ridional isomer of $[Ru(CO)_3I_3]^-$ by carbonylation. The structural integrity of the meridional isomer has been determined from its infrared and ^{13}C NMR spectra. The meridional isomer of $[Ru(CO)_3I_3]^-$ can be converted by heating it under a CO atmosphere to the thermodynamically more stable facial isomer or it can be used to regenerate $[Ru_2(CO)_4I_6]^{2-}$ by heating a THF solution containing excess iodide under an argon atmosphere.

Neither the meridional isomer of $[Ru(CO)_3I_3]^-$ nor its precursor, $[Ru_2(CO)_4I_6]^{2-}$, have been completely documented in prior literature. Thus this report represents the first completely documented syntheses of these ruthenium halo carbonyl complexes.

Acknowledgment. I thank Dr. S. W. Polichnowsi and Dr. R. L. Zimmerman for their helpful discussions and C. J. Ledford for running the ^{13}C NMR spectra.

Registry No. $[Ru(CO)_3I_2]_2$, 32423-80-6; $[Ph_3PMe][\textit{fac}\text{-}Ru(CO)_3I_3]$, 104092-01-5; $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$, 104153-54-0; $[Ph_3PMe][\textit{mer}\text{-}Ru(CO)_3I_3]$, 104092-02-6; $Ru_3(CO)_{12}$, 15243-33-1; iodine, 7553-56-2.

Supplementary Material Available: Crystal structure analysis report for $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$, Table III (anisotropic thermal parameters for non-hydrogen atoms), Table IV (idealized positions for hydrogen atoms in the cation of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$), Tables V and VI (bond lengths and bond angles in the cation of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$), and Figure 2 (ORTEP drawing for the cation of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$) (14 pages); structure factor tables for the X-ray study of $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$ (21 pages). Ordering information is given on any current masthead page.

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Multiple Routes to the Formation of a Phosphine-Bridged Trirhodium Dihydride Cation, $[Rh_3\{\mu\text{-}(Ph_2PCH_2)_2PPh\}_2(H)_2(\mu\text{-}Cl)_2(CO)_2]^+$

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Red-orange $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-}Cl)_2(CO)_2][BPh_4]$ (dpmp is bis((diphenylphosphino)methyl)phenylphosphine) is formed by treatment of dichloromethane solutions of $[Rh_3(\mu\text{-dpmp})_2(CO)_2(\mu\text{-}Cl)Cl][BPh_4]$ or $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)(CO)(\mu\text{-}Cl)Cl][BPh_4]$ with dihydrogen, by the reaction of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]$ with aqueous formaldehyde, paraformaldehyde, or acetaldehyde, or by treatment of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)_2Cl_4][BPh_4]$ with dihydrogen. Deep green $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)_2Cl_4][BPh_4]$ is formed by treatment of dichloromethane solutions of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]$ with aqueous hydrochloric acid or hydrogen chloride vapor. Spectroscopic data characterizing these complexes are reported. $[Rh_3(\mu\text{-dpmp})_2(H)_2(CO)_2(\mu\text{-}Cl)_2][BPh_4]\cdot 3CH_2Cl_2$ crystallizes in the space group $P2_1/n$ (No. 14) with $a = 14.498$ (2) Å, $b = 22.077$ (3) Å, $c = 28.353$ (3) Å, $\beta = 99.86$ (1)°, and $Z = 4$ at 130 K, $R = 0.049$, $R_w = 0.054$ for 12079 reflections with $I > 3\sigma(I)$ and 558 parameters. The complex consists of two chloro-bridged A-frame units linked side-by-side through the central rhodium. The hydrides, which were well-behaved on refinement, are primarily localized on the central rhodium; Rh(2)–H distances are 1.48 (7) and 1.55 (7) Å. Structural and ^1H NMR spectroscopic evidence suggests a semibridging interaction between these hydrides and the terminal $Rh(CO)Cl(P)_2$ units.

Introduction

We recently reported the preparation, isolation, and structural characterization of the trinuclear rhodium hydride $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-}Cl)_2(CO)_2][BPh_4]$ (**1a**) (dpmp is bis((diphenylphosphino)methyl)phenylphosphine).[1] This was the first phosphine-bridged rhodium hydride obtained directly from dihydrogen and a precursor complex, either $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl]^+$[2] (**2**) or $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)CO(\mu\text{-}Cl)Cl]^+$[3] (**3**), and its structure showed that the dihydrogen had added to the central rhodium center within the nearly linear complex. This hydride is exceptionally stable. Here we describe its preparation by a number of routes and present details of its characterization.

Results

Preparative Chemistry. Red $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-}Cl)_2(CO)_2][BPh_4]$ (**1a**) is readily prepared by a variety of procedures. The paths delineated here are summarized in Chart I.

Treatment of a red dichloromethane solution of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)(CO)(\mu\text{-}Cl)Cl][BPh_4]$ (**3**) under 1 atm of dihydrogen for 12 h produces a lighter red solution from which red-orange crystals of $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-}Cl)_2(CO)_2][BPh_4]$ (**1a**) can be isolated by the gradual addition of ethyl ether. Isolation of the same hydride from the rose-colored tricarbonyl, $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]$ (**2**), requires the use of a higher pressure of dihydrogen. After 12 h under 10 atm of dihydrogen, a dichloromethane solution of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]$ yields **1a** in comparable yield. The formation of the dihydride **1a** from $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl]^+$ is accompanied by the exchange reaction $H_2 + D_2 \rightarrow 2HD$. Thus when a sample of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl]^+$ is exposed to 2 atm of a mixture of H_2 and D_2 (ratio of H_2:D_2:HD = 42:55:3) and the gas sampled after 35 h, significant quantities of HD have formed (new ratio, 30:41:29). Consequently, sites for multiple attachment of dihydrogen must be available, or hydride and deuteride ligands must undergo interionic exchange. Sampling of reaction mixtures by ^1H NMR spectroscopy reveals the presence of small amounts of other hydrides, which have not been produced in large enough quantity for isolation and characterization. These may be involved in the exchange process.

Dihydride **1a** is also formed when $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4]$ is treated with aqueous formaldehyde in a two-phase reaction or with paraformaldehyde in a homogeneous reaction. The procedure using aqueous formaldehyde is probably the most convenient for the preparation of **1a**. These reactions are unusual. Formaldehyde has frequently been used as a source of a carbonyl ligand in preparative organometallic chemistry.[4] Here, however, is a case where a carbon monoxide ligand must be lost from the parent complex and formaldehyde is serving us a source of the hydride ligands. Oxidative addition of a formaldehyde C–H bond to low-valent metal ions has been shown to produce hydrido formyl

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(1) Balch, A. L.; Linehan, J. C.; Olmstead, M. M. *Inorg. Chem.* **1985**, *24*, 3975.

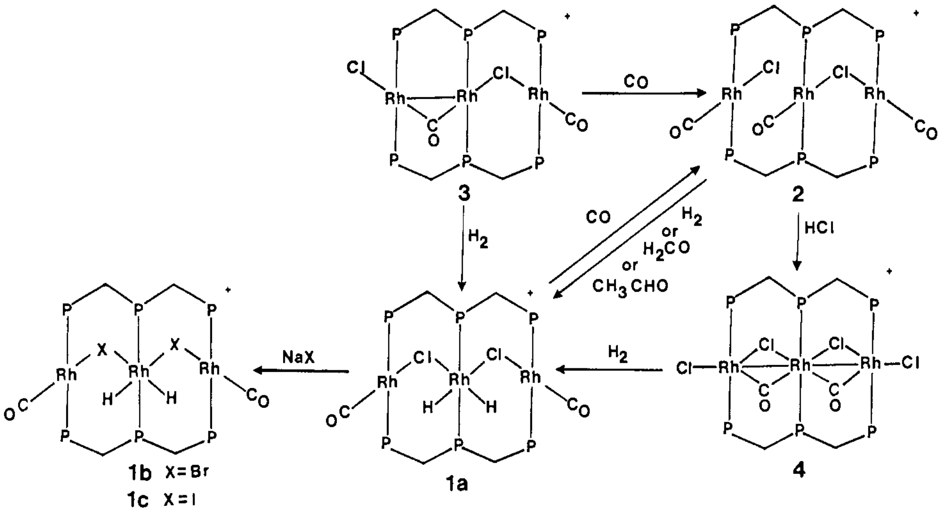
(2) Guimerans, R. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 1677.

(3) Balch, A. L.; Fossett, L. A.; Guimerans, R. R.; Olmstead, M. M. *Organometallics* **1985**, *4*, 781.

(4) Bianchini, C.; Meli, A. *Organometallics* **1985**, *4*, 1537.

0020-1669/86/1325-3937$01.50/0

Chart I



complexes.[5] Probably a similar reaction is involved here, but attempts to detect formyl intermediates in these reactions have not been successful. Acetaldehyde also reacts with $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ to yield **1a**. Again no intermediates were detectable and no attempt was made to identify organic products.

The dihydride **1a** is a remarkably stable substance. The solid is air stable for weeks, and dichloromethane solutions prepared in the atmosphere show no decomposition after 1 day. Treatment of a dichloromethane solution of **1a** with a 10-fold excess of trifluoroacetic acid at 25 °C gives no evidence for the protonation of the hydride ligands.[6] The ^1H NMR spectrum of the complex remains unaltered under these conditions. Treatment of the hydride **1a** with carbon monoxide in dichloromethane solution results in the formation of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$. Although the insertion of sulfur dioxide into metal hydride bonds has been demonstrated,[7] there is no reaction between **1a** and sulfur dioxide in dichloromethane solution at either −60 or +25 °C.

Complex **1a** undergoes metathesis of the bridging chloride ligands with other halide ions without disruption of the rest of the structural features. Thus treatment of **1a** with sodium bromide or sodium iodide yields $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-X})_2(CO)_2][BPh_4]$ (X = Br, **1b**, or I, **1c**) in high yield. The spectroscopic data on these two products are consistent with the structure shown in Chart I. Thus the change of halide ligands in **1a** does not induce a structural change as it does in the case of substitution in $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$.[8,9]

Attempts to form an analogous hydride from $[Rh_3(\mu\text{-dpma})_2(CO)_3Cl_2][BPh_4]$ (dpma is bis((diphenylphosphino)methyl)phenylarsine)[10] and dihydrogen resulted in the formation of red solutions in which $[Rh_3(\mu\text{-dpma})_2(H)_2(\mu\text{-Cl})_2(CO)_2]^+$ was detected spectroscopically. However, this complex rapidly decomposed in the absence of an atmosphere of dihydrogen, and it could not be isolated.

In an effort to see whether hydride complexes were formed from these trirhodium complexes and hydrogen halides, dichloromethane solutions of $Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ and $Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ were exposed to aqueous hydrochloric acid. Deep green complexes $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2Cl_4][BPh_4]$ (**4**) and $[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})_2Cl_4][BPh_4]$, which have very slight solubility in dichloromethane, were isolated. When hydrogen chloride vapor was passed through a dichloromethane solution of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})(Cl)][BPh_4]$, a red complex formed and then gradually converted into green $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2Cl_4][BPh_4]$. The red intermediate could not be obtained in pure form due to its conversion to the green complex, but ^1H NMR spectra indicated that it was not a hydride complex. Treatment of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2Cl_4][BPh_4]$ (**4**) with 1 atm of dihydrogen gave the dihydride **1a** in good yield.

Table I. Selected Electronic and Infrared Spectral Data

	electronic[a]		infrared[a]
	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	ν(C≡O), cm^{-1}
$[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2][BPh_4]$	472	26 000	1963
$[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Br})_2(CO)_2][BPh_4]$	484	25 000	1970
$[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-I})_2(CO)_2][BPh_4]$	492	23 000	1961
$[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2Cl_4][BPh_4]$	298	36 700	1801
	444	12 700	
	640	5 100	
$[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})_2Cl_4][BPh_4]$	298	35 600	1800
	444	12 000	
	640	5 000	

[a] Obtained from dichloromethane solutions of the complexes.

Spectroscopic Studies. Infrared and electronic spectral data for the new complexes are collected in Table I. The infrared spectra of the hydride complexes **1a–c** and the dpma analogue of **1a** show the presence of terminal carbonyl groups with ν(CO) in the range characteristic of *trans*-$Rh^I(CO)ClP_2$ groups.[11] No absorptions characteristic of the Rh–H group could be detected in these spectra. This may be consequence of the semibridging interaction with the terminal rhodium centers (vide infra). The infrared spectra of the tetrachloro complexes $[Rh_2(\mu\text{-dpmp})_2(\mu\text{-CO})_2Cl_4][BPh_4]$ (**4**) and $[Rh_2(\mu\text{-dpma})_2(\mu\text{-CO})_2Cl_4][BPh_4]$ show carbon monoxide stretching absorptions at ca 1800 cm^{-1}; consequently, bridging carbon monoxide ligands are present. The red precursor shows absorption in the range of terminal (1980, 1966 cm^{-1}) and bridging (1797 cm^{-1}) carbon monoxide ligands. As a consequence we tentatively assign these red materials the formulations $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2(CO)Cl_4][BPh_4]$ and $[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)Cl_4][BPh_4]$.

^1H and ^{31}P NMR spectral data for the new complexes are compiled in Table II. The ^1H NMR spectra of the hydride complexes show a hydride resonance in the range −10 to −15 ppm and an AB quartet for the methylene protons of the dpmp ligands. Some further splitting of the downfield half of the methylene quartet is caused by coupling to phosphorus, but in general this splitting is too small for adequate resolution. The observation of

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(5) Thorn, D. L. *Organometallics* **1982**, *1*, 197.

(6) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661. Anderson, B.; Tetrick, S. M.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1986**, 67.

(7) Kubas, G. J.; Wasserman, H. J.; Ryan, R. R. *Organometallics* **1985**, *4*, 2012.

(8) Olmstead, M. M.; Guimerans, R. R.; Balch, A. L. *Inorg. Chem.* **1983**, *22*, 2473.

(9) Balch, A. L.; Fossett, L. A.; Guimerans, R. R.; Olmstead, M. M.; Reedy, P. E., Jr.; Wood, F. E. *Inorg. Chem.* **1986**, *25*, 1248.

(10) Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Oram, D. E.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5272.

(11) Balch, A. L.; Guimerans, R. R.; Linehan, J. *Inorg. Chem.* **1985**, *24*, 290.

Table II. Multinuclear NMR Data for Trirhodium Complexes

	$^{31}P^a$			$^{1}H^a$				$^{13}C^a$	
		J, Hz			methylene				
	δ			$\delta_{hydride}$	δ_1	δ_2	J(H,E), Hz	δ	J(C,Rh), Hz
$[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2][BPh_4]$	27	114 (Rh,P)		−13.30^b	3.01	3.79	12.7	190.0	80.6
$[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Br})_2(CO)_2][BPh_4]$	27			−12.21	3.23	3.87	12.5	190.5	84.6
$[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-I})_2(CO)_2][BPh_4]$	20.8^c	106 (Rh,P)	37 (P,P)	−10.55	3.69	3.95	13.4		
	25.1^d	110 (Rh,P)	37 (P,P)						
$[Rh_3(\mu\text{-dpma})_2(H)_2(\mu\text{-Cl})_2(CO)_2][BPh_4]$	27.9^d	118 (Rh,P)		−14.34	2.85	3.66	13.5		
$[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2Cl_4][BPh_4]$	15.5^c	110 (Rh,P)			3.04	4.05	14		
	22.9^d	103 (Rh,P)							
$[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})_2Cl_4][BPh_4]$	18.1	103 (Rh,P)			3.17	4.04	12		

^{a} In dichloromethane-d_2 solution. ^{b} Coupling constants given in Figure 1 caption. ^{c} Internal PPh group. ^{d} Terminal PPh_2 group.

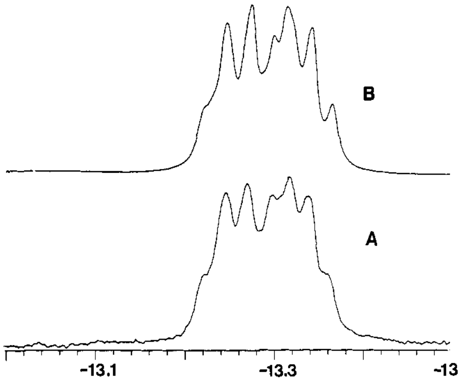
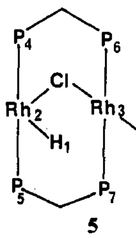


Figure 1. (A) 360-MHz ^{1}H NMR spectrum of $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2][BPh_4]$ in dichloromethane-d_2 solution at 25 °C in the region of the hydride resonance. (B) Simulated ^{1}H NMR spectrum for the following parameters: $\delta = -13.3$; $^1J(Rh_2,H) = 24.7$, $J(Rh_3,H) = 10.9$, $J(P_4,H) = J(P_5,H) = 8.6$, $J(Rh_2,P_4) = J(Rh_2P_5) = 87.0$, $J(Rh_3P_6) = J(Rh_3,P_7) = 105.0$, $J(P_4,P_5) = 250$, $J(P_6,P_7) = 340$, $J(P_4,P_6) = J(P_5,P_7) = 13$, and $J(P_4,P_7) = J(P_5,P_6) = 33$ Hz.

an AB quartet arises from the intrinsic differences between the protons within the methylene groups of the ligand itself.[3] The observation of only one AB quartet indicates that the two methylene groups in each dpmp ligand are equivalent and both dpmp ligands are equivalent, facts that are consistent with the symmetry of the complex as seen in the solid state.

The particularly well-resolved hydride resonance of **1a** is shown in Figure 1. A satisfactory simulation of this spectrum has been obtained with the seven-spin fragment **5**. The simulated spectrum



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is shown in trace B of Figure 1. The spectral parameters used to compute this spectrum are given in the figure caption, and the coupling constants used are consistent with similar parameters obtained from the spectra of other mono- and polynuclear rhodium(I) phosphine complexes.[3] The presence of two Rh–H coupling constants, 24.7 and 10.9 Hz, is particularly noteworthy. The existence of coupling of the hydride resonance to two different rhodium atoms was verified by the phosphorus decoupling experiment shown in trace A of Figure 2. The *phosphorus decoupled* ^{1}H NMR spectrum is a doublet of doublets, and from it the two Rh-H coupling constants can be measured directly. The larger coupling can be ascribed to the Rh(2)–H interaction, while the smaller coupling results from the Rh(3)···H interaction.

The ^{31}P NMR spectrum of hyride **1a** shows poor resolution of the terminal and internal phosphorus environments. The spectrum consists of a doublet with a second smaller doublet emerging to high field of the larger when the sample is cooled. Such poorly resolved spectra have been encountered previously for some trinuclear rhodium complexes of dpmp.[12] The ^{13}C NMR spectrum of ^{13}CO enriched **1a** in dichloromethane at −80 °C shows a doublet at 190.0 ppm with $^1J(Rh,C) = 80.6$ Hz.

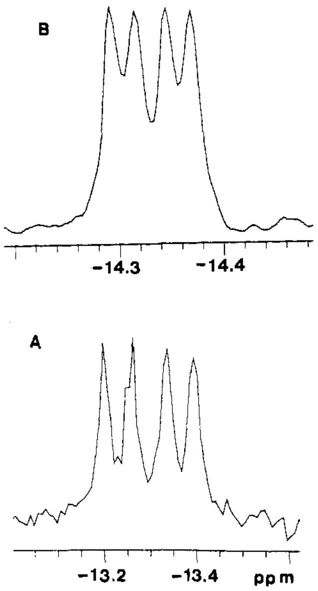

Figure 2. (A) Phosphorus-decoupled 180 MHz ^{1}H NMR spectrum in the hydride region of $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2][BPh_4]$ in dichloromethane-d_2 at 25 °C. (B) Hydride region of the 360-MHz ^{1}H NMR spectrum of $[Rh_3(\mu\text{-dpma})_2(H)_2(\mu\text{-Cl})_2(CO)_2]^+$ in dichloromethane-d_2 at 25 °C.

The NMR spectra for the corresponding bromo and iodo complexes **1b,c** show similar features. However, the hydride resonances are less well resolved, and detailed analysis of the coupling constants involved has not been possible. The ^{31}P NMR spectra show better resolution, and the spectrum of the iodide complex is sufficiently defined so that values of ^1J(Rh,P) and ^2J(P,P) can be obtained.

Because of its instability, $[Rh_3(\mu\text{-dpma})_2(H)_2(\mu\text{-Cl})_2(CO)_2]^+$ has been identified only through spectral data taken from solutions of $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl]^+$ that have been exposed to 10 atm of dihydrogen. The ^{1}H NMR spectrum in the hydride region is shown in trace B of Figure 2. The doublet of doublets occurs because of coupling of the hydride to two different rhodium atoms. Since arsenic–proton coupling is not resolved (arsenic has a quadripolar nucleus with $S = {}^3/_2$) the spectrum is analogous to the phosphorus-decoupled spectrum of **1a** shown in Figure 2, trace A. The two Rh,H coupling constants present in $[Rh_3(\mu\text{-dpma})_2(H)_2(\mu\text{-Cl})_2(CO)_2]$, 19.4 and 9.7 Hz, are similar in magnitude to those in **1a**. The methylene region of the ^{1}H NMR spectrum consists of a AB quartet, and the ^{31}P NMR spectrum is a simple doublet.

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[12] Balch, A. L.; Fossett, L. A.; Linehan, J.; Olmstead, M. M. *Organometallics* **1986**, *5*, 691.

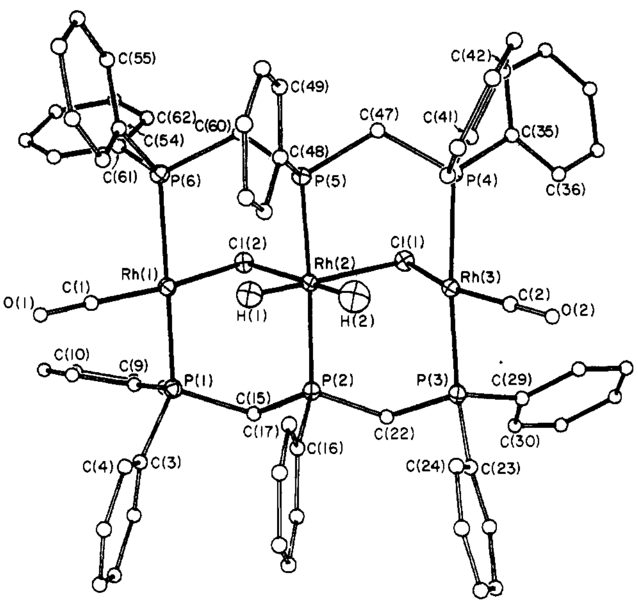

Figure 3. Perspective view of $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2]^+$, showing 50% thermal elipsoids.

The green tetrachloride complex is tentatively assigned the chloride- and carbonyl-bridged structure **4**. This arrangement, which gives each rhodium 18 electrons, is consistent with the available structural data, which require the presence of a bridging carbon monoxide and which suggest that the two ends of trirhodium chain are equivalent.

X-ray Crystal Structure of $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2][BPh_4]\cdot 3CH_2Cl_2$. The structure consists of the cation, the tetraphenylborate anion, and three dichloromethane molecules. There are no unusual contacts between these constituents. A drawing of the cation that gives the atomic numbering scheme is given in Figure 3. Atomic positional parameters are given in Table III. Tables IV and V give selected interatomic distances and angles. There is no imposed crystallographic symmetry. However, the cation has a virtual C_{2v} symmetry with an idealized mirror plane passing through the nearly planar $Rh_3H_2(CO)_2Cl_2$ unit and a second idealized mirror plane bisecting the H(1)–Rh(2)–H(2) and Cl(1)–Rh(2)–Cl(2) angles. The near-mirror symmetry extends out to include even the phenyl groups. In solution, normal molecular motion renders the phosphine ligands fully equivalent.

The central rhodium atom, Rh(2), has regular six-coordinate geometry with two hydride ligands, a pair of trans phosphine ligands, and two bridging chloride ligands. The two end rhodium atoms, Rh(1) and Rh(3), have planar geometry with coordination by a terminal carbonyl group, a pair of trans phosphines, and the bridging chloride. The Rh(1)···Rh(2)···Rh(3) angle (168.1 (1)°) is nearly linear.

It is instructive to compare the structure of $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2]^+$ (**1a**) with that of its parent, $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ (**2**).[2] A comparison of the central planar parts of these two complexes is presented in Figure 4. The two are related by the replacement of the two hydride ligands on the central rhodium by a carbon monoxide ligand. Hydride complex **1a** has two bridging chloride ligands and 16 electrons at the terminal rhodium centers and eighteen electrons for the central rhodium while the tricarbonyl has only one bridging chloride and 16 electrons at each of the three rhodium atoms. The two Rh···Rh separations (3.180, 3.164 Å) in the tricarbonyl are nearly equal in length despite the differences in bridging. These distances are considerably longer than the Rh···Rh separations (2.967, 2.948 Å) in hydride **1a**. Thus replacement of one carbon monoxide on the central rhodium by two hydride ligands results in folding of the two end rhodium atoms toward the central group. We attribute this to a semibridging interaction between the central Rh(2)–H unit and the terminal rhodium centers. The hydride ligands sit almost directly above the center of the planar $RhP_2(CO)Cl$ end groups. Therefore, they are positioned to interact with the empty, out-of-plane p_z orbital and the filled d_{z^2} orbital of the terminal rhodium atoms. The ^1H NMR spectra show significant coupling of the hydride ligands to two different rhodium atoms and therefore add evidence for the semibridging interaction. Nevertheless the interaction must be weaker than those present in normal bridging hydrides, which have shorter Rh–Rh separations (in the 2.7–2.8-Å range)[13-17] with less asymmetry in the hydride placement.

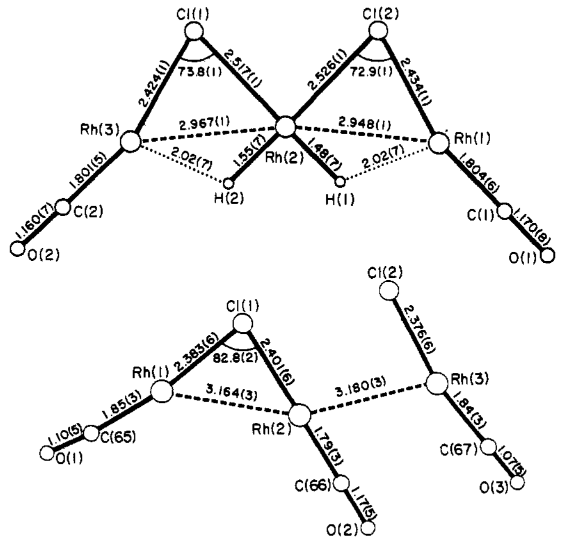

Figure 4. Comparison of planar sections of $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2]^+$ (A) and $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})(Cl)]^+$ (B) (data from ref 2).

Experimental Section

Preparation of Compounds. The compounds $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ (**2**),[2] $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)(\mu\text{-Cl})Cl][BPh_4]$ (**3**),[3] and $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$[10] were prepared as previously described. Formaldehyde, paraformaldehyde, and acetaldehyde were purchased from Mallinckrodt and used as received.

$[Rh_3(\mu\text{-dpmp})_2(CO)_2(H)_2(\mu\text{-Cl})_2][BPh_4]$ (1a). Method 1. A solution of 51 mg (0.028 mmol) of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)(\mu\text{-Cl})Cl][BPh_4]$ in 10 mL of dichloromethane was stirred overnight under 1 atm of dihydrogen. The color of the red solution lightened. Its volume was reduced to 4 mL on a rotary evaporator. After filtration, ethyl ether was added to precipitate red-orange needles of the product. The crystals were collected by filtration and recrystallized from dichloromethane and ethyl ether; yield 42 mg (84%).

Method 2. A solution of 101 mg (0.056 mmol) of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ in 15 mL of dichloromethane was placed in a 200-mL Parr pressure reactor. The atmosphere above the solution was purged with dihydrogen, and the reactor was charged to 10 atm with dihydrogen. After the reaction vessel was stirred mechanically for 28 h, it was opened and the solution removed. The light red solution was evaporated to approximately 5 mL, filtered, and treated with ethyl ether to precipitate the product, which was purified as described in method 1; yield 76 mg (76%).

Method 3. A heterogeneous mixture of 5 mL of 37% aqueous formaldehyde and 5 mL of dichloromethane containing 94 mg (0.052 mmol) of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ was stirred in a stoppered 50-mL Erlenmeyer flask for 24 h. The mixture was evaporated by using a rotary evaporator until the organic layer was gone and an orange powder remained suspended in the aqueous phase. The powder was removed by filtration and washed with 15 mL of methanol and 15 mL of ethyl ether. The remaining powder was dissolved in dichloromethane and recovered

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(13) Teller, R. G.; Williams, J. M.; Koetzle, T. F.; Burch, R. R.; Gavin, R. M.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 1806.

(14) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119.

(15) Meier, E. B.; Burch, R. R.; Muetterties, E. L.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 2661.

(16) Brown, R. K.; Williams, J. M.; Sivak, A. J.; Muetterties, E. L. *Inorg. Chem.* **1980**, *19*, 370.

(17) Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1984**, *23*, 1290.

Table III. Atom Coordinates (×10⁴) and Thermal Parameters (Å² × 10³) for $[Rh_3\{\mu\text{-}(Ph_2PCH_2)_2PPh\}_2(H)_2(\mu\text{-}Cl)_2(CO)_2][BPh_4]\cdot 3CH_2Cl_2$

atom	*x*	*y*	*z*	*U*	atom	*x*	*y*	*z*	*U*
Rh(1)	5410 (1)	6606 (1)	3361 (1)	14 (1)[a]	C(40)	4687 (4)	4034 (3)	1204 (2)	28 (1)
Rh(2)	5309 (1)	6307 (1)	2340 (1)	13 (1)[a]	C(41)	2906 (4)	5178 (3)	1183 (2)	20 (1)
Rh(3)	4858 (1)	6171 (1)	1285 (1)	15 (1)[a]	C(42)	2461 (4)	4641 (3)	1021 (2)	24 (1)
Cl(1)	6211 (1)	5742 (1)	1796 (1)	18 (1)[a]	C(43)	1482 (5)	4628 (3)	898 (2)	35 (2)
Cl(2)	6567 (1)	6013 (1)	3033 (1)	17 (1)[a]	C(44)	948 (5)	5138 (3)	933 (2)	35 (2)
Cl(3)	−846 (2)	5563 (1)	3437 (1)	61 (1)[a]	C(45)	1392 (5)	5669 (3)	1097 (2)	36 (2)
Cl(4)	−745 (2)	5405 (1)	4462 (1)	69 (1)[a]	C(46)	2359 (4)	5691 (3)	1219 (2)	25 (1)
Cl(5)	1416 (2)	1828 (1)	−55 (1)	75 (1)[a]	C(47)	4367 (4)	4930 (2)	1988 (2)	17 (1)
Cl(6)	3387 (2)	1840 (3)	333 (1)	140 (2)[a]	C(48)	3108 (4)	5655 (2)	2433 (2)	15 (1)
Cl(7)	8399 (3)	4643 (2)	265 (1)	130 (2)[a]	C(49)	2503 (4)	5170 (3)	2462 (2)	20 (1)
Cl(8)	9490 (4)	3548 (3)	158 (2)	181 (3)[a]	C(50)	1552 (4)	5278 (3)	2453 (2)	25 (1)
P(1)	6413 (1)	7414 (1)	3302 (1)	16 (1)[a]	C(51)	1212 (5)	5866 (3)	2424 (2)	28 (1)
P(2)	5961 (1)	7223 (1)	2229 (1)	15 (1)[a]	C(52)	1809 (4)	6348 (3)	2392 (2)	27 (1)
P(3)	5803 (1)	6991 (1)	1164 (1)	17 (1)[a]	C(53)	2756 (4)	6241 (3)	2398 (2)	21 (1)
P(4)	4166 (1)	5235 (1)	1367 (1)	15 (1)[a]	C(54)	3619 (4)	5572 (2)	3661 (2)	16 (1)
P(5)	4352 (1)	5516 (1)	2439 (1)	14 (1)[a]	C(55)	3369 (4)	5009 (3)	3827 (2)	24 (1)
P(6)	4784 (1)	5669 (1)	3510 (1)	15 (1)[a]	C(56)	2480 (5)	4907 (3)	3918 (2)	31 (1)
O(1)	4368 (4)	7277 (2)	4012 (2)	40 (1)	C(57)	1812 (5)	5363 (3)	3840 (2)	34 (2)
O(2)	3447 (3)	6506 (2)	442 (2)	32 (1)	C(58)	2043 (5)	5922 (3)	3671 (2)	30 (1)
C(1)	4774 (4)	7009 (3)	3757 (2)	23 (1)	C(59)	2944 (4)	6030 (3)	3578 (2)	22 (1)
C(2)	3985 (4)	6375 (3)	778 (2)	20 (1)	C(60)	4744 (4)	5126 (2)	3009 (2)	16 (1)
C(3)	6083 (4)	8205 (2)	3354 (2)	18 (1)	C(61)	5550 (4)	5313 (3)	4008 (2)	23 (1)
C(4)	5139 (4)	8377 (3)	3292 (2)	20 (1)	C(62)	6134 (4)	4841 (3)	3967 (2)	28 (1)
C(5)	4907 (5)	8987 (3)	3292 (2)	28 (1)	C(63)	6708 (5)	4589 (3)	4367 (2)	33 (2)
C(6)	5604 (5)	9425 (3)	3349 (2)	31 (1)	C(64)	6733 (5)	4827 (3)	4809 (3)	39 (2)
C(7)	6541 (5)	9254 (3)	3418 (2)	29 (1)	C(65)	6159 (7)	5312 (5)	4852 (4)	73 (3)
C(8)	6786 (4)	8647 (3)	3421 (2)	24 (1)	C(66)	5550 (7)	5549 (4)	4472 (3)	59 (2)
C(9)	7443 (4)	7317 (2)	3771 (2)	17 (1)	C(67)	9564 (4)	7188 (3)	2003 (2)	21 (1)
C(10)	7283 (5)	7376 (3)	4243 (2)	29 (1)	C(68)	9613 (4)	6770 (3)	1628 (2)	25 (1)
C(11)	8030 (5)	7288 (3)	4620 (3)	34 (2)	C(69)	9178 (5)	6210 (3)	1611 (2)	31 (1)
C(12)	8903 (5)	7120 (3)	4534 (2)	30 (1)	C(70)	8681 (5)	6032 (3)	1957 (2)	32 (1)
C(13)	9049 (5)	7068 (3)	4064 (2)	32 (1)	C(71)	8605 (5)	6423 (3)	2330 (3)	34 (2)
C(14)	8323 (4)	7166 (3)	3688 (2)	23 (1)	C(72)	9035 (4)	6995 (3)	2347 (2)	29 (1)
C(15)	6875 (4)	7429 (2)	2734 (2)	15 (1)	C(73)	10542 (4)	7997 (3)	1564 (2)	21 (1)
C(16)	5177 (4)	7877 (2)	2141 (2)	16 (1)	C(74)	10236 (5)	8438 (3)	1218 (2)	31 (1)
C(17)	4225 (4)	7805 (3)	2112 (2)	21 (1)	C(75)	10634 (5)	8499 (3)	806 (3)	41 (2)
C(18)	3620 (4)	8303 (3)	2022 (2)	26 (1)	C(76)	11343 (5)	8124 (3)	724 (3)	42 (2)
C(19)	3986 (5)	8872 (3)	1964 (2)	30 (1)	C(77)	11686 (5)	7706 (4)	1059 (3)	43 (2)
C(20)	4937 (4)	8946 (3)	1994 (2)	28 (1)	C(78)	11294 (5)	7647 (3)	1483 (3)	36 (2)
C(21)	5543 (4)	8456 (3)	2086 (2)	23 (1)	C(79)	10861 (4)	7937 (3)	2528 (2)	22 (1)
C(22)	6579 (4)	7233 (3)	1716 (2)	18 (1)	C(80)	10932 (5)	7576 (3)	2939 (2)	31 (1)
C(23)	5289 (4)	7706 (3)	928 (2)	19 (1)	C(81)	11613 (5)	7670 (3)	3339 (3)	40 (2)
C(24)	4353 (4)	7842 (3)	948 (2)	24 (1)	C(82)	12263 (5)	8120 (3)	3351 (3)	34 (2)
C(25)	3990 (5)	8406 (3)	801 (2)	30 (1)	C(83)	12208 (5)	8501 (3)	2956 (2)	29 (1)
C(26)	4550 (5)	8837 (3)	639 (2)	31 (1)	C(84)	11516 (4)	8406 (3)	2561 (2)	26 (1)
C(27)	5478 (5)	8708 (3)	607 (2)	30 (1)	C(85)	9199 (4)	8355 (3)	2085 (2)	21 (1)
C(28)	5846 (4)	8143 (3)	754 (2)	24 (1)	C(86)	8435 (4)	8427 (3)	1706 (2)	24 (1)
C(29)	6591 (4)	6782 (3)	751 (2)	23 (1)	C(87)	7716 (5)	8849 (3)	1724 (2)	28 (1)
C(30)	7538 (4)	6919 (3)	830 (2)	26 (1)	C(88)	7733 (5)	9202 (3)	2132 (2)	33 (2)
C(31)	8108 (5)	6733 (3)	515 (2)	35 (2)	C(89)	8439 (5)	9122 (3)	2519 (2)	32 (1)
C(32)	7734 (7)	6392 (4)	121 (3)	58 (2)	C(90)	9152 (4)	8707 (3)	2485 (2)	27 (1)
C(33)	6789 (7)	6244 (5)	35 (4)	69 (3)	C(91)	−1511 (6)	5491 (4)	3908 (3)	52 (2)
C(34)	6222 (6)	6446 (4)	352 (3)	53 (2)	C(92)	2280 (6)	2107 (5)	413 (3)	60 (3)[a]
C(35)	4707 (4)	4639 (3)	1064 (2)	19 (1)	C(93)	8599 (14)	3898 (8)	339 (5)	144 (9)[a]
C(36)	5219 (4)	4801 (3)	709 (2)	29 (1)	B	10049 (5)	7868 (3)	2040 (2)	23 (1)
C(37)	5712 (5)	4363 (3)	498 (3)	36 (2)	H(1)	4781 (43)	6629 (28)	2667 (22)	29 (17)
C(38)	5691 (5)	3761 (3)	643 (3)	38 (2)	H(2)	4555 (48)	6491 (30)	1908 (25)	42 (20)
C(39)	5173 (5)	3596 (3)	992 (3)	35 (2)					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

as crystals by precipitation with ethyl ether; yield 77 mg (85%).

Method 4. Paraformaldehyde, 0.5 g (17 mmol), was added to a solution of 0.103 g (0.057 mmol) of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ in 10 mL of dichloromethane and left for 48 h. The solution was filtered to remove the remaining paraformaldehyde, and the dichloromethane filtrate was concentrated by rotary evaporation. The workup under method 1 was followed to produce 65 mg (64%) of the product.

Method 5. Acetaldehyde, 0.5 mL (8.7 mmol), and 20 mL of a dichloroethane solution containing 84 mg (0.047 mmol) of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ were sealed into a Parr pressure reactor. The reactor was then heated to 40 °C for 72 h. The cooled reactor was then opened. The light red solution yielded 44 mg (54%) of product after the workup described under method 1.

$[Rh_3(\mu\text{-dpmp})_2(CO)_2(H)_2(\mu\text{-Br})_2][BPh_4]$ (1b). A solution of 500 mg (4.9 mmol) of sodium bromide in 10 mL of methanol was added to a stirred dichloromethane solution containing 132 mg (0.075 mmol) of $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2][BPh_4]$. After 10 min the dichloromethane was removed by a rotary evaporator, and the remaining slurry was filtered. The red solid was washed with three portions of 5 mL of methanol and then dissolved in a minimum of dichloromethane. After filtration, the product was precipitated as red needles from the dichloromethane solution by the slow addition of ethyl ether. The crystals were collected by filtration and recrystallized from dichloromethane and ether to yield 117 mg (85%). The iodide complex **1c** was prepared similarly. Anal. Calcd for $C_{84}H_{80}Br_2BO_2P_6Rh_3$: C, 56.47; H, 4.51; Br, 8.94. Found: C, 56.95; H, 4.50; Br, 9.01.

$[Rh_3(\mu\text{-dpma})_2(CO)_2(H)_2(\mu\text{-Cl})_2][BPh_4]$. This compound decomposes unless more than 2 atm of hydrogen pressure is continuously applied. The half-life of this compound in a solution of dichloroethane is approximately 45 min in the air. This compound was generated in situ from $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$, by method 2 described above and used immediately.

Table IV. Selected Interatomic Distances (Å) for $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2]^+$

At Rh(1)			
Rh(1)···Rh(2)	2.948 (1)	Rh(1)···H(1)	2.02 (7)
Rh(1)-P(1)	2.324 (1)	Rh(1)-P(6)	2.327 (1)
Rh(1)-Cl(2)	2.434 (1)	Rh(1)-C(1)	1.804 (6)
At Rh(3)			
Rh(3)···Rh(2)	2.967 (1)	Rh(3)···H(2)	2.02 (7)
Rh(3)-P(3)	2.330 (2)	Rh(3)-P(4)	2.327 (1)
Rh(3)-Cl(1)	2.424 (1)	Rh(3)-C(2)	1.801 (5)
At Rh(2)			
Rh(2)···Rh(1)	2.948 (1)	Rh(2)···Rh(3)	2.967 (1)
Rh(2)-P(2)	2.276 (11)	Rh(2)-P(5)	2.278 (1)
Rh(2)-Cl(1)	2.517 (1)	Rh(2)-Cl(2)	2.526 (1)
Rh(2)-H(1)	1.48 (7)	Rh(2)-H(2)	1.55 (7)
At Carbon Monoxide			
C(1)-O(1)	1.170 (8)	C(2)-O(2)	1.160 (7)

Table V. Selected Interatomic Angles (deg) in $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2]^+$

At Rh(1)			
P(1)-Rh(1)-P(6)	164.4 (1)	C(1)-Rh(1)-Cl(2)	164.1 (2)
C(1)-Rh(1)-P(1)	93.5 (2)	C(1)-Rh(1)-P(6)	93.9 (2)
Cl(2)-Rh(1)-P(1)	84.5 (1)	Cl(2)-Rh(1)-P(6)	84.6 (1)
Rh(1)-C(1)-O(1)	179.0 (6)		
At Rh(3)			
P(3)-Rh(1)-P(4)	168.2 (1)	C(2)-Rh(1)-Cl(1)	163.8 (2)
C(2)-Rh(1)-P(3)	92.3 (2)	C(2)-Rh(1)-P(4)	92 (2)
Cl(1)-Rh(1)-P(3)	87.4 (1)	Cl(1)-Rh(1)-P(4)	84.9 (1)
Rh(3)-C(2)-O(2)	177.7 (6)		
At Rh(2)			
P(2)-Rh(2)-P(5)	167.0 (1)	Cl(2)-Rh(2)-H(2)	179 (2)
Cl(1)-Rh(2)-H(1)	179 (2)	Cl(1)-Rh(2)-P(2)	94.8 (1)
Cl(1)-Rh(2)-P(5)	95.0 (1)	Cl(1)-Rh(2)-H(2)	91.3 (3)
Cl(1)-Rh(2)-Cl(2)	88.1 (1)	Cl(2)-Rh(2)-P(2)	94.3 (1)
Cl(2)-Rh(2)-P(5)	94.6 (1)	Cl(2)-Rh(2)-H(1)	91 (2)
H(1)-Rh(2)-P(2)	86 (2)	H(1)-Rh(2)-P(5)	84 (2)
H(2)-Rh(2)-P(2)	85 (2)	H(2)-Rh(2)-P(5)	86 (3)
H(1)-Rh(2)-H(2)	90 (3)		

$[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2(\mu\text{-Cl})_2Cl_2][BPh_4]$ (4). Method 1. Concentrated aqueous HCl, 5 mL, was stirred with a solution of 98 mg (0.055 mmol) of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ in 10 mL of dichloromethane in a stoppered Erlenmeyer flask for 18 h. The dichloromethane was removed from the resulting green heterogeneous mixture by rotary evaporation. The resulting aqueous slurry was filtered, and the solid was washed with three aliquots of water and then with three aliquots of methanol. A dichloromethane solution saturated with sodium tetraphenylborate was added to the green solid to form a green solution. The solution was then filtered to remove any insoluble material. The product was recovered as green crystals by the slow addition of ethyl ether; yield 48 mg (54%). Anal. Calcd for $C_{86}H_{70}BCl_4O_2P_6Rh_3$: C, 57.94; H, 3.96; Cl, 7.94. Found: C, 57.31; H, 3.90; Cl, 7.54.

Method 2. Hydrogen chloride vapor was bubbled slowly for 5 min through a solution containing 68 mg (0.038 mmol) of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ in 20 mL of dichloromethane. An unstable, red crystalline compound partially precipitated. This red compound converted to the green product after standing in solution for 30 min. The green product was recrystallized as in method 1.

$[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(\mu\text{-Cl})_2Cl_2][BPh_4]\cdot CH_2Cl_2$. This compound was made in the same fashion as the dpmp analogue by using either method 1 or 2. A yield of 43 mg (56%) of the product was isolated when 76 mg (0.043 mmol) of $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ was used and method 2 was followed. Anal. Calcd for $C_{86}H_{70}As_2BCl_4O_2P_4Rh_3\cdot CH_2Cl_2$: C, 53.46; H, 3.71; Cl, 10.88. Found: C, 52.75; H, 3.78; Cl, 10.30.

Physical and Spectroscopic Measurements. These were made as described previously.[3] The ^1H NMR spectrum shown in Figure 2 was simulated by using the 1180/1280 ITRCAL routine (an adaption of Laocoon III) of the Nicolet software. This routine is designed for simulation of systems with a maximum of seven nuclei with spin $^1/_2$. Since our complexes involve six phosphorus and three rhodium atoms and two hydrides (eleven spin-$^1/_2$ nuclei in all), we had to carry out the calculations on the smaller seven-spin fragment **5**.

Table VI. Crystal Data for $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2][BPh_4]\cdot 3CH_2Cl_2$

formula	$C_{93}H_{86}Rh_3P_6Cl_8O_2B$
fw (dimer + solvent)	2024.72
cryst syst	monoclinic
space group	$P2_1/n$
conditions	$0k0$, $k = 2n$; $h0l$, $h + l = 2n$
cryst dimens, mm	0.75 × 0.45 × 0.37
color and habit	orange needles
unit cell dimens (140 K)	
a, Å	14.498 (2)
b, Å	22.077 (3)
c, Å	28.353 (3)
β, deg	99.86 (1)
V, Å^3	8941 (2)
d(calcd), g cm^{-3} (140 K)	1.50
Z	4
radiatn (λ, Å (graphite monochromator))	Mo Kα (0.71069)
μ(Mo Kα), cm^{-1}	9.2
range of abs cor factors	1.33-1.54
scan type; $2\theta_{max}$, deg	ω; 55
scan range, deg	1.0
bkgd offset, deg	±1.0
octants	$h,k,\pm l$
scan speed, deg min^{-1}	60
no. of check reflcns interval no.	3, measured every 200 reflctns
no. of unique data	20558
no. of data with $I > 3\sigma(I)$	12079
R	0.049
R_w	0.054
no. of params	558

X-ray Data Collection, Refinement, and Solution. Well-formed red crystals were obtained by slow vapor diffusion of diethyl ether into a dichloromethane solution of $[Rh_3(\mu\text{-dpmp})_2(H)_2(\mu\text{-Cl})_2(CO)_2][BPh_4]$ **1a**. Crystal data, data collection procedure, and refinement of the structure are summarized in Table VI. The lattice was found to be monoclinic by standard procedures using the software associated with the Syntex P2$_1$ diffractometer. Quick scans of the reflections for space group determination yielded the conditions $0k0$, $k = 2n$, and $h0l$, $h + l = 2n$, consistent with the space group $P2_1/n$. The data were collected at 130 K by using a locally modified LT-1 low-temperature apparatus on the Syntex P2$_1$ diffractometer. The data were corrected for Lorentz, polarization, and extinction effects.

The structure was solved by locating the three rhodium atoms with the Patterson (FMAP8) routine of SHELXTL, version 4, 1984 (Nicolet Instrument Corporation, Madison, WI). Other atoms were located from successive difference Fourier maps. Final cycles of refinement were made with anisotropic thermal parameters for rhodium, phosphorus, and chlorine and isotropic thermal parameters for all remaining atoms. Hydrogen atoms on rhodium were refined and were well-behaved. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[18] An absorption correction (XABS) was applied.[19] A conventional R factor of 0.049 was obtained.

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Registry No. **1a**·$3CH_2Cl_2$, 103835-36-5; **1b**, 103835-38-7; **1c**, 103835-40-1; **2**, 84774-75-4; **3**, 103835-42-3; **4**, 103835-44-5; $[Rh_3(\mu\text{-dpma})_2(CO)_2(H)_2(\mu\text{-Cl})_2][BPh_4]$, 103835-46-7; $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$, 103835-48-9; $[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(\mu\text{-Cl})_2Cl_2][BPh_4]$, 103835-50-3; H_2, 1333-74-0; formaldehyde, 50-00-0; paraformaldehyde, 30525-89-4; acetaldehyde, 75-07-0.

Supplementary Material Available: Listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom positions (7 pages); a listing of structure factor amplitudes (71 pages). Ordering information is given on any current masthead page.

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(18) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(19) The method obtains an empirical absorption tensor from an expression relating F_o and F_c: Hope, H.; Moezzi, B. Department of Chemistry, University of California, Davis, CA.