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Preparation and Structural Dynamics of Phosphine-Bridged Trirhodium Chains. Observation of Facile Bridge/Terminal Interchange of Anionic Ligands or Carbon Monoxide

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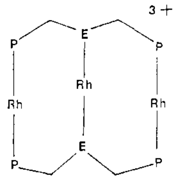
The preparations of the trirhodium chain compounds $[Rh_3(\mu\text{-dpmp})_2(CO)_3X_2][BPh_4]$ (dpmp is bis((diphenylphosphino)-methyl)phenylphosphine; X = Cl^-, Br^-, I^-, N_3^-, NCO^-) and $[Rh_3(\mu\text{-dpma})_2(CO)_3X_2][BPh_4]$ (dpma is bis((diphenylphosphino)-methyl)phenylarsine; X = Cl^-, Br^-, I^-) are reported. Infrared and multinuclear (^1H, ^{31}P, ^{13}C) NMR spectra along with the previously reported X-ray crystallographic data on $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ and $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2]^+$ allow these cations to be sorted into three classes. All classes contain a $Rh_3(dpmp)_2$ or $Rh_3(dpma)_2$ core with trans P-Rh-P and As-Rh-As units. The cations $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-X})X]^+$ (X = Cl^-, N_3^-, NCO^-) and $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-X})X]^+$ (X = Cl^-, Br^-) possess a structure with one bridging X and only terminal carbonyls. In solution these undergo rapid bridge/terminal halide exchange. The cations $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2]^+$ and $[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2]^+$ both possess a static structure in solution that is the same as the solid-state structure. One Rh-Rh unit is bridged by a carbonyl and an iodide. That iodide is close to the third rhodium, which is also bridged to the central rhodium by a shorter iodide bridge. The structure of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2Br_2]^+$ is unique. In solution it undergoes rapid bridge/terminal carbonyl exchange, which leaves one of the terminal carbonyl groups unaffected. This cation crystallizes in two modifications, a violet one without a bridging carbonyl and a tan one with an apparent structure similar to that found in solution.

Introduction

The small-bite, linear tridentate ligands bis((diphenylphosphino)methyl)phenylphosphine (dpmp)[1] and bis((diphenylphosphino)methyl)phenylarsine (dpma)[2] are backbones about which nearly linear arrays of three rhodium ions can be constructed to form the structural unit **1**.[2-12] Aggregates of this sort are expected to show behavior distinct from that of clusters supported by metal-metal bonds. In particular, the presence of the phosphine backbone should allow expansion and contraction of the metal-metal distances without disruption of the cluster. Facile metal-metal bond making and breaking have already been demonstrated in binuclear complexes based on bis(diphenylphosphino)methane (dpm) backbones.[12,13] The flexibility of the methylene connection in these ligands allows for expansion and contraction of the metal-metal separation over a wide range (2.2-4.2 Å). In trinuclear systems containing **1**, it appears that the two metal-metal separations as well as the M-M-M angle have considerable, independent latitude in the values they can assume.



1: E = P or As

Here we consider the preparation and structural dynamics of a group of tricarbonyl cations of constitution $[Rh_3(\mu\text{-dpmp})_2(CO)_3X_2]^+$ and $[Rh_3(\mu\text{-dpma})_2(CO)_3X_2]^+$ where X is one of the halides (Cl^-, Br^-, or I^-) or pseudohalides (N_3^- or NCO^-). These are readily obtained from the reaction of the phosphine backbone with $Rh_2(\mu\text{-Cl})_2(CO)_4$ followed by metathesis with the appropriate anion. In preliminary communications we have reported that the structures of these cations are dependent upon the identity of the anion X.[4,7]

Results

Treatment of dpmp or dpma in dichloromethane solution with $Rh_2(CO)_4(\mu\text{-Cl})_2$ in methanol followed by the addition of a methanol solution of sodium tetraphenylborate yields the salts $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ and $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ in good yield. Metathesis of these in dichloromethane solution with an excess of sodium salts of other simple anions (Br^-, I^-, N_3^-, NCO^-) dissolved in methanol results in the rapid replacement of both coordinated anions. The resulting complexes are readily isolated as their tetraphenylborate salts upon the addition of more methanol in which the salts have very limited solubility. Only with iodide is there a problem of precipitation of mixtures of salts containing both tetraphenylborate and the added anion. In this case the iodide salt is initially isolated. It is insoluble in dichloromethane but is readily converted into the soluble tetraphenylborate salt through the addition of an excess of sodium tetraphenylborate in methanol to a slurry of the complex in dichloromethane. Apparently because of selective ion pairing and mass action, the complex dissolves in the mixture and may be precipitated as the tetraphenylborate salt through the addition of more methanol. The salts obtained by these reactions fall into three structurally different classes, which are described below.

Cations with the $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ Structure. The structure of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$, which has previously been subject to an X-ray diffraction study[3] as the chloride salt, is shown in drawing A of Figure 1. The cation contains only terminal carbonyl groups. One bridging chloride ligand and one terminal chloride ligand are present. This structural type appears to be present in several of the other cations including $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-X})X]^+$ (X = N_3^-, NCO^-) and $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-X})X]^+$ (X = Cl^-, Br^-). Characteristic features of this

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Table I. Infrared and Electronic Spectra of Trirhodium Cations

compd	species	infrared[a] ν(CO), cm^{-1}	electronic spectra[b] λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)
$[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$		1988, 1975, 1965 sh, 1958 sh	550, 400[a]
		1989, 1975 sh[b]	534 (22 500), 391 (4000), 275 sh (26 500)
$[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}N_3)N_3][BPh_4]$		1986, 1973[c]	530 (24 900), 283 sh (23 500)
$[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-NCO})NCO][BPh_4]$		1984 sh, 1968, 1954 sh[d]	522 (24 100), 275 sh (31 200)
$[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$		1987, 1973, 1952	545, 390[a]
		1983[b]	532 (23 500), 389 sh (3700)
$[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Br})Br][BPh_4]$		1993, 1970, 1956 sh	552 (23 400), 402 sh (3800)
$[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2][BPh_4]$		1969, 1830	476 sh (4600), 332 sh (17 900), 268 (44 600)
		1973, 1842[b]	
$[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2][BPh_4]$		1974, 1831	640 sh (700), 442 sh (6600)
			397 sh (9800), 325 sh (16 500)
$[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2Br_2][BPh_4]$	tan	1977, 1962, 1813	
	violet	1990 sh, 1980, 1965 sh	
	solution	1985, 1807	550 sh (4500), 458 (9600), 400 (12 300), 284 (28 000)

[a] Mineral oil mulls. [b] Dichloromethane solutions. [c] Azide at 2082, 2035 cm^{-1}. [d] Cyanate at 2176 cm^{-1}.

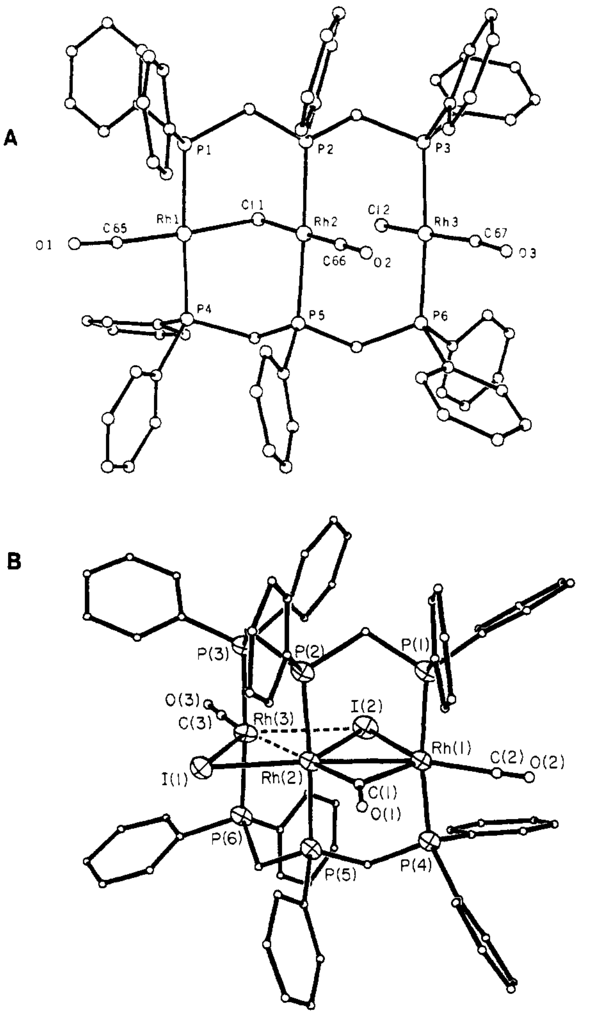


Figure 1. Perspective drawings of the structures of (A) $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ from ref 3 and (B) $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2]^+$ from ref 4.

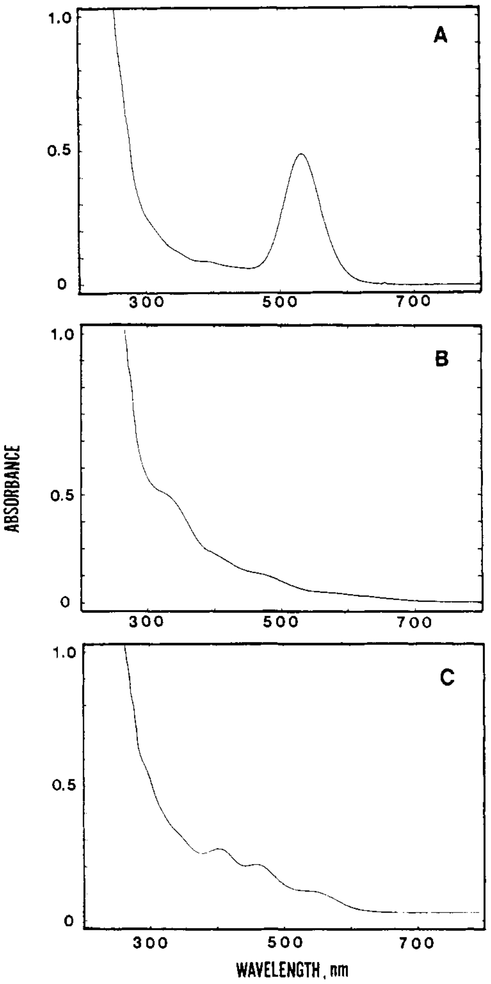


Figure 2. Electronic spectra of 2.2 mM solutions of (A) $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ (B) $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2]^+$ and (C) $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2Br_2]^+$ in dichloromethane with a 0.10-cm cell path length.

class include the presence of only terminal carbonyl absorptions at ca. 1980 cm^{-1} in the infrared spectrum both in the solid state and in dichloromethane solution and an intense, pleasing rose color, which manifests itself in an absorption band at ca. 540 nm in the electronic spectrum. The infrared and electronic spectral data are compiled in Table I. Figure 2 shows the electronic spectrum of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ (trace A) along with those of other complexes for comparison.

The NMR spectra of all of these cations show features which indicate that rapid bridge/terminal interchange of the anion is occurring. The ^{31}P NMR spectrum of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ is shown in Figure 3. Only two types of phosphorus atoms are present. The internal trans pair produces the resonances labeled P_c while the two terminal trans pairs of PPh_2 groups produce the resonances labeled $P_{a,b}$. The pattern of this spectrum contrasts sharply with those of the unsymmetrical and static cations $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2]^+$, vide infra, shown in trace B of Figure 3 and $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)(\mu\text{-I})I]^+$ (Figure 2 of ref 9). The spectrum is unaltered even when the sample is cooled to −80 °C. The ^{13}C NMR spectrum of $[Rh_3(\mu\text{-dpmp})_2(^{13}CO)_3(\mu\text{-Cl})Cl]^+$ is shown in Figure 4. Only two types of carbonyl groups are present. The doublet of triplets labeled t results from the two carbonyl groups bound to the terminal rhodium ions. The large doublet splitting results from ^1J(Rh,C) while the small triplet splitting results from ^2J(P,C). The less intense doublet of triplets labeled i results from the single

Table II. Nuclear Magnetic Resonance Data for Trirhodium Cations

	^{31}P			^{13}C (carbon monoxide)			^{1}H (methylene)
compd	δ	^{1}J(Rh,P), Hz	J(P,P),[b] Hz	δ	^{1}J(Rh,C), Hz	^{2}J(P,C), Hz	δ (no. of protons)
$[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$	23.0	118.7	25	189.7	78	11	3.25 (4)
	15.3	115.5	25	188.7	78	15	4.15 (4)
$[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-N}_3)N_3][BPh_4]$	23.7	123.8	25	191.8	72	12	3.40 (4)
	17.0	124.1	25	189.5	74	15	3.70 (4)
$[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-NCO})NCO][BPh_4]$	23.2	120.2	25	190.9	70	15	3.38 (4)
	16.3	120.8	25	189.2	71	17	3.65 (4)
$[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$	24.2	119.6		187.8	73		
				187.4	78	15	
$[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Br})Br][BPh_4]$	23.1	117.0					
$[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2][BPh_4]$	24.3	97.0	47	210.5	67, 25		3.35 (2)
	17.8	106.9	25	193.0	82	17	3.55 (2)
	13.9	100.0	47, 25	189.7	91	14	4.28 (4)
$[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2][BPh_4]$	24.8	101.7					
	17.0	109.5					
$[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2Br_2][BPh_4]$	23.5[a]	114.7	25	216.2[a]	39		2.74 (2)[a]
	18.8[a]	100.0	50, 25	188.6[a]	81		2.93 (4)[a]
	16.3[a]	105.9	50	186.0[a]	76		3.25 (2)[a]

[a] At −80 °C. [b] Apparent coupling constants.

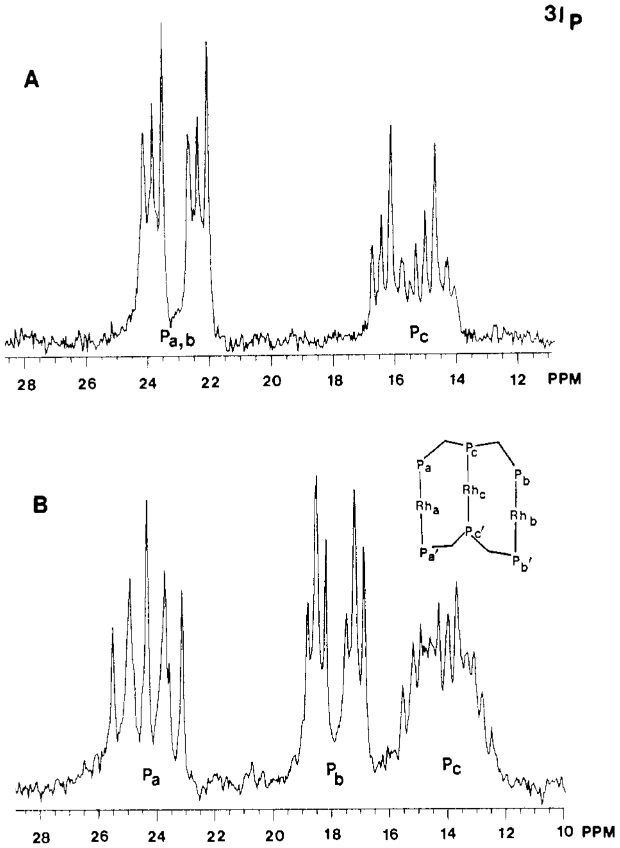


Figure 3. ^{31}P NMR spectra (A) $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ and (B) $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2]^+$ in dichloromethane solution at 23 °C.

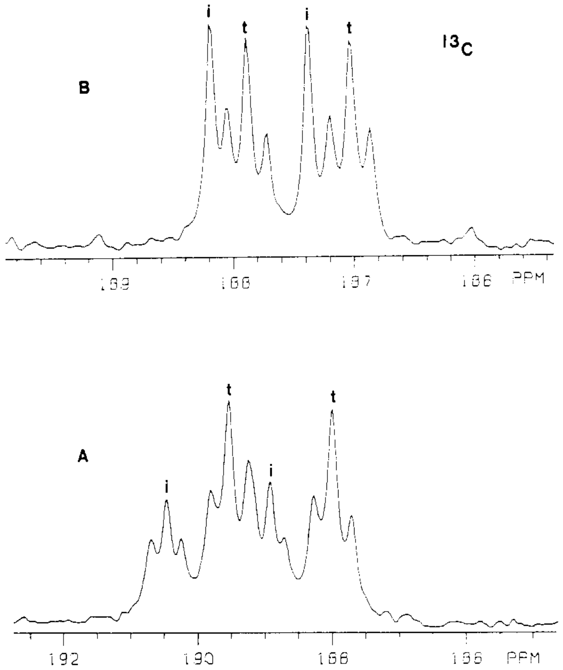
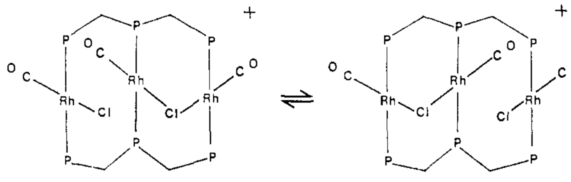


Figure 4. ^{13}C NMR spectra of (A) $[Rh_3(\mu\text{-dpmp})_2(^{13}CO)_3(\mu\text{-Cl})Cl]^+$ at 50.3 MHz and (B) $[Rh_3(\mu\text{-dpma})_2(^{13}CO)_3(\mu\text{-Cl})Cl]^+$ at 90.5 MHz in dichloromethane solutions.

carbonyl group bound to the internal rhodium ion. Again coupling to rhodium and to phosphorus is apparent. The intensity data indicate the carbonyl groups are present in a 2:1 ratio. The chemical shifts and coupling constants indicate that each is a terminal carbonyl. Again, the spectrum is unaltered over the temperature range −80 to +25 °C. The methylene region of the ^{1}H NMR spectrum contains structurally useful information. In the free ligand, the methylene protons are diastereotopic so that at least two methylene resonances are expected. When the terminal PPh_2 groups of one dpmp ligand reside in unique environments, then four methylene resonances are expected. In the case of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$, only two methylene multiplets are observed over the temperature range −80 to +25 °C. Similar features are observed for the multinuclear NMR spectra of all the other complex cations in this class. For the dpma complexes, $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-X})X]^+$ ($X = Cl^-, Br^-$), the presence of the central arsenic simplifies the ^{31}P NMR spectra by eliminating P–P coupling so that only one doublet appears in the spectrum. Likewise, the ^{13}C NMR spectrum (Figure 4) shows one doublet of triplets labeled t due to the two carbonyl groups bound to the $Ph_2P\text{–}Rh\text{–}PPh_2$ units. For the carbonyl group bound to the PhAs–Rh–AsPh unit, no coupling to phosphorus is present so a simple doublet labeled i is observed. The NMR data for this group of compounds are collected in Table II.

These NMR results all fall into a consistent pattern which indicates that, in solution, the environments of the two end rhodium ions and their ligands are equivalent. This contrasts with the solid-state structure in which Rh(1) and Rh(3) are in distinctly different sites. To explain these observations, we suggest that the cations are undergoing rapid bridge/terminal interchange of the anionic ligands. This process, which allows each rhodium ion to maintain a 16-electron count, is shown in eq 1. The motion involves displacement of the two anionic ligands and a "windshield wiper" motion of the central carbonyl group. For the chloro complex it is known that the bonded Rh(2)–Cl(1) distance, 2.401 (6) Å, is only slightly shorter than the nonbonded Rh(2)–Cl(2) distance, 3.487 (6) Å[3], so the displacements involved in altering



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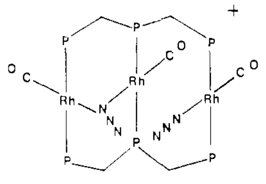
(1)

the Rh–Cl bonding in this case are quite reasonable. The two Rh···Rh separations, 3.164 (3) and 3.180 (3) Å, are similar, so no significant displacement of these or the phosphine bridge is required.

For the azide and cyanate complexes, we propose that the anions function as monatomic bridges as shown in **3** and **4**. Precedent for bridging in this fashion is available for both azide[14–16] and cyanate.[17,18] Again, with these structures, the displacements of the anion necessary to effect equivalency of the two ends of the cation are not great. For azide ligands the structural differences between the bridging and terminal forms have been noted[16] to be minor and to present no particular barrier to bridge/terminal interchange. The infrared spectrum of the azide complex is consistent with structure **3**. In particular, it contains a band at 2085 cm^{-1}, which can be assigned, on the basis of previous observations,[19] to $\nu_{as}(\mathrm{N_3})$ for the bridging azide, while the band at 2035 cm^{-1} can be assigned to $\nu_{as}(\mathrm{N_3})$ for the terminal azide. The ν(CN) band is known to be insensitive to the mode of cyanate coordination,[20] and so the presence of only one band is not inconsistent with structure **4**.



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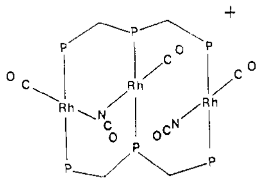

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Cations with the $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-I})_2]^+$ Structure. The structure of $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-I})_2]^+$ as determined by X-ray crystallography is shown in drawing B of Figure 1. In contrast to the group just discussed, this complex cation has one bridging carbonyl, and both of the iodide ligands are bridging. The cation $[\mathrm{Rh_3}(\mu\text{-dpma})_2(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-I})_2]^+$ has been assigned a similar structure. Both complexes are brown and produce similar electronic spectra that are more complex than those of the preceeding group as can be seen by reference to trace B of Figure 2. The infrared spectra of both iodide complexes show an absorption band in the region expected for terminal carbonyl groups and one in the region characteristic of a bridging carbonyl group. The NMR spectra of the two iodide cations in dichloromethane are in accord with a static structure that is consistent with the solid-state structure. The ^{31}P NMR spectrum of $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-I})_2]^+$ is shown in Figure 3. The three distinct phosphorus resonances (each with coupling to a directly bound rhodium) are readily apparent. The ^{31}P NMR spectrum of $[\mathrm{Rh_3}(\mu\text{-dpma})_2(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-I})_2]^+$ consists of a pair of doublets, again a feature indicative of inequivalence of the two end phosphorus and rhodium environments. These spectra are unchanged over the temperature range −80 to +25 °C.

The ^{13}C NMR spectrum of ^{13}CO enriched $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-}^{13}\mathrm{CO})(^{13}\mathrm{CO})_2(\mu\text{-I})_2]^+$ is shown in trace A of Figure 5. Three carbonyl environments, two terminal and one bridging, are clearly resolved. The terminal resonances show both one-bond Rh–C and two-bond C–P coupling. The resonance of the bridging carbonyl shows inequivalent, one-bond coupling of carbon to the two rhodium atoms. This spectrum is unaltered over the temperature range +25 to −80 °C.

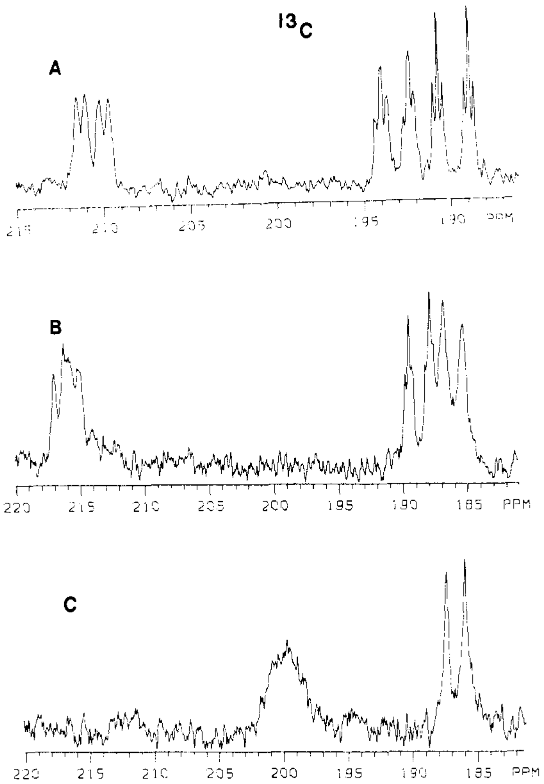

Figure 5. 50.3-MHz ^{13}C NMR spectra of (A) $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-}^{13}\mathrm{CO})(^{13}\mathrm{CO})_2(\mu\text{-I})_2]^+$ at 23 °C, (B) $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-}^{13}\mathrm{CO})(^{13}\mathrm{CO})_2\mathrm{Br_2}]^+$ at −80 °C, and (C) $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-}^{13}\mathrm{CO})(^{13}\mathrm{CO})_2\mathrm{Br_2}]^+$ at 23 °C in dichloromethane solutions.

$[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2\mathrm{Br_2}]^+$. The structure and structural dynamics of this cation are unique. Crystals suitable for X-ray diffraction have not been obtained, and so its structure must be inferred from spectroscopic data taken from solution. The electronic spectrum, shown in trace C of Figure 2, shows that this cation is clearly different from the $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}]^+$ class. The infrared spectrum shows the presence of both terminal and bridging carbonyl groups. This is confirmed by the ^{13}C NMR spectra. The spectrum recorded at −80 °C is shown in trace B of Figure 5. The pattern closely resembles that of the corresponding iodide shown in trace A. However, on warming, the spectrum shows significant differences. Trace C shows the ^{13}C NMR spectrum of the same sample at 23 °C. One of the terminal carbon monoxide resonances has coalesced with that of the bridging carbon monoxide. However, the resonance of the other terminal carbonyl remains distinct. Consequently, that group must not be involved in the exchange process. The ^{31}P NMR spectra of $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2\mathrm{Br_2}]^+$ at +23 and −80 °C are shown in Figure 6. They are also indicative of the occurrence of a dynamic process. At the lower temperature the spectrum is partially resolved into three multiplets, which have been assigned to three distinct phosphorus environments. When the sample is warmed to room temperature, the spectrum collapses into a rather featureless mass. We believe that this results from a coalescence of the two terminal phosphorus environments with the resulting average chemical shift lying very near to the chemical shift of the interior phosphorus. Finally, the ^{1}H NMR spectrum of $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2\mathrm{Br_2}]^+$ shows two methylene resonances at 23 °C in a pattern indicative of a complex with equivalent ends of the phosphine ligand. When the sample is cooled to −80 °C, the spectrum broadens and separates into three groups of methylene resonances in a 1:2:1 intensity ratio.

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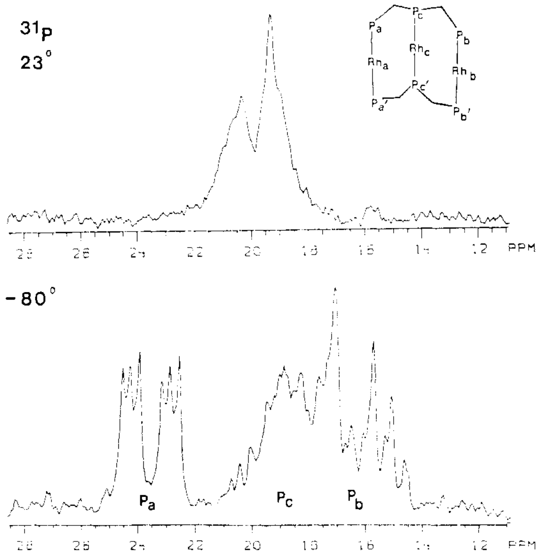
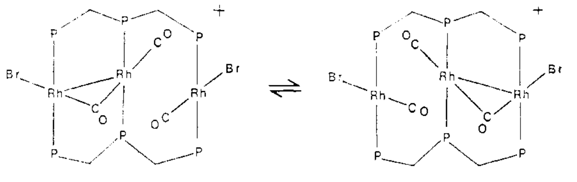


Figure 6. 81-MHz ^{31}P NMR spectra of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2Br_2]^+$ at +23 and −80 °C in dichloromethane solutions.

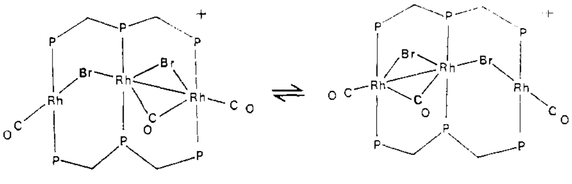
From these results we infer that the bromo complex has a unique structure **5**, which undergoes the dynamic process shown in eq 2. This process is similar to that shown in eq 1 except that the roles of two of the carbonyl groups and the two halide ligands have been interchanged. In this system we have bridge/terminal carbon monoxide exchange, which makes the two terminal phosphorus environments equivalent and interchanges the environments of one bridging and one terminal carbonyl. The other carbonyl group on the opposite side of the cation cannot become involved in the exchange because of its location. This process renders the two ends of the molecule equivalent and accounts for the observed temperature dependence of the ^{31}P, ^{13}C, and ^{1}H NMR spectra. Structure **5** is also appealing because it is built of structural units previously encountered in binuclear complexes. We have noted earlier that many trirhodium complexes of this sort contain units that correlate with binuclear analogues.[3,9] Thus, the left side of **5** contains a carbonyl-bridged A-frame like that in $Rh_2(\mu\text{-dpm})_2(\mu\text{-CO})Br_2$,[21] and the right side resembles the face-to-face dimer $Rh_2(\mu\text{-dpm})_2(CO)_2Cl_2$.[22]


(2)

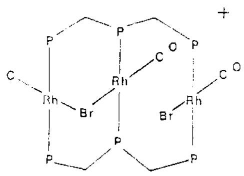
5

Previously, on the basis of the ^{31}P NMR data and the infrared spectrum, particularly the similarity of the infrared spectrum to that of the iodide complex, we had proposed[4] that the cation had a structure similar to that of the iodide complex. A structure identical with that of the iodide is unlikely because there appears to be no pathway readily accessible to interchange bridging and terminal carbon monoxide ligands and to render the two ends of the cation equivalent. However, by reversing the positions of the bridging carbonyl and iodide that lie between Rh(1) and Rh(2) it is possible to create structure **6**. We originally suggested that this structure coupled with the dynamic process shown in eq 3 could account for the spectroscopic data on this complex. The ^{13}C NMR data, however, rule out this process. The requirement of eq 3 that the two terminal carbonyl environments become equivalent while the bridging carbonyl migrates but remains bridging is clearly incompatable with the ^{13}C NMR spectra.

The complex $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2Br_2]^+$ crystallizes in two distinct forms. Precipitation from dichloromethane by the addition of methanol or from dimethylformamide by addition of ethyl ether gives tan crystals, which have color and infrared spectra similar to those of the dichloromethane solutions. However, precipitation from acetone solution through the addition of ethyl ether produces violet crystals, which have an infrared spectrum that has terminal carbonyl bands but lacks bridging carbonyl absorptions. By analogy with $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$, which has similar spectral features, we suggest that this violet solid contains the isomeric cation **7**.


(3)

6



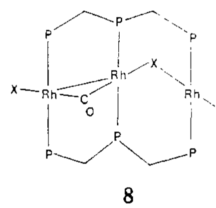
7

Both forms dissolve in dichloromethane to give solutions with identical spectroscopic properties. The two forms are readily transformed into each other. Dissolution of the tan form in acetone followed by the addition of ether gives violet crystals. Dissolution of the violet form in dichloromethane followed by the addition of methanol produces the tan modification.

Discussion

The sensitivity of the structure of this group of cations to changes in the two anionic ligands is remarkable. To some extent the structural variation introduced by the iodide ligands can be attributed to a size effect. Only with iodide is it possible for an anion in the position of I(2) to make contact with all three rhodium centers. However, the unique structural variation exhibited by $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)_2Br_2]^+$ is more difficult to explain. Clearly, the structure must lie in a shallow minimum since it can be converted to the violet isomer **7**. Moreover, note that changing the central phosphorus atoms to arsenic also results in a structural change. Thus $[Rh_3(\mu\text{-dpma})_2(CO)_3(\mu\text{-Br})Br]^+$ has the $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ structure and lacks carbonyl bridges.

Despite the structural variation within the cations $[Rh_3(\mu\text{-dpmp})_2(CO)_3X_2]^+$ for X = Cl^-, Br^-, and I^-, they undergo reversible loss of carbon monoxide to form the cations $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)(\mu\text{-X})X]^+$ **8**, which have a common structure for each of the three halides.[9] Likewise, these same cations, $[Rh_3(\mu\text{-dpmp})_2(CO)_3X_2]^+$, undergo reversible carbon monoxide addition to form tetracarbonyls **9** that also possess a common structure for all three anions.[6,23] Thus, the remarkable sensitivity of structure to anionic ligand is shown only by the $n = 3$ member of the cluster family $[Rh_3(\mu\text{-dpmp})_2(CO)_nX_2]^+$ (n = 2, 3, or 4).



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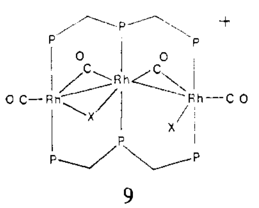

9

The dynamic behavior of the cations of the class $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl]^+$ represents an example of bridge/terminal

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anion interchange that we believe proceeds through an intraionic process. It has not been possible to slow this process so that kinetic parameters can be obtained. However, it is apparent that bridge/terminal anion exchange must be faster than bridge/terminal carbon monoxide interchange, since the latter process has been slowed, on cooling, to the point where the inequivalence of the two end environments of the cation becomes spectroscopically evident. This is reasonable since bridge/terminal carbon monoxide interchange requires electronic changes in the rhodium–rhodium interactions and probably introduces larger geometric alterations within the cation core than does the interchange of the anions. While bridge/terminal carbon monoxide interchange has been a well-studied phenomenon,[2,4] the present case is unusual because it is accompanied by metal–metal bond formation and breaking.

The intense rose color of the cations of the $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}]^+$ class results from metal–metal interactions. These cations can be viewed as stacks of three planar $\mathrm{Rh(CO)ClP_2}$ units. Perturbation of the out-of-plane orbitals (Rh d_{z^2} and p_z, ligand π) is expected to result due to the closeness of the rhodium ions.[25-27] The effect is clearly seen by considering the lowest allowed transitions in the series: $\mathrm{Rh(CO)Cl(PPh_3)_2}$, 364 nm;[26] $\mathrm{Rh_2}(\mu\text{-dpm})_2(\mathrm{CO})_2\mathrm{Cl_2}$, 450 nm[26] (Rh···Rh = 3.2386 (5) Å);[22] $[\mathrm{Rh_2}(\mu\text{-dpm})_2(\mu\text{-Cl})(\mathrm{CO})_2]^+$, 442 nm (Rh···Rh = 3.1520 (8) Å);[21] $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}]^+$, 534 nm. The proximity shift for the trinuclear complexes is the greatest simply because there are three interacting centers present and the HOMO/LUMO gap narrows as the number of metal ions in the chain increases. The transition involved is analogous to the $2a_{1g}$ (Rh d_{z^2}, σ^*) $\rightarrow$ $2a_{2u}$ (Rh p_z, ligand π) transition (D_{4h} symmetry, z being the stacking direction) seen at 727 nm in the related linear chain $[\mathrm{Rh_3(CNPh)_{12}}]^{3+}$.[23] While the electronic spectra of the other cations prepared here are useful in their qualitative and quantitative identification, the spectra themselves are much more complex due to the variety of metal–metal interactions and metal–bridging ligand interactions present.

Experimental Section

Preparation of Compounds. The ligands dpmp[1] and dpma[2] were prepared according to previous reports. The complexes reported here all have good stability toward the atmosphere, and consequently no special precautions were taken to exclude dioxygen or moisture during their preparation.

$[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}][\mathrm{BPh_4}]$. A solution of 300 mg (0.59 mmol) of dpmp dissolved in 10 mL of dichloromethane was added rapidly to a stirred solution of 150 mg (0.38 mmol) of $\mathrm{Rh_2(CO)_4}(\mu\text{-Cl})_2$ in 25 mL of methanol. After gas evolution ceased, a solution of 0.5 g (1.5 mmol) of sodium tetraphenylborate in 5 mL of methanol was gradually added. After standing for 1 h, the red, crystalline product was collected by filtration and washed successively with methanol and acetone, which removed an intensely red impurity. The product was purified by dissolving it in a minimum quantity of dichloromethane, filtering, and slowly adding ethyl ether. The crystalline product was collected by filtration and washed with ethyl ether; yield 300 mg (66%). Anal. Calcd for $\mathrm{C_{91}H_{78}BCl_2O_3P_6Rh_3}$: C, 60.86; H, 4.38; Cl, 3.95; P, 10.35. Found: C, 60.85; H, 4.20; Cl, 3.87; P, 10.09.

$[\mathrm{Rh_3}(\mu\text{-dpma})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}][\mathrm{BPh_4}]$. This was prepared from dpma by using the procedure described above for $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}][\mathrm{BPh_4}]$; yield 85%. Anal. Calcd for $\mathrm{C_{91}H_{78}As_2BCl_2O_3P_4Rh_3}$: C, 58.00; H, 4.17; Cl, 3.76. Found: C, 57.40; H, 4.26; Cl, 3.72.

$[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-I})_2][\mathrm{BPh_4}]$. A solution of 0.20 g (1.2 mmol) of sodium iodide in 3 mL of methanol was added to a solution of 0.15 g (0.083 mmol) of $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}][\mathrm{BPh_4}]$ in 12 mL of dichloromethane. The brown solution was filtered, and 30 mL of methanol was gradually added to the filtrate. The dense black precipitate (largely the iodide salt of the desired cation) was removed by filtration and washed with methanol. A solution containing 0.25 g (0.73 mmol) of sodium tetraphenylborate in 3 mL of methanol was added to a slurry of the black solid in 10 mL of dichloromethane. The resulting brown solution was filtered, and 20 mL of methanol was gradually added to the filtrate to precipitate brown crystals of the product. These were purified by dissolving them in dichloromethane, filtering, and then adding ethyl ether to precipitate the product. After filtration and washing with ethyl ether, the yield of the product was 0.14 g (85%). Anal. Calcd for $\mathrm{C_{91}H_{78}BI_2O_3P_6Rh_3}$: C, 55.24; H, 3.97; I, 12.83. Found: C, 55.02; H, 3.82; I, 12.35.

$[\mathrm{Rh_3}(\mu\text{-dpma})_2(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-I})_2][\mathrm{BPh_4}]$. This was prepared from $[\mathrm{Rh_3}(\mu\text{-dpma})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}][\mathrm{BPh_4}]$ by the method used for $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-I})_2][\mathrm{BPh_4}]$; yield 80%. Anal. Calcd for $\mathrm{C_{91}H_{78}As_2BI_2O_3P_4Rh_3}$: C, 52.89; H, 3.80; I, 12.28. Found: C, 52.33; H, 3.65; I, 12.38.

$[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2\mathrm{Br_2}][\mathrm{BPh_4}]$. A solution of 0.20 g (1.9 mmol) of sodium bromide in 10 mL of methanol was added to a solution of 0.15 g (0.084 mmol) of $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}][\mathrm{BPh_4}]$ in 10 mL of dichloromethane. The brown solution was filtered, and 20 mL of methanol was added to the filtrate. After the mixture was stored at 5 °C for 2 h, it was filtered to remove the tan crystalline product. Purification was accomplished by dissolving the solid in dichloromethane, filtering, and reprecipitating it by the addition of methanol. After the tan product was collected by filtration and washed with methanol and ether, the yield was 0.075 g (47%). The product may also be obtained as violet crystals through precipitation from an acetone solution by the gradual addition of ethyl ether. The violet crystals are readily converted back to the tan form by dissolving them in either dichloromethane or dimethylformamide and precipitating them by the addition of methanol or ethyl ether. Anal. Calcd for $\mathrm{C_{91}H_{78}BBr_2O_3P_6Rh_3}$: C, 57.99; H, 4.17; P, 9.86. Found: C, 57.73; H, 4.54; P, 9.86.

$[\mathrm{Rh_3}(\mu\text{-dpma})_2(\mathrm{CO})_3(\mu\text{-Br})\mathrm{Br}][\mathrm{BPh_4}]$. This was obtained from $[\mathrm{Rh_3}(\mu\text{-dpma})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}][\mathrm{BPh_4}]$ by the method described for $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2\mathrm{Br_2}][\mathrm{BPh_4}]$; yield 80%. Anal. Calcd for $\mathrm{C_{91}H_{78}As_2BBr_2O_3P_4Rh_3}$: C, 55.41; H, 3.99. Found: C, 55.41; H, 3.81.

$[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-N_3})\mathrm{N_3}][\mathrm{BPh_4}]$. This was obtained from $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}][\mathrm{BPh_4}]$ and sodium azide by the method used for the preparation of $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2\mathrm{Br_2}][\mathrm{BPh_4}]$ except that the purification involved the use of dichloromethane and ethyl ether; yield 45%. Anal. Calcd for $\mathrm{C_{91}H_{78}BN_6O_3P_6Rh_3}$: C, 60.42; H, 4.35; N, 4.65; P, 10.27. Found: C, 61.11; H, 4.40; N, 4.49; P, 10.11.

$[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-NCO})\mathrm{NCO}][\mathrm{BPh_4}]$. This was obtained from $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}][\mathrm{BPh_4}]$ and sodium cyanate by the method used for the preparation of $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mathrm{CO})_3(\mu\text{-N_3})\mathrm{N_3}][\mathrm{BPh_4}]$; yield 74%. Anal. Calcd for $\mathrm{C_{93}H_{78}BN_2O_5P_6Rh_3}$: C, 61.75; H, 4.35; N, 1.55; P, 10.27. Found: C, 61.35; H, 4.36; N, 1.56; P, 10.44.

^{13}CO Enrichment. All samples for ^{13}C NMR spectroscopy were enriched in ^{13}CO. A sample of ca. 85% enriched $[\mathrm{Rh_3}(\mu\text{-dpmp})_3(^{13}\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}][\mathrm{BPh_4}]$ was prepared by stirring a 0.1–0.2-g sample of the complex in 20 mL of dichloromethane under 1 atm of 98% enriched ^{13}CO in a closed 100-mL flask for 12 h. The complex was isolated by precipitation with ethyl ether. This sample was subsequently converted into the other complexes by anion metathesis. A sample of $[\mathrm{Rh_3}(\mu\text{-dpma})_2(^{13}\mathrm{CO})_3(\mu\text{-Cl})\mathrm{Cl}][\mathrm{BPh_4}]$ was prepared similarly.

Spectroscopic Measurements. The ^{1}H NMR spectra were recorded at 360 MHz on a Nicolet NT-360 Fourier transform spectrometer. The ^{13}C and ^{31}P NMR spectra were recorded on either a NT-360 Fourier transform spectrometer (at 90.5 and 145.8 MHz, respectively) or a NT-200 Fourier transform spectrometer (at 50.3 or 81 MHz). The references were as follows: ^{13}C and ^{1}H, internal tetramethylsilane; ^{31}P, external 85% phosphoric acid. The high-frequency-positive convention, recommended by IUPAC, has been used in recording all chemical shifts. Infrared spectra were recorded from mineral oil mulls or dichloromethane solutions on a Perkin-Elmer 180 spectrometer. Electronic spectra were obtained on a Hewlett-Packard 8450A spectrometer.

Acknowledgment. We thank the National Science Foundation (Grant CHE 8217954) for financial support, M. V. Nguyen for experimental assistance, and Dow Corning Corp. for a fellowship for P.E.R.

Registry No. **2**·BPh$_4$ (L = dpmp), 84774-75-4; **2**·BPh$_4$ (L = dpma), 100082-61-9; **3**·BPh$_4$ (L = dpmp), 100681-26-3; **4**·BPh$_4$ (L = dpmp), 100681-28-5; **5**·BPh$_4$ (L = dpmp), 100655-35-4; **7**·BPh$_4$ (L = dpma), 100655-37-6; $[\mathrm{Rh_3}(\mu\text{-dpmp})_2(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-I})_2][\mathrm{BPh_4}]$, 100655-31-0; $[\mathrm{Rh_3}(\mu\text{-dpma})_2(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-I})_2][\mathrm{BPh_4}]$, 100655-33-2; $\mathrm{Rh_2(CO)_4}(\mu\text{-Cl})_2$, 14523-22-9.

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