HFB)(DPM)$_2$] (X = Cl, Br, I; 10, 11, 12). The hexafluoro-2-butyne species were all prepared in a manner analogous to that for the DMA species except that 1 atm of the acetylene gas was placed above a suspension of 1 or above a solution of either 2, 3, 4, 5, or 6. All of the above acetylene complexes are dark green.

Infrared and $^{31}P\{^{1}H\}$ NMR spectra for all compounds are given in Table I. All elemental analyses except for those of [Rh$_2$I$_2$(μ-CO)(μ-HFB)(DPM)$_2$] prepared from 5 were consistent with the formulations given. The $^{31}P\{^{1}H\}$ NMR spectra of the HFB complex 12, prepared from 5, always showed an additional resonance of

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(33) Abbreviations used: DPM = bis(diphenylphosphino)methane; DMA = dimethyl acetylenedicarboxylate; HFB = hexafluoro-2-butyne, Cp = η^5-C$_5$H$_5$.

comparable intensity due to $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)(DPM)_2]^+$,[4] accounting for the unsatisfactory elemental analyses.

(d) $[Rh_2Cl_2(\mu\text{-}HFB)(DPM)_2]$ (13). A suspension of $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}HFB)(DPM)_2]$ (10) (200 mg, 0.162 mmol) in 50 mL of $CHCl_3$ was refluxed under dinitrogen for 24 h, during which time all of the starting material entered into solution. Removal of the solvent under an N_2 bleed and washing with diethyl ether gave a light green solid whose infrared and $^{31}P\{^1H\}$ NMR spectra were identical with those of an authentic sample, which was prepared by an alternate route and characterized by elemental analyses, spectral studies, and an X-ray structure determination.[34]

The ^{13}CO-substituted acetylene complexes **7–12** were prepared as shown above, starting with ^{13}CO-substituted complexes **2–6**.

Hydrogenation Studies. A typical experiment consisted of weighing accurately approximately 10 mg of compound **2** into a two-neck flask, which was then placed on a hydrogen-uptake apparatus (gas buret) and flushed several times with hydrogen. A 50-mL sample of previously degassed methanol was then injected into the flask and was left overnight to equilibrate. During this time the red-brown solid entered into solution, giving a light yellow solution. Approximately 0.15 mL of the substrate was then injected into the flask, and the volume of hydrogen was monitored at regular time intervals. When hydrogenation of this aliquot of substrate had ceased, another 0.15 mL was injected, and this procedure was repeated until hydrogenation had slowed to about one-tenth of the initial rate, after which time no further readings were taken. In subsequent runs a three-necked reaction flask was fitted with a buret to allow simple addition of the aliquots of substrate without having to repeatedly syringe in the small volumes. Throughout the run the temperature of the reaction flask was monitored along with the atmospheric pressure. Turnover numbers were calculated both on the number of moles of substrate used and on the number of moles of hydrogen used. The numbers based on hydrogen uptake were 10–15% greater than those based on substrate used. At the end of the run the solvent was removed by vacuum distillation. The hydrogenated products were then removed by extracting with diethyl ether and were analyzed by GLC techniques.

For each run the 0.15-mL aliquot of substrate, the hydrogen uptake was linear up to the point where all phenylacetylene had been converted into styrene, at which point hydrogen uptake essentially stopped. The analysis of hydrogenation products showed the major product to be styrene with about 10% ethylbenzene. Turnover numbers (mol of substrate used/mol of catalyst) exceeded 1350, and in a typical run using a 2.1×10^{-4} M solution of the catalyst the initial hydrogen uptake was ca. 4.85 mL min^{-1} (14.3 turnover numbers min^{-1}).

Cyclotrimerization Studies. The cyclotrimerization of DMA was carried out in a manner analogous to the preparation of $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}DMA)(DPM)_2]$ but by using a 200-fold excess of DMA and only ca. 10 mg of **2** in 50 mL of MeOH. The reaction was monitored by ^1H NMR spectroscopy and the product characterized by both ^1H NMR spectroscopy and mass spectrometry. The ^1H NMR chemical shifts for the DMA and the hexamethyl mellitate are δ 3.82 and 4.75 ppm, respectively, in CD_3OD. Turnover numbers of about 60 were obtained within 30 min at room temperature. Similar reactions were attempted in CH_2Cl_2 by using both $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ and $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}DMA)(DPM)_2]$ as catalyst precursors. In both cases no observable amount of hexamethyl mellitate was detected even after 24 h. The reaction using the acetylene complex as catalyst precursor in methanol also yielded no hexamethyl mellitate under the above conditions.

X-ray Data Collection. Suitable-quality crystals of $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}DMA)(DPM)_2]$ were obtained by allowing diethyl ether to slowly diffuse into a saturated CH_2Cl_2 solution of the complex.

Preliminary film data showed that the crystals belonged to the tetragonal system with extinctions ($h00$, h odd; $00l$, $l \neq 4n$) characteristic of the space group $P4_12_12$ or $P4_32_12$. Accurate cell parameters were obtained by a least-squares analysis of 12 carefully centered reflections chosen from diverse regions of reciprocal space ($50° \leq 2\theta \leq 70°$; Cu K$\alpha_1$ radiation) and obtained with use of a narrow X-ray source. See Table II for pertinent crystal data and the details of data collection.

Data were collected on a Picker four-circle automated diffractometer equipped with a scintillation counter and a pulse height analyzer tuned to accept 90% of the Cu Kα peak. Background counts were measured

Table II. Summary of Crystal Data and Intensity Collection

compd	$Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}DMA)(DPM)_2$
fw	1215.64
formula	$Rh_2Cl_2P_4O_5C_{57}H_{50}$
cell parameters	
a	15.021 (2) Å
c	25.738 (5) Å
V	5807 Å^3
Z	4
density	1.390 g cm^{-3} (calcd)
space group	$P4_12_12$
cryst dimens	0.039 × 0.042 × 0.069 cm
cryst shape	distorted octahedron with faces of forms $\{101\}$ and $\{011\}$
cryst vol	0.039 mm^3
temp	22 °C
radiation	Cu Kα (λ = 1.540 562 Å) filtered with 0.5-mil Ni foil
μ	69.811 cm^{-1}
range in abs cor factors	0.117–0.258
receiving aperture	4 × 4 mm
takeoff angle	6.3°
scan speed	2° in 2θ/min
scan range	1.1° below Kα_1 to 1.1° above Kα_2
bkgd counts	$3° \leq 2\theta \leq 60°$, 10 s; $60° < 2\theta \leq 104°$, 20 s; $104 < 2\theta \leq 124°$, 40 s
2θ limits	$3° \leq 2\theta \leq 124°$
unique data used ($F_o^2 \geq 3\sigma(F_o^2)$)	4566
final no. of parameters varied	146
error in observn of unit wt	1.832
R	0.049
R_w	0.066

at both ends of the scan range with both crystal and counter stationary. The intensities of three standard reflections were measured every 100 reflections throughout the data collection and were found to remain constant to within 1.5% of the mean. The intensities of 5023 unique reflections ($3° \leq 2\theta \leq 124$) were measured by using Cu Kα radiation and processed in the usual manner with $\sigma(F_o^2)$ calculated by using a value of 0.05 for p.[35] Of these, 4566 had $F_o^2 \geq 3\sigma(F_o^2)$ and were used in subsequent calculations. Absorption corrections were applied to the data by using Gaussian integration.[36]

Structure Solution and Refinement. The structure was solved in the space group $P4_12_12$ by using a sharpened Patterson synthesis to locate the independent rhodium atom. Subsequent refinements and difference-Fourier calculations led to the location of all remaining atoms. Atomic scattering factors were taken from Cromer and Waber's tabulation[37] for all atoms except hydrogen, for which the values of Stewart et al.[38] were used. Anomalous dispersion[39] terms for Rh, Cl, and P were included in F_c. The carbon atoms of all phenyl rings were refined as rigid groups having D_{6h} symmetry, C–C distances of 1.392 Å, and independent isotropic thermal parameters. All hydrogen atoms of the DPM ligands were located, were included in their idealized positions calculated from the geometry about their attached carbon atom by using a C–H distance of 0.95 Å, and were not refined. These hydrogen atoms were assigned isotropic thermal parameters of 1 Å^2 greater than the isotropic thermal parameter (or the equivalent isotropic thermal parameter of anisotropic atoms) of their attached carbon atom. The hydrogen atoms of the acetylene ligand were not located and so were not included in the least-squares calculations. The carbomethoxy groups of the acetylenic moiety were disordered between two positions and were refined by assuming a 50% occupancy at each site. The disordered atoms were refined with isotropic thermal parameters. The final model in the space group $P4_12_12$ with 146 parameters refined converged to R = 0.049 and R_w = 0.066,[40] and

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Table III. Positional and Thermal Parameters for the Nongroup Atoms of $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-DMA})(DPM)_2]$

atom	x^a	y	z	$U_{11}{}^b$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	0.72152 (3)	0.62524 (3)	−0.05164 (2)	2.97 (2)	3.08 (2)	3.29 (2)	−0.12 (2)	0.10 (2)	0.06 (2)
Cl	0.8575 (1)	0.6386 (1)	−0.10268 (6)	3.89 (8)	6.0 (1)	4.84 (8)	−0.01 (7)	1.04 (6)	0.58 (7)
P(1)	0.7908 (1)	0.5279 (1)	0.00723 (6)	3.28 (7)	3.34 (7)	3.78 (7)	0.11 (6)	0.27 (6)	0.37 (6)
P(2)	0.7161 (1)	0.6307 (1)	0.10345 (5)	3.64 (7)	3.46 (7)	3.50 (6)	0.11 (6)	−0.02 (6)	0.34 (6)
O(1)	0.7774 (3)	0.7774	0	3.9 (2)	3.9	4.9 (3)	−0.9 (3)	0.8 (2)	−0.8
C(1)	0.7227 (4)	0.7227	0	3.4 (2)	3.4	2.7 (4)	0.5 (4)	−0.5 (2)	0.5
C(2)	0.7390 (4)	0.5229 (4)	0.0725 (2)	4.1 (3)	4.1 (3)	4.5 (3)	0.4 (3)	−0.1 (3)	1.7 (3)
C(3)	0.6091 (4)	0.5752 (4)	−0.0215 (2)	2.9 (3)	3.8 (3)	4.5 (3)	−0.4 (2)	−0.2 (2)	−0.1 (3)
C(4)	0.5682 (5)	0.4997 (5)	−0.0508 (3)	6.6 (5)	5.3 (4)	5.6 (4)	−1.7 (4)	0.6 (4)	−0.6 (4)

atom	x	y	z	$B, \text{Å}^2$	atom	x	y	z	$B, \text{Å}^2$
O(2a)	0.573 (1)	0.423 (1)	−0.0282 (7)	7.3 (4)	O(2b)	0.6177 (7)	0.4746 (7)	−0.0879 (4)	4.5 (2)
O(3a)	0.514 (1)	0.516 (1)	−0.0862 (7)	8.3 (4)	O(3b)	0.526 (1)	0.439 (1)	−0.0268 (8)	9.0 (4)
C(5a)	0.517 (2)	0.355 (2)	−0.060 (1)	10.6 (7)	C(5b)	0.588 (2)	0.395 (2)	−0.1183 (9)	7.4 (5)

^{a} Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. ^{b} The form of the thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^2$.
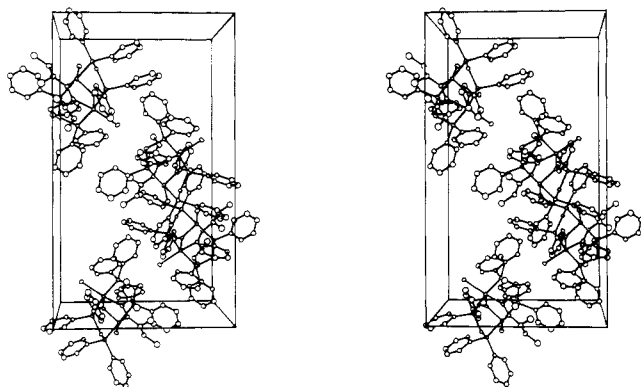

Figure 1. Stereoview of the cell of $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-DMA})(DPM)_2]$. The x axis is horizontal to the left, the z axis runs from top to bottom, and the y axis runs into the page. 20% thermal ellipsoids are used with the exception of the methylene hydrogen atoms, which are drawn artificially small in this and all subsequent drawings.

on a final Fourier difference map, the 20 highest residuals (1.73–0.76 e/Å^{-3}) were mainly in the vicinity of the disordered carbomethoxy groups, indicating that the model used did not completely account for the disorder. A typical carbon atom on earlier syntheses had an electron density of about 4.0 e/Å^3.

Refinement of the structure in the space group $P4_32_12$ converged at $R = 0.066$ and $R_w = 0.091$, suggesting that the original choice was probably correct.

The final positional parameters of the individual nonhydrogen atoms and the phenyl groups are given in Tables III and IV, respectively. The derived hydrogen positions, their thermal parameters, and a listing of observed and calculated structure factor amplitudes used in the refinement are available.[41]

Discussion

Description of Structure. The structure of $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-DMA})(DPM)_2]$, shown in Figure 1, consists of four discrete molecules in the cell, situated on the crystallographic 2-fold axes. There are no unusually short intermolecular contacts (Table V). Figure 2 presents a perspective view of the molecule, including the numbering scheme (phenyl hydrogen atoms have the same number as their attached carbon atoms). The plane of the acetylene and the rhodium atoms is shown in Figure 3 along with some relevant bond lengths and angles.

$[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-DMA})(DPM)_2]$ consists of two rhodium centers bridged by two transoid DPM ligands. In the equatorial plane, approximately perpendicular to the Rh–P vectors, the rhodium atoms are bridged by a carbonyl ligand and an
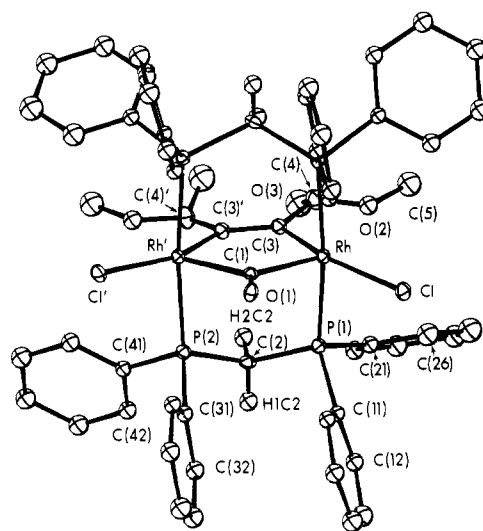
(40) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.
(41) Supplementary material.

Figure 2. Perspective view of $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-DMA})(DPM)_2]$ showing the numbering scheme. The numbering on the phenyl carbon atoms starts at the carbon bonded to the phosphorus and increases sequentially around the ring. 50% thermal ellipsoids are shown.
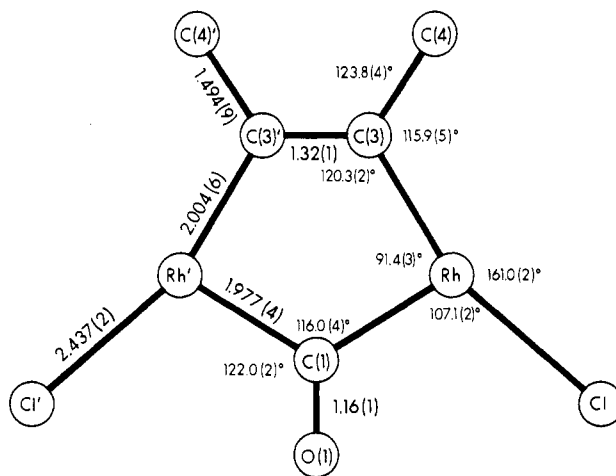

Figure 3. Inner coordination sphere of $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-DMA})-(DPM)_2]$ drawn in the plane of the metals and the acetylene ligand. Some relevant bond lengths and angles are shown.

acetylene ligand, the latter of which is bonded as a cis-dimetalated olefin. A terminal chloro ligand completes the coordination sphere of each rhodium atom and is almost trans to the metalated olefin. The molecules of the complex have crystallographically imposed 2-fold symmetry, with the 2-fold

Table IV

<p style="text-align:center">Derived Parameters for the Rigid Groups of $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-DMA})(DPM)_2]$</p>

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.9091 (2)	0.5383 (3)	0.0211 (1)	3.1 (1)	C(31)	0.8250 (2)	0.6717 (3)	0.1239 (1)	3.3 (1)
C(12)	0.9560 (3)	0.4649 (2)	0.0396 (2)	4.0 (1)	C(32)	0.8847 (3)	0.6158 (2)	0.1492 (2)	4.4 (1)
C(13)	1.0439 (3)	0.4746 (3)	0.0558 (2)	5.6 (2)	C(33)	0.9658 (3)	0.6490 (3)	0.1669 (2)	5.3 (2)
C(14)	1.0848 (2)	0.5576 (3)	0.0536 (1)	5.5 (2)	C(34)	0.9871 (2)	0.7382 (3)	0.1592 (1)	5.8 (2)
C(15)	1.0380 (3)	0.6310 (2)	0.0351 (2)	4.6 (1)	C(35)	0.9273 (3)	0.7942 (2)	0.1339 (2)	4.9 (2)
C(16)	0.9501 (3)	0.6213 (3)	0.0189 (2)	3.5 (1)	C(36)	0.8463 (3)	0.7610 (3)	0.1162 (2)	3.7 (1)
C(21)	0.7822 (4)	0.4151 (3)	−0.0180 (2)	3.5 (1)	C(41)	0.6634 (3)	0.6004 (3)	0.1645 (1)	3.2 (1)
C(22)	0.7388 (4)	0.3460 (4)	0.0076 (1)	4.3 (1)	C(42)	0.6848 (3)	0.5230 (3)	0.1914 (2)	4.0 (1)
C(23)	0.7321 (4)	0.2627 (3)	−0.0157 (2)	5.5 (2)	C(43)	0.6479 (4)	0.5071 (3)	0.2402 (2)	5.1 (2)
C(24)	0.7689 (4)	0.2484 (3)	−0.0646 (2)	5.9 (2)	C(44)	0.5897 (3)	0.5687 (3)	0.2620 (1)	5.3 (2)
C(25)	0.8123 (4)	0.3175 (4)	−0.0903 (1)	7.3 (2)	C(45)	0.5683 (3)	0.6462 (3)	0.2351 (2)	5.4 (2)
C(26)	0.8190 (4)	0.4009 (3)	−0.0670 (2)	6.2 (2)	C(46)	0.6052 (4)	0.6620 (3)	0.1863 (2)	4.4 (1)

Rigid-Group Parameters

	$x_c{}^a$	y_c	z_c	δ^b	ϵ	η
ring 1	0.9970 (2)	0.5479 (2)	0.0374 (1)	3.342 (3)	2.814 (3)	6.389 (2)
ring 2	0.7755 (2)	0.3318 (2)	−0.0413 (1)	0.276 (3)	1.114 (4)	1.934 (3)
ring 3	0.9060 (2)	0.7050 (2)	0.1415 (1)	3.374 (3)	2.694 (3)	0.377 (3)
ring 4	0.6266 (2)	0.5846 (2)	0.2132 (1)	2.653 (3)	1.062 (4)	6.088 (3)

^{a} x_c, y_c, and z_c are the fractional coordinates of the centroid of the rigid group. ^{b} The rigid group orientation angles δ, ϵ, and η (radians) are the angles by which the rigid body is rotated with respect to a set of axes X, Y, and Z. The origin is the center of the ring; X is parallel to a^*, Z is parallel to c, and Y is parallel to the line defined by the intersection of the plane containing a^* and b^* with the plane containing b and c.

Table V. Selected Interatomic Distances (Å) in $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-DMA})(DPM)_2]$

Bonded

Rh–Cl	2.437 (2)	O(2a)–C(5a)	1.55 (3)
Rh–P(1)	2.348 (2)	C(4)–O(2b)	1.27 (1)
Rh–P(2)$^{\prime b}$	2.346 (2)	C(4)–O(3b)	1.27 (2)
Rh–C(1)	1.977 (4)	O(2b)–C(5b)	1.49 (2)
Rh–C(3)	2.004 (6)	P(1)–C(2)	1.852 (6)
C(1)–O(1)	1.162 (10)	P(1)–C(11)	1.820 (3)
C(1)–O(1)^a	1.179 (10)	P(1)–C(21)	1.819 (4)
C(3)–C(3)$'$	1.322 (12)	P(2)–C(2)	1.838 (7)
C(3)–C(4)	1.494 (9)	P(2)–C(31)	1.825 (4)
C(4)–O(2a)	1.29 (2)	P(2)–C(41)	1.817 (3)
C(4)–O(3a)	1.25 (2)		

Nonbonded

Rh···Rh$'$	3.3542 (9)	C(2)···H(42)	2.76
P(1)···P(2)	3.126 (2)	O(1)···H(16)	2.65
Cl···H(36)	2.66	O(1)···H(43)^c	2.81
Cl···H1C2^c	2.72	C(21)···H(12)	2.67
Cl···H(46)	2.81	O(3a)···H(35)^d	2.62
C(2)···H(22)	2.66	O(1)···H(36)	2.60

^{a} Bond length corrected for thermal motion; atom 2 riding on atom 1. ^{b} The two sets of disordered positions are designated a and b. Primed atoms are related to unprimed atoms by a 2-fold axis in this and all subsequent tables. ^{c} Atom located at $^1/_2 + y$, $^3/_2 - x$, $z - ^1/_4$. ^{d} Atom located at $y - ^1/_2$, $^3/_2 - x$, $z - ^1/_4$.

axis bisecting the Rh–Rh$'$ and C(3)–C(3)$'$ vectors and being collinear with the bridging carbonyl group. Each metal is five-coordinate with a geometry resembling a distorted tetragonal pyramid having the carbonyl ligand at the apex and the other ligands in the basal plane. The somewhat analogous carbonyl-free species $[Pd_2Cl_2(\mu\text{-HFB})(DPM)_2]^{21}$ has a slightly distorted square-planar geometry about each Pd atom, which does not differ much from the corresponding part of the present species. Geometrically, the title compound corresponds to the palladium complex with a bridging carbonyl ligand occupying the apical site above each metal.

The rhodium–DPM framework is much like those observed in similar DPM-bridged complexes of rhodium.[1-6,34] As is commonly observed in these systems, the methylene linkages of the DPM groups are folded toward the more crowded side of the molecule[1-3,5,34] (that having the coordinated acetylene) allowing the bulky phenyl rings to avoid unfavorable contacts with the acetylene molecule. In addition the phenyl groups

are arranged such that they are staggered with respect to the equatorial ligand positions thus minimizing short contacts with these groups. The Rh–P distances (average 2.347 (2) Å) (see Table V) are quite typical but are at the long end of those observed in similar systems where a range of 2.303 (2)–2.367 (8) Å has been observed.[1-6,34] It seems that the longer Rh–P distances are associated with complexes having the metals in a higher formal oxidation state; in the present species the metals can be considered as formally Rh(III) (vide infra).

The long Rh–Rh separation is believed to be the largest yet observed in a dirhodium DPM-bridged species and is probably a result of the bridging acetylene ligand forcing the two metals apart. This long rhodium–rhodium separation corresponds to no formal metal–metal bond and can be contrasted to typical Rh–Rh separations where a metal–metal bond is present (2.7566 (9)–2.8415 (7) Å).[1,2,5,6] In $[Pd_2Cl_2(\mu\text{-HFB})(DPM)_2]^{21}$ the large Pd–Pd separation of 3.492 (1) Å again results from the bridging acetylene ligand forcing the metals apart. The shorter separation in the present compound compared to the Pd complex seems to be due to the requirements of the bridging carbonyl ligand. As it is, this is the largest metal–metal separation to be bridged by a carbonyl group.[42] The absence of a metal–metal bond in the title compound is substantiated by the observed diamagnetism, the electron count, which yields a 16-electron configuration at each rhodium center without the inclusion of such a bond, and the intraligand P–P separation (3.126 (2) Å), which is much shorter than the metal–metal separation and indicates no mutual attraction of the metals. Furthermore the fact that the metals tend to be forced so far apart by the acetylene ligand indicates the absence of a direct metal–metal interaction. By comparison, in $[Rh_2Cl_2(\mu\text{-HFB})(DPM)_2]$,[34] where the acetylene is analogously bound, a direct metal–metal bond holds the metals 2.7447 (9) Å apart.

The long Rh–Cl distance (2.437 (2) Å) is consistent with it being opposite a σ-bound carbon atom[6,43-45] of high trans

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Table VI. Selected Angles (Deg) in [Rh₂Cl₂(μ-CO)(μ-DMA)(DPM)₂]

Bond Angles

P(1)-Rh-P(2)	170.63 (5)	C(1)-Rh-C(3)	91.4 (3)	C(4)-O(2a)-C(5a)	109 (2)	C(11)-P(1)-C(2)	103.6 (3)
P(1)-Rh-Cl	91.58 (5)	Rh-C(1)-Rh'	116.0 (4)	C(3)-C(4)-O(2b)	111.3 (7)	C(21)-P(1)-C(2)	104.8 (3)
P(1)-Rh-C(1)	91.31 (5)	Rh-C(1)-O(1)	122.0 (2)	C(3)-C(4)-O(3b)	121 (1)	C(11)-P(1)-C(21)	102.6 (2)
P(1)-Rh-C(3)	83.7 (2)	Rh-C(3)-C(3)'	120.3 (2)	O(2b)-C(4)-O(3b)	116 (1)	Rh'-P(2)-C(2)	112.0 (2)
P(2)-Rh-Cl	97.66 (5)	Rh-C(3)-C(4)	115.9 (5)	C(4)-O(2b)-C(5b)	117 (1)	Rh'-P(2)-C(31)	119.3 (1)
P(2)-Rh-C(1)	87.51 (4)	C(3)'-C(3)-C(4)	123.8 (4)	P(1)-C(2)-P(2)	115.8 (3)	Rh'-P(2)-C(41)	112.6 (2)
P(2)-Rh-C(3)	87.0 (2)	C(3)-C(4)-O(2a)	115 (1)	Rh-P(1)-C(2)	115.1 (2)	C(31)-P(2)-C(2)	104.8 (3)
Cl-Rh-C(1)	107.1 (2)	C(3)-C(4)-O(3a)	119 (1)	Rh-P(1)-C(11)	120.4 (1)	C(41)-P(2)-C(2)	103.7 (2)
Cl-Rh-C(3)	161.0 (2)	O(2a)-C(4)-O(3a)	123 (1)	Rh-P(1)-C(21)	108.5 (2)	C(31)-P(2)-C(41)	103.0 (2)

Torsion Angles

Rh-C(3)-C(3)'-C(4)'	-170.9 (4)	C(11)-P(1)-P(2)'-C(41)'	107.6 (2)	C(11)-P(1)-Rh-C(1)	-75.5 (3)
Rh-C(3)-C(3)'-Rh'	8.8 (1.0)	C(21)-P(1)-P(2)'-C(2)'	101.0 (3)	C(21)-P(1)-Rh-C(1)	166.8 (3)
C(4)-C(3)-C(3)'-C(4)'	9.4 (1.4)	C(21)-P(1)-P(2)'-C(31)'	-137.4 (2)	C(31)-P(2)-Rh'-C(1)	58.8 (3)
C(2)-P(1)-P(2)'-C(2)'	-13.4 (2)	C(21)-P(1)-P(2)'-C(41)'	-12.8 (2)	C(41)-P(2)-Rh'-C(1)	179.7 (3)
C(2)-P(1)-P(2)'-C(31)'	108.2 (3)	C(11)-P(1)-Rh-Cl	31.6 (2)	C(11)-P(1)-Rh-C(3)	-166.8 (2)
C(2)-P(1)-P(2)'-C(41)'	-127.3 (3)	C(21)-P(1)-Rh-Cl	-86.0 (2)	C(21)-P(1)-Rh-C(3)	75.5 (2)
C(11)-P(1)-P(2)'-C(2)'	-138.6 (3)	C(31)-P(2)-Rh'-Cl'	-48.1 (2)	C(31)-P(2)-Rh'-C(3)'	150.4 (2)
C(11)-P(1)-P(2)'-C(31)'	-17.0 (3)	C(41)-P(2)-Rh'-Cl'	72.7 (2)	C(41)-P(2)-Rh'-C(3)'	-88.8 (2)

influence. In contrast, a normal terminal Rh–Cl distance in these systems is ca. 2.34–2.39 Å.[2,4,46,47]

As noted earlier, the acetylene molecule is bound as a cis-dimetalated olefin with the acetylene molecule essentially parallel to the rhodium atoms, rather than as the more commonly observed μ_2–η^2 bonding mode where the acetylene molecule lies perpendicular to the metal–metal axis.[7-18] Actually, the acetylene molecule in the present complex is twisted somewhat from the metal–metal axis as is shown by the torsion angles about C(3)–C(3)' (e.g., Rh–C(3)–C(3)'–C(4)') of approximately 9°. The C(3)–C(3)' bond at 1.32 (1) Å is in the range previously observed (ca. 1.27–1.34 Å)[7-22] for both types of acetylene coordination modes and is comparable to a normal C–C double bond.[23] This distance is consistent with the dimetalated olefinic formulation, implying significant activation of the acetylene molecule. By comparison, the C–C triple bond in free acetylenes is ca. 1.20 Å, and this bond lengthens to ca. 1.29 Å when coordinated to only one metal.[24] Also consistent with the olefinic formulation of this ligand are the angles about C(3), which are close to 120° (see Table VI), indicating sp² hybridization of this atom. The rhodium–olefinic bond (Rh–C(3) = 2.004 (6) Å) is comparable to the analogous distances in other complexes exhibiting the cis-dimetalated olefinic coordination modes of an acetylene ligand[19-22] but is significantly shorter than the distances observed (ranging from 2.023 (5) to 2.128 (5) Å) when the acetylene ligand is μ_2–η^2 bound in rhodium complexes.[7-18] The C(3)–C(4) bond is normal for a single bond between sp² hybridized carbon atoms;[48] however, the rest of the acetylene molecule is less than ideally described owing to the disorder of the carbomethoxy groups. In particular, the coordination about C(4) is not exactly planar, and the bond lengths within this part of the molecule, although not unusual, are not exactly as expected. In spite of the disorder, however, the geometry of the carbomethoxy group is quite clearly defined.

An unexpected feature of this structure is the discovery of a carbonyl ligand bridging the two metal centers, which are not bonded to each other (a ketonic carbonyl). This is only the third structural determination of such a ligand and is the first observed for rhodium. As such, it is important to compare the structural features of this carbonyl ligand to those of conventional bridging carbonyls, i.e., those accompanied by a metal–metal bond. The most obvious difference lies in the metal–carbon–metal angles. In the present complex this angle is 116.0 (4)°, comparable to the two previous determinations and near the value expected for an sp²-hybridized carbon atom as observed in organic carbonyl groups. In contrast, this value in conventional carbonyls is much lower, varying from ca. 70° to 90°.[42] This very wide carbonyl angle in the present structure presents further evidence that no metal–metal bond is present. The C(1)–O(1) distance (1.162 (10) Å) is not significantly different from the analogous distance in conventional carbonyls, and even when corrected for thermal motion (with O(1) riding on C(1)), this distance (1.18 (1) Å), although nearer the value expected on the basis of very low infrared stretching frequency (ca. 1700 cm⁻¹), is still not unusual. Significantly, the Rh–C(1) distance (1.977 (4) Å) is shorter than the equivalent distances in complexes containing conventional bridging carbonyl groups, where values such as those observed in [Rh₂(CO)₂(μ-CO)(μ-Cl)(DPM)₂]⁺ (2.034 (7) and 2.104 (7) Å) are more typical.[1] We suggest that the shorter Rh–C distances for ketonic carbonyls result from the bonding differences between these species and carbonyl ligands accompanied by metal–metal bonds. In the latter cases the bonding is generally considered to involve three-center bonding between the metals and the carbonyl group, whereas we propose that in ketonic carbonyl complexes the carbonyl ligand bonds to the metal via two localized electron-pair bonds. As such, both the acetylene and carbonyl ligands in this complex can be considered as dianionic ligands with both metals in the +3 formal oxidation state. This view is consistent with the structural parameters, including the long Rh–P distances and the lack of reactivity of this species with H₂ (vide infra).

Spectroscopic Studies. The structural parameters of the title complex verify the presence of a ketonic carbonyl ligand, as initially suggested by the low values of ν(CO) for these species (ca. 1700 cm⁻¹). These values are in the range expected for organic carbonyls and in compounds 7–9 are in fact masked by the vibrations of the carboxylate carbonyl groups. Although the infrared results can be useful, they are not unambiguous. For example, in [Rh₂Br₂(μ-CO)(DPM)₂][5] the carbonyl stretch is observed near the above values, at 1750 cm⁻¹, yet this species has a metal–metal bond. Furthermore, the carbonyl vibrations for [Pt₂Cl₂(μ-CO)(DAM)₂][31] and [Mn₂(CO)₄(μ-CO)(DPM)₂][49] are observed at 1638 and 1645 cm⁻¹, respectively, yet the first is a ketonic carbonyl complex and the second has another unusual carbonyl bonding mode in which the carbonyl group is terminally bound to one metal and side-on bound to the other. ¹³C NMR spectroscopy is also known to be useful in characterizing the bonding mode of carbonyl ligands.[50] As

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Table VII. Spectral Parameters for the Carbonyl Ligands

| compd | infrared[a] | | ^{13}C NMR | |
	ν(CO), cm^{-1}	ν(^{13}CO), cm^{-1}	^{13}C$\{^{31}$P$\{^{1}$H$\}\}$ δ	$\vert ^{1}J_{Rh-C}\vert$, Hz
[Rh$_2$(CO)$_2$(μ-CO)(μ-Cl)(DPM)$_2$]$^+$	2008 (sh), 1991 (vs)[b]	1961 (sh), 1945 (vs)	186.9 (m)[c]	85.0
	1873	1824	203.2 (m)	43.0
[Rh$_2$I(CO)(μ-CO)(DPM)$_2$]$^+$ (5)	1960 (s)[b]	1920 (s)	187.6 (dd)	79.0
	1820	1780	212.8 (ddd)	30.5, 67.3
[Rh$_2$Cl$_2$(μ-CO)(DPM)$_2$] (2)	1750	1720	228.9 (t)	45.1
[Rh$_2$Br$_2$(μ-CO)(DPM)$_2$] (3)	1750	1720	227.5 (t)	45.8
[Rh$_2$Cl$_2$(μ-CO)(μ-DMA)(DPM)$_2$] (6)	1690	1655	179.7	d
[Rh$_2$Br$_2$(μ-CO)(μ-DMA)(DPM)$_2$] (7)	1690	1655	184.5 (t)	36.5
[Rh$_2$I$_2$(μ-CO)(μ-DMA)(DPM)$_2$] (8)	1690	1655	191.8 (t)	34.3

[a] Infrared spectra recorded in CH$_2$Cl$_2$. [b] Terminal carbonyl ligands. Abbreviations: vs = very strong; s = strong; sh = shoulder. All bridging carbonyl bands are of medium intensity. [c] Abbreviations used: dd = doublet of doublets; ddd = doublet of doublet of doublets; m = multiplet; t = triplet. [d] Unresolved multiplet owing to very low solubility. Recorded on WH200 at room temperature with no phosphorus decoupling.

the electron density on the carbonyl carbon increases, via increased metal–carbonyl back bonding, the ^{13}C chemical shift should move to lower field (become more positive), and at the same time the carbonyl stretching frequency should decrease. Consistent with this, the ^{13}C chemical shifts for the bridging CO ligands in a series of similar rhodium species, [Rh$_2$-(CO)$_2$(μ-CO)(μ-Cl)(DPM)$_2$][BPh$_4$], [Rh$_2$I(CO)(μ-CO)-(DPM)$_2$][I], [Rh$_2$Br$_2$(μ-CO)(DPM)$_2$], and [Rh$_2$Cl$_2$(μ-CO)(DPM)$_2$], increase in an essentially linear manner as their carbonyl stretching frequencies decrease (Table VII). In keeping with this trend we would have expected the ketonic carbonyl complexes, with values of ν(CO) near 1700 cm^{-1}, to have very low-field ^{13}C shifts, near 240 ppm. However, as shown in Table VII, chemical shifts near 180 ppm are observed instead. These values are in the region commonly associated with terminally bound metal carbonyls[50] but are also close to the values observed[51] for organic carbonyl groups. It is tempting to attribute this significantly different chemical shift compared to other bridging carbonyl groups to a different environment about the carbonyl carbon atom, specifically to sp^2 rather than the conventional sp hybridization. This view would be consistent with our suggestion that the bonding in these ketonic carbonyl species is analogous to that in organic carbonyls, having two localized-electron-pair bonds to the metals, rather than the three-center bonding model proposed for conventional bridging carbonyls.[52] Certainly the structural parameters of [Rh$_2$Cl$_2$(μ-CO)(μ-DMA)(DPM)$_2$] support this view. In a series of related cationic species having bridging carbonyl and acetylene ligands, not thought to be accompanied by metal–metal bonds, the ^{13}C chemical shifts have also been found[53] to be at higher field than expected on the basis of relatively low carbonyl stretching frequencies. However, no structural confirmation of these species is yet available. A study to experimentally determine the bonding-electron density in the regions of the metals and the bridging carbonyl ligands would be of significant value, as would theoretical calculations to determine the nature of the bonding in the regions of the bridging carbonyl groups.

No evidence of a perturbed acetylene stretching vibration is observed in the region 2300–1600 cm^{-1} for any of the ketonic carbonyl species. In some previous characterizations involving acetylenes bound as cis-dimetalated olefins these vibrations were also unobserved.[21,22] However, in [Rh$_2$Cl$_2$(μ-HFB)-(DPM)$_2$][34] and [Cp$_2$Rh$_2$(CO)$_2$(μ-HFB)][54] this vibration was observed at 1638 and 1653 cm^{-1}, respectively.

Catalytic Studies. (a) Cyclotrimerization. The complex [Rh$_2$Cl$_2$(μ-CO)(DPM)$_2$] is a catalyst or catalyst precursor for the cyclotrimerization of dimethyl acetylenedicarboxylate to hexamethyl mellitate at room temperature in methanol. This reaction is complete in about 30 min with between 20 and 25 mol of product formed/mol of complex used. By comparison, the analogous reaction using either [Pd$_2$Cl$_2$(DPM)$_2$] or [Pd$_2$Cl$_2$(μ-DMA)(DPM)$_2$] as the catalyst gave turnovers of 15–20 mol of product/mol of catalyst, but elevated temperatures were used (398 K) and the reaction time was 1.6 h.[21]

Significantly, in our studies cyclotrimerization does not occur in CH$_2$Cl$_2$ at room temperature after 24 h nor does it occur when the acetylene complex [Rh$_2$Cl$_2$(μ-CO)(μ-DMA)-(DPM)$_2$] is used as catalyst precursor. It seems therefore that the acetylene complex is not involved in the catalytic process. Maitlis has established that with Pd(II) complexes the cyclotrimerization of DMA involves insertion into the Pd–Cl bonds.[28] Such a mechanism is also consistent with our observation of cyclotrimerization in methanol, where some chloride ion dissociation may occur, but no cyclotrimerization in CH$_2$Cl$_2$. The chloride dissociation may facilitate the initial "insertion" proposed by Maitlis.[28] In methanol the cyclotrimerization probably occurs until the active catalytic species is transformed into the inactive acetylenic complex [Rh$_2$Cl$_2$-(μ-CO)(μ-DMA)(DPM)$_2$], which is isolated from solution after the cyclotrimerization reaction is complete. At the present time none of the other starting materials (1, 3–6) have been tested as a cyclotrimerization catalyst although this will subsequently be investigated.

(b) Hydrogenation. Compound 2 acts as a catalyst or catalyst precursor for the hydrogenation of phenylacetylene to styrene. In addition, preliminary studies have shown that complex 2 catalytically hydrogenates diphenylacetylene under the same conditions.[55] Significantly, no hydrogenation of dimethyl acetylenedicarboxylate is observed: cyclotrimerization instead occurs under these conditions. It is not surprising that hydrogenation of DMA is not observed. This highly electron-withdrawing acetylene would be expected to deactivate the complex toward oxidative addition of hydrogen, a necessary step in the hydrogenation reaction. Similar reasoning has been used to explain the very slow hydrogenation of ethylene by Wilkinson's catalyst.[56] Furthermore, the complex [Rh$_2$Cl$_2$-(μ-CO)(μ-DMA)(DPM)$_2$] is formally a Rh(III) species and would not be expected to readily oxidatively add H$_2$.

The hydrogenation reaction is found to be very dependent on the order in which the reagents are added; adding the substrate before the hydrogen or adding too large an excess of substrate effectively reduces the hydrogen-uptake rate to

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zero. However, when hydrogen is introduced first and substrate is kept below an approximate 150-fold excess, turnover numbers greater than 1350 have been obtained. It should be noted that we have made no effort yet to optimize hydrogenation conditions. The dependence of the hydrogenation on the order of H_2 addition strongly suggests the initial involvement of a metal hydride species. However, we have been unable to detect hydride species in either CD_2Cl_2 or CD_3OD solutions of $[Rh_2Cl_2(\mu-CO)(DPM)_2]$ under approximately 600 mm of H_2 with use of ^1H NMR spectroscopy, even after 1000 scans on a Bruker WH-400 spectrometer. Poisoning of the catalyst by too large an excess of phenylacetylene suggests to us that an acetylene complex is in equilibrium with small amounts of the catalytically active species. Too large an excess of PhC≡CH suppresses the formation of this active species and reduces the hydrogenation rate. The nature of the phenylacetylene complex, which we assume poisons the reaction, is unknown. However, preliminary investigations indicate that the catalyst precursor $[Rh_2Cl_2(\mu-CO)(DPM)_2]$ reacts with phenylacetylene, yielding a carbonyl-free species possibly containing two phenylacetylene molecules.[57] Further investigations of the chemistry of binuclear rhodium complexes with phenylacetylene are currently under way in attempts to answer some of the above questions regarding the hydrogenation reaction.

Summary

The reactions of *trans*-$[RhCl(CO)(DPM)]_2$ (**1**) and $[Rh_2Cl_2(\mu-CO)(DPM)_2]$ (**2**) with the activated acetylenes DMA and HFB yield the final products $[Rh_2Cl_2(\mu-CO)(\mu$-acetylene)(DPM)_2]$. In the reactions involving **1**, attack is probably terminal followed by Cl⁻ loss and rearrangement of the acetylene to the bridging site, followed by Cl⁻ recoordination and loss of one carbonyl ligand. This route has been established for the reactions of **1** with SO_2[4] and CS_2.[6] Attempts are now under way to isolate and characterize the initial red-brown species in this reaction, which may be the product before rearrangement. In the reaction of **2** with the acetylene molecules, the product results from what seems to be direct insertion of the acetylene into the Rh–Rh bond. However, on the basis of the rearrangement observed with **1**, terminal attack and rearrangement cannot be ruled out.

The final acetylenic product $[Rh_2Cl_2(\mu-CO)(\mu$-DMA)(DPM)_2]$ is the first structurally characterized complex of rhodium containing a ketonic carbonyl ligand and is only the third such compound characterized. However, the observation of a ketonic carbonyl ligand in the present species is even more significant when one considers that this unusual carbonyl bonding mode and associated cis-dimetalated olefin coordination of the acetylene molecule are favored over those of the alternate structure, which would have a stable closed-shell

configuration, a "normal" bridging carbonyl ligand, a formal metal–metal bond, and a μ_2-η^2 acetylene coordination as was observed in $[Cp_2Rh_2(\mu-CO)(\mu$-HFB)]$.[18] On the basis of these observations and on those in the related Pt[30] and Pd[31] complexes, it is clear that bridging carbonyl ligands do not require an accompanying metal–metal bond as was previously believed.[52,58] However, it seems that other bridging groups such as DPM or DAM are still required to stabilize these unusual species. These bridging DPM or DAM ligands, it seems, have just the right bite to hold the metals at the required separation to allow the observation of this carbonyl bonding mode. It is now of interest to establish if the chemistry of the ketonic carbonyl ligand is different from that of conventional bridging carbonyl ligands and specifically if this chemistry resembles that of an organic carbonyl group. The present series of compounds is particularly important in this regard since in the two previously characterized ketonic carbonyl complexes the carbonyl ligands are quite labile and are lost too readily to allow their reactions to be investigated. We have therefore initiated a study into the chemistry of this unusual carbonyl ligand.

It is especially interesting that the activated acetylenes (DMA and HFB) display significantly different chemistries compared to that of the nonactivated phenylacetylene molecule. In particular, the activated acetylenes are catalytically cyclotrimerized but are not noticeably hydrogenated whereas phenylacetylene and diphenylacetylene are hydrogenated under the same conditions and no cyclotrimerization is observed. Consistent with these differences in their catalytic reactions, the stoichiometric reaction of complex **2** with phenylacetylene yields a product very different from that formed in the DMA or HFB reaction. It is anticipated that further studies with the phenylacetylene reaction will help clarify some of the present uncertainties and perhaps prove useful in understanding the hydrogenation reaction.

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