back-bonding to the phosphites, which is greater than the $d-d_\pi$ back-bonding to the phosphines, would produce a bigger synergic increase in the σ donation, increasing the shielding at carbon C4.

According to the bonding scheme proposed, the overall electron density at the metal atom is controlled by the interactions of the metal orbitals with the HOMO and LUMO of BDA and with the σ and π orbitals of carbon monoxide and phosphorus ligands. It can be seen in Table I that there are no significant trends in the chemical shifts of the carbonyls within the series. This suggests that the changes in the electron density at the metal atom are controlled mainly by the interactions of the iron orbitals with the orbitals of BDA and phosphorus ligands. Plots of $\Delta C4/\Delta C3$ vs. ν presented in Figure 3 show that the relative complex shifts increase linearly with the overall electron density at the metal atom. The effect is larger for the phosphites than for the phosphines. This is again contrary to that expected on the basis of the greater iron–phosphorus π back-bonding in the phosphite complexes. An explanation could be given on the basis of a stronger interaction between the HOMO of BDA and the empty metal orbitals in the phosphite complexes. Since the oxygen atom is the major donor center and the C4 carbon atom the major acceptor center of BDA, the effect on $\Delta C4/\Delta C3$ would reflect a net transfer of electron density from the oxygen atom to the C4 carbon atom through the iron atom.

The results discussed above seem to indicate that the BDA ligand acts as a "sink" for the negative charge placed on the iron atom by the phosphorus ligand via a $P \xrightarrow{\sigma} Fe \xrightarrow{\pi} BDA$ mechanism. This is in contrast with that observed in (π-cyclopentadienyl)iron carbonyl complexes.[19] In these complexes, the iron–cyclopentadienyl π back-bonding is not important and the electronic effects of the substituents on the cyclopentadienyl group are transmitted to the carbonyls.

On the basis of the results discussed in this paper we agree with Pearson and Raithby[10] that ^{13}C NMR spectroscopy provides an exceedingly sensitive means of detecting relatively small electronic perturbations in organometallic systems that are not always possible to detect by X-ray methods.

Acknowledgment. We thank the Conselho Nacional de Desenvolvimento Científico (CNPq), Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), and Financiadora de Estudos e Projetos (FINEP) for financial support.

Registry No. (BDA)Fe(CO)$_3$, 38720-22-8; (BDA)Fe(CO)$_2$P(OPh)$_3$, 93984-14-6; (BDA)Fe(CO)$_2$P(OMe)$_3$, 93984-15-7; (BDA)Fe(CO)$_2$P(OEt)$_3$, 93923-25-2; (BDA)Fe(CO)$_2$PPh$_3$, 93984-16-8; (BDA)Fe(CO)$_2$PMePh$_2$, 88760-06-9; (BDA)Fe(CO)$_2$P(*o*-tol)$_3$, 93923-26-3; (BDA)Fe(CO)$_2$PMe$_2$Ph, 89230-56-8; (BDA)Fe(CO)$_2$PEt$_3$, 89230-55-7; (BDA)Fe(CO)$_2$PCy$_3$, 93923-27-4; Fe(CO)$_4$PCy$_3$, 18474-81-2; Fe(CO)$_4$P(*o*-tol)$_3$, 40697-06-1; dodecacarbonyltriiron, 17685-52-8.

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Mono- and Polynuclear Transition-Metal Complexes of the Linear, Small-Bite Tris(phosphine) Bis((diphenylphosphino)methyl)phenylphosphine

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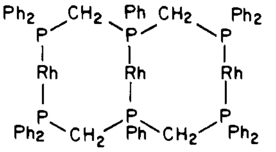
Bis((diphenylphosphino)methyl)phenylphosphine (dpmp) forms chelated complexes Pt(dpmp)(CH$_3$)$_2$, Pt(dpmp)(CN)$_2$, Pd(dpmp)X$_2$ (X = Cl, Br, I) and M(dpmp)(CO)$_4$ (M = Cr, Mo, W) in which the internal phosphorus atom is uncoordinated. Spectroscopic characterization by ^{31}P and ^1H NMR and infrared is reported. In solution, Pd(dpmp)X$_2$ (X = Cl, Br) reacts with itself to form PdX$_2$(μ-dpmp)Pd(dpmp)X]X, which has been identified by ^{31}P NMR spectroscopy. These chelated monomers react with other d^8 metal ions to form trinuclear complexes: *trans*-Rh(CO)Cl[(μ-dpmp)ML$_n$]$_2$, ML$_n$ = Pt(CH$_3$)$_2$, PtCl$_2$, PdCl$_2$, Mo(CO)$_4$; *cis*-PtCl$_2$[(μ-dpmp)ML$_n$]$_2$, ML$_n$ = Pt(CH$_3$)$_2$, PdCl$_2$, Mo(CO)$_4$; *trans*-PdCl$_2$[(μ-dpmp)ML$_n$]$_2$, ML$_n$ = Pt(CH$_3$)$_2$, PdCl$_2$, Mo(CO)$_4$. NMR spectroscopic properties indicative of the formation of these trinuclear complexes include a downfield shift of the ^{31}P resonance of the internal phosphorus atom of dpmp, a reduction of J(P,P) from 60–80 Hz in the bidentate chelates to less than 5 Hz in the dpmp-bridged complexes, and increased complexity in the upfield methylene resonance in the ^1H NMR spectrum. The metal centers appear to be remote from one another and noninteracting in these trinuclear complexes.

Introduction

While the behavior of polydentate ligands toward a single metal center has been an area of careful, detailed study for a long time,[1] the binding of polydentate ligands to several metal centers has only recently begun to be studied. Polydentate ligands, particularly poly(phosphine) ligands, can be used to prepare[2,3] and stabilize[4] metal clusters, to promote metal–metal interactions,[5] and to facilitate the formation of novel ligand bridges between metal centers.[6]

In this article we are concerned with the behavior of the linear, small-bite tris(phosphine) bis((diphenylphosphino)methyl)phenylphosphine (dpmp), in the context of building complex structures from monomeric fragments. Two questions emerge in this context. How does this ligand prefer to bind a single metal ion? How can these monomeric poly(phosphine) complexes be used to create new multicentered assemblages? We have demonstrated that this ligand is capable of forming a group of reactive trirhodium complexes in which the framework, **1**, remains intact while other ligands, which coordinate perpendicularly to this unit, readily undergo substitution and exchange.[2,7-9] Additionally dpmp



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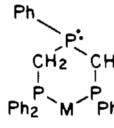

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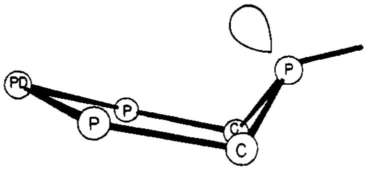
forms monomeric complexes that incorporate the chelated fragment **2**.[10] This unit, with its uncoordinated central phosphorus atom, can be used to construct more complex aggregates, particularly mixed-metal species. Two complexes containing chelating dpmp have been structurally characterized by X-ray diffraction.[11] In Pd(dpmp)Cl_2, the chelate ring adopts the boat conformation (**3**) so that the lone pair on the central phosphorus atom is directed over and above the chelate ring. In $(CH_3CN)Cl_2Pd(\mu\text{-dpmp})PdCl_2$, where dpmp bridges two metal ions, the ligand adopts the skew-boat conformation (**4**), which allows for maximal separation of the two palladium ions. In this article we describe the preparation of complexes involving chelated dpmp and use these to construct polynuclear complexes. We also compare and contrast the coordination behavior of this triphosphine ligand with other closely related ones: the linear ligands $Ph_2P(CH_2)_nPPh(CH_2)_nPPh_2$ (n = 2, 3) and the tripod ligand $(Ph_2P)_3CH$.



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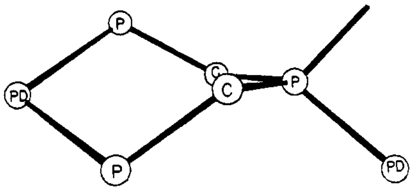

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Experimental Section

Preparation of Compounds. dpmp,[12] Pd(dpmp)Cl_2,[11] (1,5-COD)$PtCl_2$ (1,5-COD = 1,5-cyclooctadiene)[13] and Mo(2,5-nor)$(CO)_4$ (2,5-nor = 2,5-norbornadiene),[14] were prepared by established procedures.

Pd(dpmp)Br_2. A solution of 327 mg (0.647 mmol) of dpmp in 7 mL of dichloromethane was added to 242 mg (0.647 mmol) of solid (1,5-COD)$PdBr_2$, which then dissolved. A yellow precipitate formed after the reaction mixture had stirred at room temperature for 20 min. The precipitate was collected by filtration and washed with ethyl ether. No recrystallization was necessary: yield 84%. Anal. Calcd for $C_{32}H_{29}Br_2P_3Pd$: C, 49.74; H, 3.78; Br, 20.68. Found: C, 49.47; H, 3.77; Br, 20.69.

Pt(dpmp)Cl_2. A solution of 150 mg (0.296 mmol) of dpmp in 10 mL of dichloromethane was added to 111 mg (0.350 mmol) of (1,5-COD)-$PtCl_2$, which dissolved. After the mixture was stirred for about 1 h, the volume was reduced to one-third with the use of a rotary evaporator. Addition of ethyl ether precipitated a white compound that was collected by filtration, washed with ether, and vacuum-dried; yield 70%. Anal. Calcd for $C_{32}H_{29}Cl_2P_3Pt$: C, 49.75; H, 3.79. Found: C, 49.74; H, 3.88.

Pt(dpmp)$(CN)_2\cdot CH_2Cl_2$. A solution of 200 mg (0.259 mmol) of Pt(dpmp)Cl_2 in 40 mL of a 1:1 mixture of dichloromethane/ethanol was added dropwise to an ethanol solution of 26.7 mg (0.508 mmol) of sodium cyanide. The reaction mixture was heated under reflux for 8 h. After the mixture was cooled, its volume was reduced to half by rotary evaporation. The mixture was cooled in an ice bath. The white precipitate that formed was collected by filtration and washed with ether; yield 95%. Anal. Calcd for $C_{35}H_{31}Cl_2N_2P_3Pt$: C, 50.13; H, 3.73; Cl, 8.46; N, 3.34. Found: C, 50.25; H, 3.84; Cl, 7.90; N, 3.06.

Pt(dpmp)$(CH_3)_2$. Excess methyllithium in ethyl ether (2.25 mL, 1.5 M, 3.4 mmol) was added to a suspension of 0.654 g (0.85 mmol) of Pt(dpmp)Cl_2 in 70 mL of dry, degassed ether ethyl, which had been cooled to 0 °C. The mixture was stirred for 1 h at 0 °C. Most of the solid dissolved. Five milliliters of a 10 M solution of ammonium chloride in water was added to hydrolyze any unreacted methyllithium. The ether layer was separated, and the aqueous layer was washed twice with dichloromethane. The organic solutions were combined and evaporated to dryness. The air-stable, white solid that remained was recrystallized from dichloromethane and methanol to give colorless plates, which were collected by filtration, washed with methanol, and vacuum-dried; yield 0.575 g (93%). Anal. Calcd for $C_{34}H_{35}P_3Pt$: C, 55.81; H, 4.82. Found: C, 55.08; H, 4.89.

Mo(dpmp)$(CO)_4$. A solution of 508 mg (1.00 mmol) of dpmp in 10 mL of dichloromethane was added to a solution of 301 mg (1.00 mmol) of Mo(2,5-nor)$(CO)_4$ in 3 mL of dichloromethane. After the mixture was stirred for 2 h, the volume was reduced to less than one-fourth with the use of a rotary evaporator. Addition of *n*-hexane and cooling precipitated a yellow solid that was collected by filtration and washed with *n*-hexane; yield 94%. Anal. Calcd for $C_{36}H_{29}MoO_4P_3$: C, 60.57; H, 4.10. Found: C, 61.18; H, 4.40. IR ($CHCl_3$ solution): ν(CO) 2010, 1923, 1900, 1895 sh cm^{-1}.

Cr(dpmp)$(CO)_4$. A toluene solution containing 0.140 g (0.60 mmol) of chromium hexacarbonyl and 0.322 g (0.60 mmol) of dpmp was heated under reflux for 30 h. The hot solution was then evaporated until its volume reached 5 mL. During this process unreacted chromium hexacarbonyl sublimed from the reaction mixture. The crude product was precipitated from solution by the addition of *n*-hexane. The solid was recrystallized from chloroform/methanol to give 0.132 (31%) of the yellow crystalline complex. Anal. Calcd for $C_{36}H_{29}CrO_4P_3$: C, 64.28; H, 4.35; P, 13.82. Found: C, 62.87; H, 4.04; P, 13.75. IR ($CHCl_3$ solution): ν(CO) 2010, 1922, 1889 cm^{-1}.

W(dpmp)$(CO)_4$. This was prepared from 0.202 g (0.57 mmol) of tungsten hexacarbonyl and 0.290 g (0.57 mmol) of dpmp to give 0.197 g (43%) of product by the method described to form the chromium analogue. Anal. Calcd for $C_{36}H_{29}O_4P_3W$: C, 53.88; H, 3.64; P, 11.58. Found: C, 53.18; H, 3.70; D, 11.69. IR ($CHCl_3$ solution): ν(CO) 2019, 1924, 1893 cm^{-1}.

***trans*-Rh(CO)Cl[(μ-dpmp)$PdCl_2$]$_2$.** A solution of 9.98 mg (0.026 mmol) of $[Rh(CO)_2(\mu\text{-Cl})]_2$ in a 3 mL of dichloromethane was added dropwise to a solution of 70.15 mg (0.091 mmol) of Pd(dpmp)Cl_2 in 25 mL of dichloromethane. After the mixture was stirred for $^1/_2$ h, the product had precipitated as a yellow solid in almost quantitative yield. The product was recovered by filtration and washed with ether; yield 92%. Anal. Calcd for $C_{65}H_{58}Cl_5OP_6Pd_2Rh$: C, 50.89; H, 3.78; Cl, 11.56. Found: 50.01; H, 3.83; Cl, 11.90.

***trans*-Rh(CO)Cl[(μ-dpmp)$PtCl_2$]$_2$.** A solution of 4.7 mg (0.012 mmol) of $[Rh(CO)(\mu\text{-Cl})]_2$ in 3 mL of dichloromethane was added dropwise to a solution of 37.3 mg (0.048 mmol) of Pt(dpmp)Cl_2 in 15 mL of dichloromethane. After the solution was stirred for 2 h, a yellow solid had been formed. The precipitate was collected by filtration and washed with ethyl ether; yield 90%. Anal. Calcd for $C_{65}H_{58}Cl_5OP_6Pt_2Rh$: C, 45.61; H, 3.39; Cl, 10.36. Found: C, 45.35; H, 3.37; Cl, 10.52.

***trans*-Rh(CO)Cl[(μ-dpmp)Mo$(CO)_4$]$_2\cdot CH_2Cl_2$.** A solution of 13.62 mg (0.035 mmol) of $[Rh(CO)_2(\mu\text{-Cl})]_2$ in 3 mL of dichloromethane was added to a solution of 100 mg (0.140 mmol) of Mo(dpmp)$(CO)_4$ in 7 mL of dichloromethane. After 2 h of stirring the volume of the mixture was reduced to one-fourth in a rotary evaporator. After addition of ethyl ether and cooling an orange compound precipitated. The solid product was removed by filtration and washed with ether; yield 70%. Anal. Calcd for $C_{74}H_{60}Cl_3O_9P_6Mo_2Rh$: C, 52.90; H, 3.60. Found: C, 53.10; H, 3.74. IR: ν(CO) 2020, 1980, 1930, 1900 br cm^{-1}.

***trans*-Rh(CO)Cl[(μ-dpmp)Pt$(CH_3)_2$]$_2$.** The compound was prepared by adding 0.027 g (0.069 mmol) of $[Rh(\mu\text{-Cl})(CO)_2]_2$ in 2 mL of dichloromethane to a solution of 0.201 g (0.275 mmol) of Pt(dpmp)$(CH_3)_2$ in 2 mL of dichloromethane. The reaction mixture was stirred for 10 min. Yellow plates of the product were precipitated by addition of ethyl ether. These were collected by filtration and recrystallized from dichloromethane and methanol; yield 0.191 g (84%). Anal. Calcd for $C_{70}H_{72}Cl_3OP_6Pt_2Rh$: C, 49.03; H, 4.23; Cl, 6.20. Found: C, 49.34; H, 4.50; Cl, 6.64.

***cis*-$PtCl_2$[(μ-dpmp)Pt$(CH_3)_2$]$_2$.** A 3-mL solution of 0.0172 g (0.0457 mmol) of (1,5-COD)$PtCl_2$ in dichloromethane was added dropwise to a 2-mL dichloromethane solution of 0.0669 g (0.0914 mmol) of Pt(dpmp)$(CH_3)_2$. The resulting solution was stirred 15 min. The solution was evaporated to 2 mL, and ethyl ether was added to precipitate the product. The white compound was recrystallized from dichloromethane and ether to yield 0.055 g (50%) of white needles. Anal. Calcd for $C_{68}H_{70}Cl_2P_6Pt_3$: C, 47.24; H, 4.08; Cl, 4.10; P, 10.70. Found: C, 47.00; H, 4.02; Cl, 4.43; P, 10.58.

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Table I. ^{31}P and ^{1}H NMR Spectral Data for dpmp Complexes in Dichloromethane Solution

	^{31}P				^{1}H			
	terminal		internal		methylene		methyl	
compd	δ^a	J, Hz	δ^a	J, Hz	δ		δ	J, Hz
$Pt(dpmp)(CH_3)_2$	8.1 d	71 (J(P,P)) 1838 (^1J(Pt,P)	−39.2	71 (J(P,P)) 49 (J(Pt,P))	2.95 m	2.54 d	2.25 m	68 (J(Pt,H))
$Pt(dpmp)(CN)_2$	−4.1 d	62 (J(P,P)) 2437 (^1J(Pt,P))	−40.0 d	62 (J(P,P), J(Pt,P))	2.84 m	2.62 d		
$Pd(dpmp)Cl_2$	18.3 d	62 (J(P,P))	−40.7 t	62 (J(P,P))	2.77 m	2.54 d		
$Pd(dpmp)Br_2$	15.4 d	67 (J(P,P))	−41.6 t	67 (J(P,P))				
$Pd(dpmp)I_2$	9.0 d	61 (J(P,P))	−45.3 t	61 (J(P,P))				
$Cr(dpmp)(CO)_4$	45.4 d	60 (J(P,P))	−39.1 t	60 (J(P,P))	2.80 m	2.70 d		
$Mo(dpmp)(CO)_4$	23.3 d	79 (J(P,P))	−40.7 t	79 (J(P,P))	2.97	2.70 d		
$W(dpmp)(CO)_4$	6.8 d	74 (J(P,P)) 231 (J(W,P))	−38.1 t	74 (J(P,P))	3.03 m	2.73 d		
trans-$Rh(CO)Cl[(\mu\text{-dpmp})Pt(CH_3)_2]_2$	6.6 s	1816 (^1J(Pt,P))	11.4 d	126 (^1J(Rh,P))	3.44 m	3.15 m	0.28 m	70 (J(Pt,H))
trans-$Rh(CO)Cl[(\mu\text{-dpmp})PtCl_2]_2$	0.0 s	3525 (^1J(Pt,P))	5.9 d	128 (^1J(Rh,P))				
trans-$Rh(CO)Cl[(\mu\text{-dpmp})PdCl_2]_2$	19.3 s		9.3 d	128 (^1J(Rh,P))				
trans-$Rh(CO)Cl[(\mu\text{-dpmp})Mo(CO)_4]_2$	23.8 s		9.8 d	125 (^1J(Rh,P))				
cis-$PtCl_2[(\mu\text{-dpmp})Pt(CH_3)_2]_2$	5.4 s	108 (^3J(Pt,P)) 1788 (^1J(Pt,P))	−5.7 s	3672 (^1J(Pt,P))	3.45 m	2.71 m	0.18 m	70 (J(Pt,H))
cis-$PtCl_2[(\mu\text{-dpmp})PdCl_2]_2$	14.6 s	95 (^3J(Pt,P))	−10.1 s	3666 (^1J(Pt,P))				
cis-$PtCl_2[(\mu\text{-dpmp})Mo(CO)_4]_2$	23.5 s	101 (^3J(Pt,P))	7.9 s	3623 (^1J(Pt,P))	3.53 m	2.62 m		
trans-$PtCl_2[(\mu\text{-dpmp})Mo(CO)_4]_2$	25.0 s	62 (^3J(Pt,P))	−5.5 s	2513 (^1J(Pt,P))				
$PdCl_2(\mu\text{-dpmp})PdCl_2(NCCH_3)$	22.4 s		5.6 s					
$PdCl_2[(\mu\text{-dpmp})PdCl_2]_2$	23.0 s		−5.3 s					
$PdCl_2[(\mu\text{-dpmp})Pt(CH_3)_2]_2$	8.4 s	1802 (^1J(Pt,P))	1.6 s		3.34 m	3.26 m	0.20 m	69 (J(Pt,H))
$PdCl_2[(\mu\text{-dpmp})Mo(CO)_4]_2$	25.6 s		1.1 s					

[a] s = singlet, d = doublet, t = triplet, and m = multiplet; ^{195}Pt satellites not included.

***cis*-$PtCl_2[(\mu\text{-dpmp})PdCl_2]_2$.** This compound was formed by slow addition of a solution of 0.0412 g (0.11 mmol) of $(1,5\text{-COD})PtCl_2$ in 5 mL of dichloromethane to a stirred solution of 0.150 g (0.220 mmol) of $Pd(dpmp)Cl_2$ in 5 mL of dichloromethane. The yellow product was isolated by addition of ethyl ether followed by filtration. The solid was purified by washing with 30 mL of hot methanol, followed by recrystallization from dichloromethane and methanol; yield 0.061 g (33%) of yellow plates. Anal. Calcd for $C_{64}H_{58}Cl_6P_6Pd_2Pt$: C, 47.05; H, 3.58; Cl, 13.02; P, 11.38. Found: C, 46.92; H, 3.30; Cl, 13.19; P, 10.80.

***cis*-$PtCl_2[(\mu\text{-dpmp})Mo(CO)_4]_2$.** A 3-mL solution of 0.0143 g (0.038 mmol) of $(1,5\text{-COD})PtCl_2$ in dichloromethane was added dropwise to 0.0542 g (0.076 mmol) of $Mo(dpmp)(CO)_4$ in 1 mL of dichloromethane. The reaction mixture was stirred 10 min. The addition of ethyl ether precipitated white needles, which were collected by filtration. The product was recrystallized from dichloromethane and ether to yield 0.050 g (77%) of colorless crystals. Anal. Calcd for $C_{72}H_{58}Cl_2Mo_2O_8P_6Pt$: C, 51.02; H, 3.45; Cl, 4.18. Found: C, 51.34; H, 3.82; Cl, 4.44. IR: ν(CO) 2026, 1933, 1891 br cm^{-1}.

$PdCl_2[(\mu\text{-dpmp})Pt(CH_3)_2]\cdot{}^1/_2CH_2Cl_2$. This yellow compound was formed by slow addition of 0.0195 g (0.068 mmol) of $(1,5\text{-COD})PdCl_2$ in 3 mL of dichloromethane to a solution of 0.10 g (0.137 mmol) of $Pt(dpmp)(CH_3)_2$ in 2 mL of dichloromethane. Crystals were isolated by partial evaporation of the solvent followed by addition of ethyl ether. The yellow plates were collected by filtration and recrystallized from dichloromethane and ether; yield 0.089 g (79%). Anal. Calcd for $C_{69}H_{71}Cl_3P_6PdPt_2\cdot{}^1/_2CH_2Cl_2$: C, 48.89; H, 4.25; Cl, 6.32. Found: C, 48.45; H, 4.20; Cl, 6.43.

$PdCl_2[(\mu\text{-dpmp})Mo(CO)_4]_2$. This material was prepared via the method used for *cis*-$PtCl_2[(\mu\text{-dpmp})Mo(CO)_4]_2$. Yellow plates of the product, 0.035 g (62%), were obtained from 0.0496 g (0.070 mmol) of $Mo(dpmp)(CO)_4$ and 0.010 g (0.035 mmol) of $(1,5\text{-COD})PdCl_2$. Anal. Calcd for $C_{72}H_{58}Cl_2Mo_2O_8Pd$: C, 53.84; H, 3.64; Cl, 4.41; P, 11.57. Found: C, 54.01; H, 3.71; Cl, 4.10; P, 11.35. IR: ν(CO) 2022, 1930, 1900 br cm^{-1}.

Physical Measurements. The ^{31}P NMR spectra were recorded at 81 MHz on a Nicolet NT-200 Fourier transform spectrometer. All ^{31}P spectra wre proton decoupled. An external 85% phosphoric acid reference was used. The ^1H NMR spectra were recorded at 360 MHz on a Nicolet NT-360 Fourier transform spectrometer. The high-frequency-positive convention, recommended by IUPAC, has been used in reporting all chemical shifts. Infrared spectra were recorded from mineral oil mulls with a Perkin-Elmer 180 spectrometer. Electronic spectra were obtained with a Hewlett-Packard 8450A spectrometer.

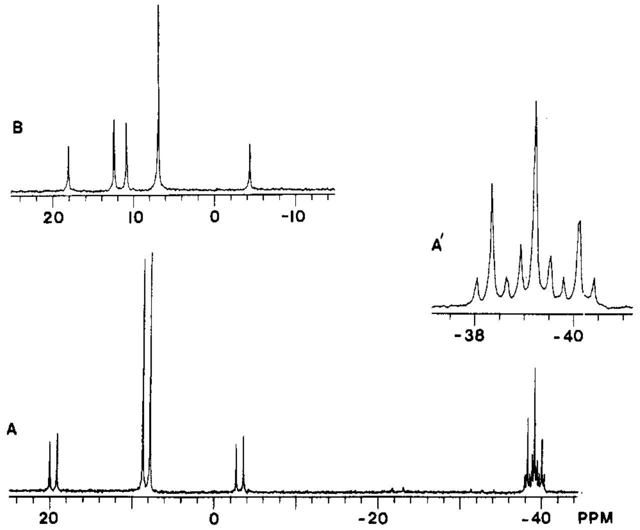
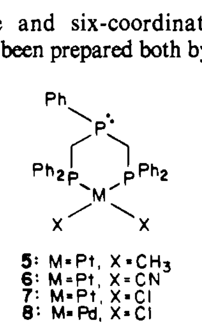


Figure 1. 81-MHz ^{31}P NMR spectra of (A) $Pt(dpmp)(CH_3)_2$ and (B) *trans*-$Rh(CO)Cl[(\mu\text{-dpmp})Pt(CH_3)_2]_2$ in dichloromethane solution. The inset on the upper right (A′) shows an expansion of the low-frequency multiplet for $Pt(dpmp)(CH_3)_2$.

Results

Bidentate Chelated Complexes. dpmp readily forms chelated monomers that leave the central phosphorus uncoordinated, with both four-coordinate and six-coordinate metal ions. $Pt(dpmp)(CH_3)_2$ (**5**) has been prepared both by the addition of dpmp to $Pt(1,5\text{-COD})(CH_3)_2$ and by the reaction of methyllithium with $Pt(dpmp)Cl_2$ (vide infra). The latter method is preferred and is the one described here. The ^{31}P NMR spectrum of **5**, which is



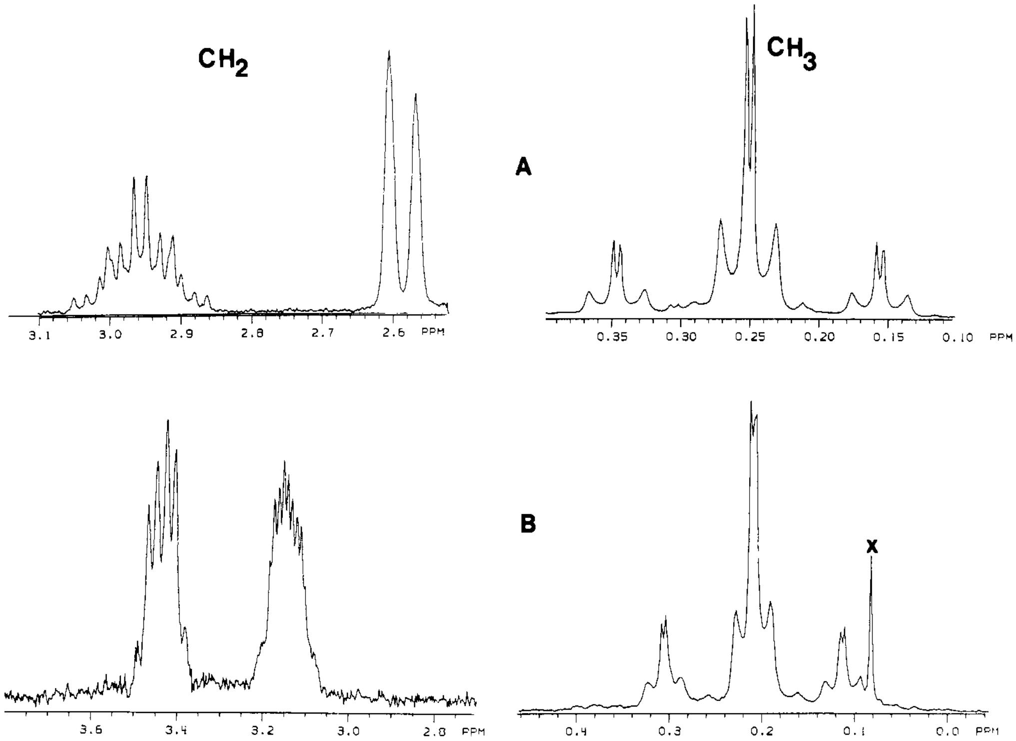
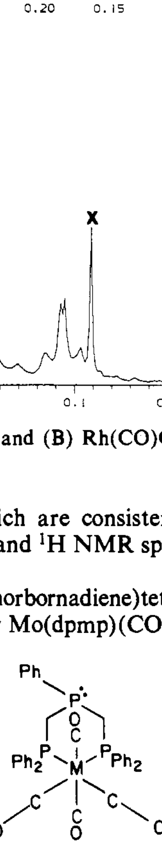


Figure 2. 360-MHz ^{1}H NMR spectra of the methylene and methyl regions of (A) Pt(dpmp)$(CH_3)_2$ and (B) Rh(CO)Cl[(μ-dpmp)Pt$(CH_3)_2]_2$ in dichloromethane solution.

typical for the chelated species reported here, is reproduced in Figure 1. Table I contains numerical data for this and other new compounds. The two equivalent terminal phosphorus atoms have experienced a large downfield shift relative to the free ligand. Such a shift is expected when the phosphorus atom is coordinated to a metal. The magnitude of coupling to ^{195}Pt (33.8% natural abundance, spin $^1/_2$) is also indicative of coordination. The internal phosphorus atom, however, has experienced a slight upfield shift relative to the free ligand. Although satellites due to coupling to ^{195}Pt are present on the resonance of the internal phosphorus atom, the magnitude of J(Pt,P) indicates that this central phosphorus is not directly bound to platinum. The magnitude of the phosphorus–phosphorus coupling in Pt(dpmp)$(CH_3)_2$ is lower than that found in the free ligand (114 Hz)[2] but is in the range 60–80 Hz, which is characteristic of the chelated form of this ligand. The ^{1}H NMR spectrum consists of a methyl multiplet at 0.25 ppm and methylene resonances shown in Figure 2 as well as the generally uninformative phenyl resonances in the range 7–8 ppm. The methylene resonances are somewhat indicative of structure. In the free ligand the two methylene groups are equivalent but within each methylene group the two protons are diastereotopic. This remains true for the chelated ligand. Moreover, the high-field resonance in the simple chelates appears as a sharp doublet (^2J(H,H) ≈ 14 Hz) without resolvable phosphorus–proton coupling while the lower field methylene proton appears as a 12-line multiplet due to proton–phosphorus coupling. The sharp doublet character of the high-field resonance appears to be a characteristic of the chelated form of dpmp. This simple doublet is replaced by a more complex multiplet in molecules containing the framework **1** or in the case when another metal is bound to the central phosphorus of the chelate ring. The methyl resonance shows satellite splitting consistent with expectations for methyl–platinum complexes. The fine structure on each feature results from coupling to the two phosphorus atoms and possibly to the protons of the phosphine ligand as described elsewhere.[15]

Treatment of Pd(dpmp)Cl_2 with 2 equiv of sodium cyanide yields Pt(dpmp)$(CN)_2$. The infrared spectrum of this colorless compound exhibits two weak cyanide stretching bands (ν(CN) 2142, 2138 cm^{-1}), which are consistent with the cis chelate structure (**6**). The ^{31}P and ^{1}H NMR spectra are similar to that of Pt(dpmp)$(CH_3)_2$.

The reaction of (2,5-norbornadiene)tetracarbonylmolybdenum with dpmp yields yellow Mo(dpmp)$(CO)_4$ (**11**). The chromium



11: M = Mo
12: M = Cr
13: M = W

and tungsten analogues have been obtained, albeit in modest yields, from the reaction of dpmp with the appropriate hexacarbonyls. The infrared spectra of **11–13** show a pattern of carbonyl absorptions that is characteristic of a *cis*-$ML_2(CO)_4$ species. In the chromium and tungsten complexes the lowest energy band appears as a broad and barely perceptible shoulder on the low-energy side of the carbonyl absorption. The ^{31}P NMR spectra (Table I) indicate that the central phosphorus atom is uncoordinated in each complex since it has experienced a slight upfield shift relative to the free ligand. The two equivalent terminal phosphorus atoms have resonances that are shifted significantly downfield from their ligand position. The ^{1}H NMR spectra show the upfield methylene doublet that is characteristic of chelated complexes.

It is noteworthy that in examining the complexes **5–13** we have found no tendency for the central phosphorus to become attached to the chelated metal. In particular, attempts to prepare Mo(dpmp)$(CO)_3$ by photolysis of Mo(dpmp)$(CO)_4$ or by the reaction between dpmp and (mesitylene)tricarbonylmolybdenum have been unsuccessful. In the latter case Mo(dpmp)$(CO)_4$ is formed in good yield, probably with the scarifice of some (mesitylene)tricarbonylmolybdenum as the source of the added carbon monoxide.

Solution Behavior of Pd(dpmp)X_2. While complexes such as **5**, **6**, **11**, **12**, and **13** with strongly bound ancillary ligands display relatively simple NMR spectroscopic behavior, the halo complexes of platinum and palladium—Pt(dpmp)Cl_2, Pd(dpmp)Cl_2, Pd-

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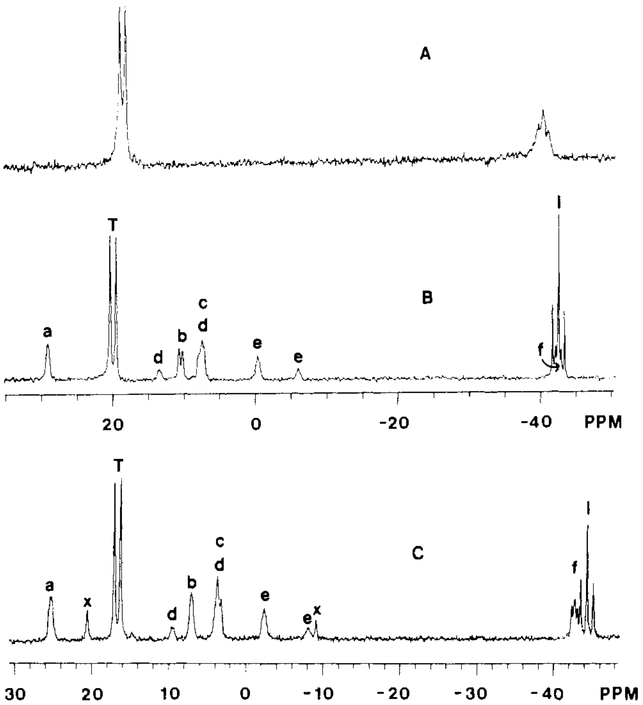
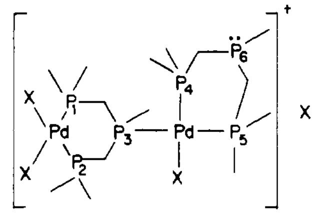


Figure 3. 81-MHz ^{31}P NMR spectra of dichloromethane solutions of (A) Pd(dpmp)Cl$_2$ at 25 °C, (B) Pd(dpmp)Cl$_2$ at -80 °C, and (C) Pd(dpmp)Br$_2$ at -80 °C. The peaks in trace C labeled X are due to an impurity of PdBr$_2$[(μ-dpmp)PdBr$_2$]$_2$. Other resonance assignments are explained in the text.

(dpmp)Br$_2$, and Pd(dpmp)I$_2$—exhibit more complex spectra.

The ^{31}P NMR spectra of Pd(dpmp)Cl$_2$ in dichloromethane solution at -80 and at +25 °C are shown in Figure 3. At the lower temperature, two species are present. Resonances labeled T and I are the resonances of the terminal and internal phosphorus atoms of the chelate monomer **8**. The resonance positions as well as the magnitude of ^2J(P,P) are consistent with such a structure. The less intense resonances labeled a–f are ascribed to the binuclear compound **14**, which can form from the attack of one chelated monomer upon another with displacement of halide. Complex **14** contains six unique phosphorus environments. The uncoordinated phosphorus atom, P$_6$, is expected to resonate at highest field and is associated with the resonance f, which overlaps with feature I of **8**. This resonance is more readily identified in the spectrum of the bromo analogue (vide infra). The trans phosphorus atoms P$_3$ and P$_5$ are expected to be strongly coupled. These produce the AB quartet labeled d and e in Figure 3. Analysis of these features yields the following: δ_d, 9.7; δ_e, -2.9; $J(P_dP_e)$, 456 Hz. The remaining phosphorus atoms (P$_1$, P$_2$, and P$_4$) produce the three broad resonances labeled a (28.9 ppm), b (10.1 ppm), and c (7.2 ppm). More specific assignments of these resonances cannot be definitively made at this time.



14: X=Cl
15: X=Br

Upon warming, the spectrum shown in trace B of Figure 3 broadens and the features a–f eventually merge into the base line so that at 25 °C only the broadened spectrum shown in trace A appears. We ascribe this behavior to rapid occurrence of reaction 1, which leads to the equilibration of resonance T with resonances a, b, c, and d (or e) and of resonance I with resonances f and e (or d).

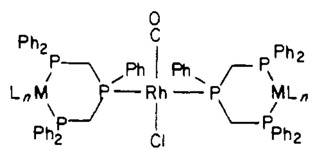
$$2\mathrm{Pd(dpmp)X_2} \rightleftharpoons [\mathrm{X_2Pd}(\mu\text{-dpmp})\mathrm{Pd(dpmp)X}]^+ + \mathrm{X}^- \quad (1)$$

Similar data are observed for the bromo analogue. The relevant spectrum is shown in trace C of Figure 3. At -80 °C the pattern of resonances is extremely similar to that seen in trace B, but the high-field resonance f is more clearly discernible. We propose an analogous interpretation of this spectrum. Resonances T and I arise from monomer **9** while a (25.3 ppm), b (6.9 ppm), c (3.5 ppm), d (5.6 ppm, $J(P_e,P_d)$ = 470 Hz), e (-4.6 ppm), and f (-42.9 ppm) come from the salt **15**. At 25 °C, reaction 1 with X = Br$^-$ is occurring rapidly and a broad triplet and a broad doublet are observed.

Somewhat similar features are present in the ^{31}P NMR spectrum of Pt(dpmp)Cl$_2$, but here the spectra are more complex and a wholly satisfactory set of assigments has not been made. It appears that the equilibrium shown by reaction 1 may be complicated in the case of platinum by the presence of a third species resulting from further attack on platinum by an uncoordinated phosphorus.

Polynuclear Complexes. The presence of an uncoordinated phosphorus atom in the chelated monomers **5–13**, allows them to be used as ligands toward a second metal ion. Since the phosphorus lone pair in **3** is directed over and above the chelate ring and the palladium ion, it appears possible that there would be significant metal–metal interaction when a second metal ion was bound to the central phosphorus atom. However, by conversion to a skew-boat chelate ring conformation (**4**) the metal–metal separation can be maximized. The following compounds were prepared to test the ability of the central phosphorus to function in this fashion and to examine metal–metal interactions in the products.

Reaction of the monomers **5**, **7**, **8**, and **11** with Rh$_2$(μ-Cl)$_2$(CO)$_4$ in a 4:1 molar ratio yields the yellow trinuclear complexes **16–19**.



16: ML$_n$ = Pt(CH$_3$)$_2$
17: ML$_n$ = PtCl$_2$
18: ML$_n$ = PdCl$_2$
19: ML$_n$ = Mo(CO)$_4$

The ^{31}P NMR spectral changes that accompany the formation of **16** are shown in Figure 1. The pattern of metal–phosphorus coupling firmly establishes the mode of phosphine coordination in **16**. Coordination to rhodium causes a large downfield shift in the position of the resonance of the unique internal phosphorus atom. Most significantly, coupling to ^{103}Rh (100% natural abundance, spin $^1/_2$) is clearly discernible in this resonance and the magnitude of J(Rh,P) is indicative of direct Rh–P bonding. The chemical shift and ^1J(Pt,P) of the terminal phosphorus atoms have undergone only minor changes upon the conversion of **5** into **16**. However, the magnitude of ^2J(P,P) has been appreciably reduced to the point where it is less than the natural line width (<5 Hz) and is therefore undetected.

In most respects the ^{1}H NMR spectrum of **16** resembles that of **5** as can be seen in Figure 2. The methyl resonance shows the expected coupling to platinum and phosphorus, and the phenyl resonances in the 7–8 ppm region, while more complex and spread out in **16**, are largely uninformative. The pattern of the methylene resonances, however, shows one significant change upon rhodium binding. Two methylene resonances are present in **16**, but both are complex multiplets showing coupling to each other and to phosphorus. The sharp, higher field doublet that was present in **5** is replaced in **16** by a broader, more complex feature.

The changes noted above for the conversion of **5** into **16** are similar to those noted in the formation of the other rhodium compounds. In pararticular, the ^{31}P NMR resonance of the internal phosphorus atom is shifted downfield and shows Rh–P coupling appropriate for an Rh–P bond. Also, the higher field methylene doublet in the ^{1}H NMR spectrum of the monomers

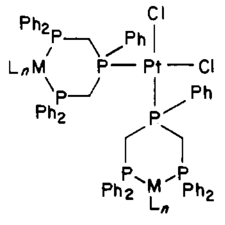
Table II. Spectroscopic Data for Rhodium Complexes

compd	^1J(Rh,P), Hz	ν(CO), cm^{-1}	λ_{max}, nm (ϵ)
trans-$Rh(CO)Cl[(\mu\text{-dpmp})Pt(CH_3)_2]_2$	126	1971	360 (3000), 416 sh (530)
trans-$Rh(CO)Cl[(\mu\text{-dpmp})PtCl_2]_2$	128	1980	361 (4700)
trans-$Rh(CO)Cl[(\mu\text{-dpmp})PdCl_2]_2$	128	1975	350 sh
trans-$Rh(CO)Cl[(\mu\text{-dpmp})Mo(CO)_4]_2$	125	1980	350 (7000)
trans-$Rh(CO)Cl[PPh_3]_2$	127	1976	364 (3300), 410 sh (570)

becomes complex upon binding rhodium.

Spectroscopic features of the rhodium center that are sensitive to its environment indicate that it is remote from, and noninteracting with, the other metal centers in the trinuclear complexes **16–19**. Data that substantiate this are presented in Table II. The carbonyl stretching frequency of the rhodium-bound carbon monoxide is sensitive to the electron density at rhodium and hence to the rhodium oxidation state. All of the complexes **16–19** exhibit ν(CO) in the range expected for Rh(I), close to that of the prototypical *trans*-$Rh(CO)Cl(PPh_3)_2$. Likewise ^1J(Rh,P) for these complexes also is in the range characteristic of a *trans*-$Rh^I(CO)ClP_2$ unit.[16] Finally, the electronic spectra of the $Rh^I(CO)ClP_2$ unit are sensitive to the close approach of a second planar d^8 metal ion.[17,18] Generally this causes a shift (proximity shift) of the lowest energy (metal d_{z^2} to ligand π/metal p_z) transition to lower energy by 100–200 nm. Comparison of the data in Table II, particularly the similarity of the electronic spectra of **16–19** to that of *trans*-$Rh(CO)Cl(PPh_3)_2$, shows that no proximity shift is operating in these molecules.

Polynuclear complexes have also been constructed about a $PtCl_2$ center. Treatment of $Pt(1,5\text{-COD})Cl_2$ with **5**, **8**, and **11** yields the trinuclear complexes **20**, **21**, and **22**, respectively. The downfield shift of the resonance of the internal phosphorus atom and most importantly the presence of satellites indicative of a one-bond Pt–P coupling demonstrate that the internal phosphorus is bound to platinum. The magnitude of ^1J(Pt,P) for the internal phosphorus atoms is indicative of a cis structure for each of these species. For comparison, ^1J(Pt,P) is 3669 Hz for *cis*-$PtCl_2(PPh_3)_2$ while it is 2634 Hz for the trans isomer.[18] Both **20** and **21** appear to be isomerically pure. However, $PtCl_2[(\mu\text{-dpmp})Mo(CO)_4]_2$ as isolated contains a small quantity of the trans isomer along with the predominant cis isomer. The spectral differences (Table I) between the cis and trans isomers include a decrease in ^1J(Pt,P), as expected, as well as a decrease in ^3J(Pt,P) for the terminal phosphorus atoms. For two different preparations the cis-to-trans ratio was 10:1, and so it appears that this may represent an equilibrium mixture. While it may be somewhat surprising to find these rather bulky phosphines (**5**, **8**, and **11**) in cis orientations, complexes of the type $PtCl_2$(tertiary phosphine)$_2$ are generally more thermodynamically stable as the cis isomer even for bulky lignads like triphenylphosphine. The detection of some *trans*-$PtCl_2[(\mu\text{-dpmp})Mo(CO)_4]_2$ is probably a consequence of the extremely large size of the $Mo(dpmp)(CO)_4$ ligand, which is expected to be more bulky than **5–10** with only planar, four-coordinate metal ions. The spectroscopic properties of the ML_n portions of these complexes indicate that they experience little perturbation in these trinuclear complexes.

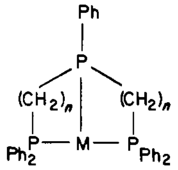


20: $ML_n = Pt(CH_3)_2$
21: $ML_n = PdCl_2$
22: $ML_n = Mo(CO)_4$

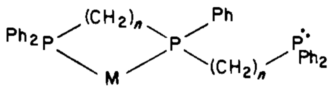
Another group of polynuclear complexes can be formed with a $PdCl_2$ central, planar unit. Thus, treatment of $Pd(COD)Cl_2$ with **5** or **11** yields $PdCl_2[(\mu\text{-dpmp})Pt(CH_3)_2]_2$ or $PdCl_2[(\mu\text{-dpmp})Mo(CO)_4]_2$, respectively. The bright yellow color of these compounds suggests that they are most likely formed as the trans isomers. The ^{31}P NMR spectra indicate that they are isomerically pure. Comparison of the ^{31}P NMR spectra for $Pd_3(dpmp)_3Cl_6$, which was prepared previously,[8] with other compounds in Table I indicates that it has the $PdCl_2[(\mu\text{-dpmp})_2PdCl_2]_2$ structure incorporating the chelated form of dpmp rather than a structure (considered earlier[8]) involving a unit analogous to **1**.

Discussion

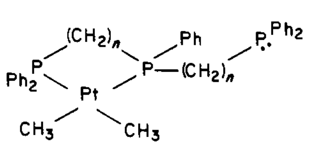
These studies demonstrate that dpmp readily and preferentially forms the bidentate chelate structure **2** when it binds to a single metal center. Alternate modes of chelation, which include tridentate **23** (with either facial or meridional disposition) or bidentate **24**, have not been found. The preference for structure **2** is a consequence of chelate ring sizes. Formation of **2** produces a highly favorable six-membered ring, whereas either **23** or **24** requires the formation of more highly strained four-membered rings. The presence of adjacent four-membered rings in **23** is a source of further strain. However, for the linear tris(phosphines) with longer spacings between phosphorus donors, these alternate coordination modes become possible and indeed preferred. While significant ring strain has been anticipated[20] in complexes of $PhP[(CH_2)_2PPh_2]_2$ in the tridentate mode **23**, numerous planar tridentate complexes of $PhP[(CH_2)_3PPh_2]_2$ are known.[20–22] Particularly germane to our work is the observation that $Pt(1,5\text{-COD})Cl_2$ reacts with $PhP[(CH_2)_3PPh_2]_2$ to yield the salt $[PhP[(CH_2)_3PPh_2]_2PtCl]Cl$, which contains structural unit **23**.[23] When forced to act as bidentate ligands, these longer tris(phosphines) prefer to leave a dangling terminal phosphine rather than to form an 8- or 10-membered ring that would be required if the internal phosphorus atom were to remain uncoordinated. Thus with $Pt(1,5\text{-COD})(CH_3)_2$ these tris(phosphines) form **25** and **26**.[24]



23



24



25: $n = 2$
26: $n = 3$

In contrast to **5**, in which the central phosphorus atom always remains uncoordinated, **25** and **26** show fluxional behavior that

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involves exchange between the dangling phosphorus atoms and the coordinated terminal phosphorus atoms. In the process the central phosphorus atom remains coordinated.

The stability of the six-membered chelate ring in these complexes limits their manipulation. The four-membered chelate rings formed by 2-(diphenylphosphino)pyridine[25] and bis(diphenylphosphino)methane (dpm)[26,27] are rather easily opened in reactions with other metal ions to give binuclear (particularly heterobinuclear) complexes. In the process a chelated ligand is converted into a bridging ligand. In contrast with dpmp we have not as yet encountered examples of such ring opening. Similarly it is possible to convert chelating dpm into a bridging form by choosing ancillary ligands that prefer to bind in a mutually trans fashion. For example, treatment of $Pt(dpm)Cl_2$ with sodium cyanide yields *trans*-$Pt(CN)_2(\mu\text{-dpm})_2$-*trans*-$Pt(CN)_2$.[28] In contrast, $Pt(dpmp)(CN)_2$ has a chelated structure and cis cyanide ligands.

Once formed, these chelate rings can act as additional ligands. The spectroscopic behavior of the polynuclear complexes described here indicates little if any interaction between the metal centers of these complexes. The spectroscopic data suggest that all of the chelated monomers exist with the boat conformation found crystallographically for $Pd(dpmp)Cl_2$. The conversion of the chelating ligand into a bridging ligand appears to be accompanied by a change of ring conformation to the skew-boat conformation **4**. This change in ring conformation is interpreted as causing the diminution in the magnitude of J(P,P) seen on complexation of the internal phosphorus atom and also causing the increase in the magnitude of J(P,H), which results in increased complexity of the upfield methylene resonance in the polynuclear complexes.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE8217954) for generous financial support and F. E. Wood, M. W. Renner, and A. J. Fossett for experimental assistance.

Registry No. **5**, 93862-09-0; **6**, 93842-01-4; **7**, 86217-37-0; **8**, 84751-00-8; **9**, 93842-02-5; **10**, 93842-03-6; **11**, 86217-32-5; **12**, 93842-04-7; **13**, 93842-05-8; **14**, 93842-12-7; **15**, 93842-13-8; **16**, 93842-06-9; **17**, 93921-89-2; **18**, 93921-90-5; **19**, 93921-91-6; **20**, 93842-07-0; **21**, 93842-08-1; **22**, 93842-09-2; *trans*-$PtCl_2[(\mu\text{-dpmp})Mo(CO)_4]_2$, 93921-92-7; $PdCl_2(\mu\text{-dpmp})PdCl_2(NCCH_3)$, 86217-33-6; $PdCl_2[(\mu\text{-dpmp})PdCl_2]_2$, 93921-93-8; $PdCl_2[(\mu\text{-dpmp})Pt(CH_3)_2]_2$, 93842-10-5; $PdCl_2[(\mu\text{-dpmp})Mo(CO)_4]_2$, 93842-11-6; (1,5-COD)$PdBr_2$, 12145-47-0; (1,5-COD)$PtCl_2$, 12080-32-9; Mo(2,5-nor)$(CO)_4$, 12146-37-1; $[Rh(CO)_2(\mu\text{-Cl})]_2$, 14523-22-9; (1,5-COD)$PdCl_2$, 12107-56-1; chromium hexacarbonyl, 13007-92-6; tungsten hexacarbonyl, 14040-11-0.

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Kinetic Study of the Reaction of Ferric Porphyrin Fluorides and Imidazole

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A kinetic study is reported for the reaction of Fe(porphyrin)F (porphyrin = dianion of tetraphenylporphyrin (TPP) and protoporphyrin IX dimethyl ester (PPIXDME)) with imidazole (HIm) in acetone at 25 °C to give $Fe(porphyrin)(HIm)_2^+F^-$. The reaction rate shows a complex dependence on the HIm concentration, being second order in HIm at low concentrations and progressing to zero order at high concentrations of HIm. With Fe(TPP)F, optical spectra at 25 and −78 °C show the existence of two reaction intermediates. The first intermediate to form is the six-coordinate high-spin Fe(TPP)(HIm)F and the second is Fe(TPP)(HIm)F···HIm, in which an external imidazole is hydrogen bonded to the fluoride. Thus, hydrogen bonding is shown to play a major role in assisting ionization of the fluoride. A comparison to analogous Fe(porphyrin)Cl complexes shows that hydrogen bonding is much more important with the fluoride, as expected for the stronger Brønsted base (F^- compared to Cl^-). A complete analysis of the data is provided that yields rate constants as well as equilibrium constants for the formation of both intermediates. The relevance of these reactions to hydrogen bonding to superoxide in oxymetalloporphyrins is noted.

Introduction

The reaction of ferric porphyrin chlorides, Fe(Por)Cl, with imidazoles, RIm, according to eq 1 has been the subject of numerous thermodynamic[3-8] and kinetic[9-12] studies.

$$Fe(Por)Cl + 2RIm \rightarrow Fe(Por)(RIm)_2^+Cl^- \qquad (1)$$

The initial step in the reaction is the rapid and reversible conversion of high-spin Fe(Por)Cl to the transient high-spin six-coordinate intermediate Fe(Por)(RIm)Cl, which then dissociates chloride in the rate-determining step before combining with another RIm to give the low-spin product. The mechanistic interest in this reaction has focused on the chloride ionization from the transient intermediate. It has been demonstrated[9-12] that hydrogen bonding to the developing chloride ion can have a major effect on the reaction dynamics. This distal-type hydrogen bonding most clearly manifests itself in the rate laws for unsubstituted imidazole (HIm) and the N-methylated analogue (*N*-MeIm). Thus, the reaction

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