Platinum(II) Dimethyl Complexes of Chelating Polyphosphine Ligands. A ^{31}P NMR Investigation of Their Dynamic Behavior

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Abstract: A series of $Pt(CH_3)_2$(polyphosphine) complexes was prepared and studied by $^{31}P\{^1H\}$ NMR spectroscopy. The diphosphine ligands $\{Ph_2PCH_2CH_2P(Ph)neo\text{-}C_{10}H_{19}$, $(CH_3)_2PCH_2CH_2PPh_2$, and $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2\text{-}CH{=}CH_2\}$, as well as all of the triphosphine ligands $\{CH_3C(CH_2PPh_2)_3$, $PhP(CH_2CH_2CH_2PPh_2)_2$, $PhP(CH_2\text{-}CH_2CH_2PCy_2)_2$, $PhP(CH_2CH_2PR_2)_2$ (R = Ph, Me), and $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2PPh_2\}$ and a tetraphosphine $\{P(CH_2CH_2PPh_2)_3 = PP_3\}$ function as bidentate ligands at low temperature. For the complexes containing the triphosphine ligands, one terminal phosphine group remains unbonded, while the $Pt(CH_3)_2(PP_3)$ complex has two terminal groups unbonded at low temperatures in solution and in the solid state. Some of the tri- and tetradentate ligands undergo rapid exchange of the terminal phosphorus atoms. On the basis of line-shape analyses of the ^{31}P NMR spectra, which show large negative $\Delta S^{\ddagger}$ values, an associative mechanism involving five-coordinate platinum(II) is proposed to explain the exchange process. Additional support for an associative mechanism is deduced from comparisons between ligands of differing steric requirements and chelate-bite angles. A five-member chelate ring containing two phosphine groups is thermodynamically preferable to a six-member ring in these platinum(II) compounds, and the cis phosphorus-phosphorus coupling constants vary in a regular and predictable manner for five- and six-member chelate rings. The changes in the phosphorus-phosphorus coupling constants are factored into "through-the-backbone" and "through-the-metal" components.

Introduction

Chelating polyphosphine ligands are useful for stabilizing unusual coordination numbers and geometries in transition-metal complexes. The chelating nature of the ligands often prevents phosphine dissociation, in contrast to the behavior of analogous complexes of monophosphine ligands. For example, the mechanism of catalysis by $RhCl(PPh_3)_3$ is thought to involve dissociation of one PPh_3 ligand,[1] whereas the triphosphine complex, RhCl(ttp), ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$, is inert to dissociation.[2] Similarly, complexes of formulation $Pt(tripod)(PR_3)$, where tripod = $CH_3C(CH_2PPh_2)_3$, are dissociatively stable, in contrast to their $Pt(PR_3)_4$ analogues.[3]

Taking advantage of this strong chelating tendency of polyphosphines and the strong covalent Pt-C bond, we have prepared a series of potentially five- and six-coordinate Pt(II) complexes, some of which show fluxional behavior. By examination of the variable-temperature ^{31}P NMR spectra of these complexes, a mechanism is proposed which can account for the exchange process. A preliminary account of this work has appeared.[4]

In addition, we have been able to determine the relative stabilities of five- and six-member chelate rings in these Pt(II) complexes. ^{31}P NMR parameters for these and other complexes are presented.

Experimental Section

Reagents. Bis(3-diphenylphosphinopropyl)phenylphosphine (ttp), bis(3-dicyclohexylphosphinopropyl)phenylphosphine (Cyttp), 3-diphenylphosphinopropylphenylphosphine (PPH), bis(2-dimethylphosphinoethyl)phenylphosphine (dmetp), 3-diphenylphosphinopropyl-2-diphenylphosphinoethylphenylphosphine (eptp), and (3-diphenylphosphinopropyl)(3-butenyl)phenylphosphine (ppol) were prepared by published procedures.[5] Tris(1,1,1-diphenylphosphinomethyl)ethane (tripod), tris(2-diphenylphosphinoethyl)phosphine (PP_3), bis(2-diphenylphosphinoethyl)phenylphosphine (etp), and bis(1,3-diphenylphosphino)propane (dppp) were purchased from either Strem Chemical Co. or Pressure Chemical Co. and were used as obtained. The ligands 2-dimethylphosphinoethyldiphenylphosphine (dmdpe) and 2-diphenylphosphinoethylneomenthylphenylphosphine (P P*) were kindly supplied by Professor R. B. King of the University of Georgia. The complex $PtMe_2(COD)$ was prepared from $PtCl_2(COD)$ (COD = 1,5-cyclooctadiene) by the published procedure.[6] All solvents are reagent grade and were dried and degassed prior to use.

Spectral Characterization. Infrared spectra of the solids were measured on a Perkin-Elmer 337 grating spectrophotometer from 400 to 4000 cm^{-1} as Nujol mulls and/or KBr pellets. Fourier-mode proton magnetic resonance and proton noise-decoupled, ^{31}P NMR spectra were collected on a Bruker HX-90 spectrometer operating at 90.00 or 36.43 MHz, respectively. The proton spectra were standardized relative to Me_4Si as an internal standard. Variable-temperature, ^{31}P spectra were obtained on samples in 10-mm tubes with concentric 5-mm inserts [containing $(CD_3)_2CO$ for the deuterium lock and trimethyl phosphate as a secondary standard]. Positive chemical shifts are downfield, and they are reported relative to δ H_3PO_4 0.0 ppm. The chemical shifts are reproducible to ± 0.05 ppm, and the coupling constants are accurate to ± 1.0 Hz.

Computer simulation of experimental spectra was performed with the ITRCAL program provided by the Nicolet Instrument Corp. ITRCAL is an adaptation of the LAOCOON III program.[7a] Line-shape analysis was performed using the DNMR program of G. Binsch and D. A. Klein of the University of Notre Dame that was adapted for the IBM-360 by K. Christensen of The Ohio State University.[7b] Simulations of spectra of platinum compounds were performed in three separate steps: (1) the central portion of the spectrum was simulated, ignoring any coupling to platinum; (2) the satellite portion of the spectrum was simulated by introducing the $^{195}Pt-^{31}P$ coupling constants; (3) the two spectra were added together in a 2:1 area ratio to account for the relative abundance of ^{195}Pt (33.7%).

Syntheses of Platinum Complexes. 1. $Pt(CH_3)_2$(tripod). To a solution of $CH_3C(CH_2PPh_2)_3$ (0.6600 g) in benzene (30 mL) was added 0.3525 g of $Pt(CH_3)_2$(COD). The resulting solution was heated under reflux for 3 h and then most of the benzene was removed on a rotary evaporator. To the remaining solution was added diethyl ether (80 mL); crystals started appearing after 5 min. After the resulting mixture sat in a refrigerator overnight, the crystals were collected on a sintered-glass frit, washed with ether, and dried in vacuo, yield 0.7148 g (79%).

Anal. Calcd for $C_{43}H_{45}P_3Pt$: C, 60.77; H, 5.35. Found: C, 60.77; H, 5.29.

2. $Pt(CH_3)_2$(ttp). A solution of $Pt(CH_3)_2$(COD) (0.3300 g) in benzene (20 mL) was treated with a ttp solution (10.0 mL, 0.117 M in benzene) and then heated under reflux for 2 h at 80-90 °C (oil bath temperature). The solvent was removed under reduced pressure and the residual oil was extracted with diethyl ether (ca. 60 mL). After the ether solution was filtered, methanol (50 mL) was added to the filtrate. The ether was allowed to evaporate from the resulting solution

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in the hood for 24 h. A white, crystalline precipitate was collected; it was washed with methanol (20 mL) and hexane (20 mL) and then dried in air, yield 0.4033 g (52%).

Anal. Calcd for $C_{38}H_{43}P_3Pt$: C, 57.93; H, 5.51. Found: C, 58.17; H, 5.64.

3. $Pt(CH_3)_2$(etp). A solution of $PhP(CH_2CH_2PPh_2)_2$ (etp, 0.5839 g) in toluene (30 mL) was treated with $Pt(CH_3)_2$(COD) (0.3641 g) and then stirred for 2 h at 70–95 °C (oil bath temperature). The resulting solution was concentrated under reduced pressure until an oil was formed. The oil was extracted with three 25-mL portions of diethyl ether. The ether was evaporated by bubbling N_2 gas through the solution, and the resultant oil was treated with absolute ethanol (50 mL). Four hours later, a white precipitate was collected on a filter, washed with hexane, and then dried in air, yield 0.6244 g (75%).

Anal. Calcd for $C_{36}H_{39}P_3Pt$: C, 56.91; H, 5.18. Found: C, 57.16; H, 5.33.

4. $Pt(CH_3)_2$(ppol), ppol = $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH{=}CH_2$. A solution of $Pt(CH_3)_2$(COD) (0.5039 g) in benzene (25 mL) was treated with a ppol solution (3.0 mL, 0.5271 M in benzene) and then heated under reflux for 4 h. The resulting solution was concentrated to ca. 5 mL under reduced pressure and then treated with absolute ethanol (30 mL). The white precipitate was collected on a filter, washed with absolute ethanol (30 mL) and hexane (50 mL), and dried in air. Recrystallization from benzene and ethanol gave a white solid.

Anal. Calcd for $C_{27}H_{34}P_2Pt$: C, 52.67; H, 5.58. Found: C, 52.82; H, 5.76.

5. Reaction of $Pt(CH_3)_2$(COD) with $PhP(CH_2CH_2PMe_2)_2$(dmetp). **A.** A solution of $Pt(CH_3)_2$(COD) (0.3520 g, 1.056 mmol) in toluene (10 mL) was treated with dmetp (2.0 mL, 0.2828 M in benzene), and then heated under reflux for 3 h. The solvent was removed in vacuo until a glassy solid formed. This solid was then dissolved in acetone and acetone-d_6 for ^{31}P NMR spectroscopy.

B. A benzene solution of dmetp (6.0 mL, 0.2828 M in benzene) was treated with $Pt(CH_3)_2$(COD) (0.2759 g, 0.8277 mmol) and heated under reflux for 2 h. After the solvent was removed in vacuo, the oil was then dissolved in acetone and acetone-d_6 for ^{31}P NMR spectroscopy. A similar sample solution with excess dmetp ligand in toluene and benzene-d_6 was also prepared for a high-temperature ^{31}P NMR study.

6. Reaction of $Pt(CH_3)_2$(COD) with $Ph_2P(CH_2)_3P(Ph)(CH_2)_2PPh_2$(eptp). **A.** A solution of $Pt(CH_3)_2$(COD) (0.2293 g, 0.6879 mmol) in toluene (10 mL) was treated with eptp (3.2 mL, 0.4051 M in benzene) and then heated under reflux for 2 h. The resulting solution was concentrated in vacuo until an oil formed. The oil was dissolved in acetone and acetone-d_6 for ^{31}P NMR spectroscopy.

B. A solution of $Pt(CH_3)_2$(COD) (0.1667 g, 0.5 mmol), 0.81 mL of eptp (>0.5 mmol), and 10 mL of toluene was heated to reflux for 20 min. The volume was reduced to 1.5 mL, and 5 mL of toluene-d_8 was added. This solution was used directly for ^{31}P NMR studies. In order to obtain a 1:1 stoichiometry, small amounts of $Pt(CH_3)_2$(COD) were added until the ^{31}P resonances due to excess ligand disappeared. The solvents were then removed in vacuo and the remaining oil was extracted with ether (~500 mL). After the volume of ether was reduced to 80 mL, 20 mL of ethanol was added, and the volume of the solution was reduced to ~15 mL; subsequently, a white solid, which was used for ^{31}P NMR studies, precipitated.

7. $Pt(CH_3)_2[Ph_2PCH_2CH_2P(Ph)neo\text{-}C_{10}H_{19}]$. A 0.6426-g portion (1.397 mmol) of ligand was added to 0.4650 g (1.395 mmol) of $Pt(CH_3)_2$(COD) in 25 mL of benzene, and the solution was heated under reflux for 3 h. After the solution was cooled, the volume was reduced to ~5 mL, 20 mL of high-boiling petroleum ether was added, and a white solid precipitated. This solid was collected on a frit, washed with petroleum ether, and dried with air, yield (first crop) 0.5167 g (54%).

Anal. Calcd for $C_{32}H_{34}P_2Pt$: C, 56.04; H, 6.48; P, 9.03. Found: C, 55.95; H, 6.53; P, 9.25.

8. $Pt(CH_3)_2((CH_3)_2PCH_2CH_2PPh_2)$. To a Schlenk flask containing 0.4012 g of $Pt(CH_3)_2$(COD) were added 25 mL of benzene and 0.33 mL of pure ligand. The solution was stirred under reflux for 3 h. After the volume was reduced to ~5 mL and 20 mL of petroleum ether was added, the flask was cooled. The resultant white solid was collected on a frit, washed with petroleum ether, and dried in vacuo, yield 0.50 g (83%).

9. $Pt(CH_3)_2$(Cyttp). A solution of 0.209 g of $Pt(CH_3)_2$(COD) (0.63 mmol) and 3.0 mL of stock ligand solution (0.75 mmol of Cyttp) in 15 mL of benzene was heated under reflux for 30 min. The solution was evaporated to dryness to give a pale-yellow paste. The paste was extracted with three 60-mL portions of ether. A white solid separated after 10 mL of methanol was added to this extract and the ether was removed in vacuo.

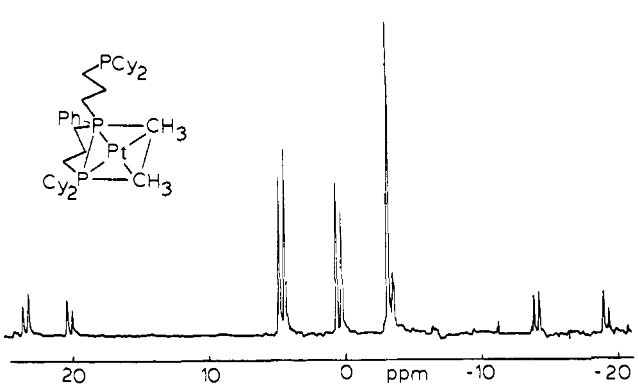


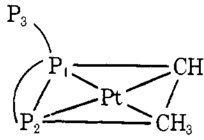
Figure 1. The ^{31}P{^{1}H} NMR spectrum of $Pt(CH_3)_2$(Cyttp) in toluene at 100 °C; Cyttp = $PhP[CH_2CH_2CH_2P(C_6H_{11})_2]_2$.

10. $Pt(CH_3)_2(PP_3)$. A solution of 0.153 g of $Pt(CH_3)_2$(COD) (0.46 mmol) and 0.313 g of PP_3 (0.47 mmol) in 10 mL of toluene was heated under reflux for 30 min. A portion of this solution was used for ^{31}P NMR spectroscopy.

Results and Discussion

Chelating polyphosphine ligands easily displace 1,5-cyclooctadiene from $Pt(CH_3)_2$(COD) to give the corresponding phosphine complexes. When the polyphosphine ligand used in the reaction is etp, ttp, eptp, dmetp, or PP_3, the ^{31}P{^{1}H} NMR spectrum of the resulting complex is temperature dependent. For complexes of the other ligands, the ^{31}P spectra are invariant over the temperature range studied.

The type of ^{31}P{^{1}H} NMR spectrum exhibited by the nonfluxional complexes is shown by the spectrum of $Pt(CH_3)_2$(Cyttp) (Figure 1). The spectrum consists of an AB pattern accompanied by satellites due to coupling to ^{195}Pt (33.7% natural abundance) and a single sharp peak. The AB portion of the spectrum can be assigned to two phosphorus atoms which are bonded to the metal, mutually coupled ($^2J_{AB}$ = 19.0 Hz), and coupled to platinum-195 ($^1J_{Pt\text{-}P_A}$ = 1798, $^1J_{Pt\text{-}P_B}$ = 1900 Hz). The remaining phosphorus resonance occurs at nearly the identical chemical shift as the dicyclohexylphosphino group in the free ligand, and it is not coupled to the platinum nucleus; thus, it is not attached to the metal. A structure such as **1** is indicated for $Pt(CH_3)_2$(Cyttp) in



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which one of the arms of the chelate is dangling free and the geometry about the metal is four coordinate and planar.

With the tripod ligand $CH_3C(CH_2PPh_2)_3$, a similar spectrum is obtained in which only two of the three phosphorus atoms are coupled to the platinum nucleus. In order to determine whether the four-coordinate geometry persisted in the solid state, an X-ray structure determination was performed by Dr. R. M. Kirchner.[8] The diagram of the inner coordination sphere of $Pt(CH_3)_2$(tripod) presented in Figure 2 shows that the ligand is coordinated to the platinum atom in a bidentate fashion. The remaining arm of the ligand extends away from the metal, similar to what was observed in $Pt(tripod)_2$.[9] The structure observed in solution by ^{31}P NMR is thus maintained in the solid state.

The low-temperature limiting ^{31}P NMR spectra of the

Table I. NMR Spectral Data on the $Pt(CH_3)_2$(polyphosphine) Complexes

	chemical shifts, ppm[a]			coordination chemical shifts, Δ[b]		coupling constants, Hz			
complex	P_1[c]	P_2[c]	P_3[c]	ΔP_1	ΔP_2	P_1-P_2	P_1-P_3	Pt-P_1	Pt-P_2
$Pt(CH_3)_2$(ttp)	−3.7	3.5	−18.9	24.5	21.6	18.0	0	1807	1850
$Pt(CH_3)_2$(Cyttp)	4.0	0.2	−7.9	32.1	8.0	19.0	0	1798	1900
$Pt(CH_3)_2$(etp)	49.4	48.5	−15.2	66.0	61.3	0.8	37.5	1838	1853
$Pt(CH_3)_2(PP_3)$	31.5	32.4	−35.0	49.0	45.5	~0	32.8	1773	1853
$Pt(CH_3)_2$(eptp)	44.0	47.4	−18.9	66.6	60.6	3.7	0	1824	1841
$Pt(CH_3)_2$(dppm)[d,e]	−40.4			−17.4				1434	
$Pt(CH_3)_2$(dppe)[d,f]	45.4			59.7				1794	
$Pt(CH_3)_2$(dppp)	3.3			20.6				1766	
$Pt(CH_3)_2$(dmdpe)[g]	47.2	26.8		63.8	78.3	3.6		1812	1738
$Pt(CH_3)_2$(P-P*)[h]	48.3	45.1		*i*	*i*	4.4		1854	1724
	49.8	43.0		*i*	*i*	7.3		1859	1704
$Pt(CH_3)_2$(tripod)[j]	4.5		−28.8	30.1			2.4	1816	
$Pt(CH_3)_2$(ppol)[k]	−2.6	3.4		24.5	21.6	18.0		1789	1827

[a] Chemical shifts are relative to 85% H_3PO_4; positive shifts are downfield. [b] $\Delta = \delta P_{coord} - \delta P_{free\ ligand}$. [c] The numbering scheme for the phosphorus atoms is as indicated in **1**. [d] Data from ref 15. [e] dppm = $Ph_2PCH_2PPh_2$. [f] dppe = $Ph_2PCH_2CH_2PPh_2$. [g] dmdpe = $Ph_2PCH_2CH_2P(CH_3)_2$; P_1 is the diphenylphosphino group. [h] P–P* = $Ph_2PCH_2CH_2P(Ph)neo\text{-}C_{10}H_{19}$; we have not determined which is P_1 or P_2. [i] An unambiguous determination of P_1 and P_2 is required to calculate ΔP_1 and ΔP_2. [j] In this case P_1 represents the two equivalent, coordinated phosphorus atoms. [k] ppol = $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH{=}CH_2$; P_2 is the diphenylphosphino group.

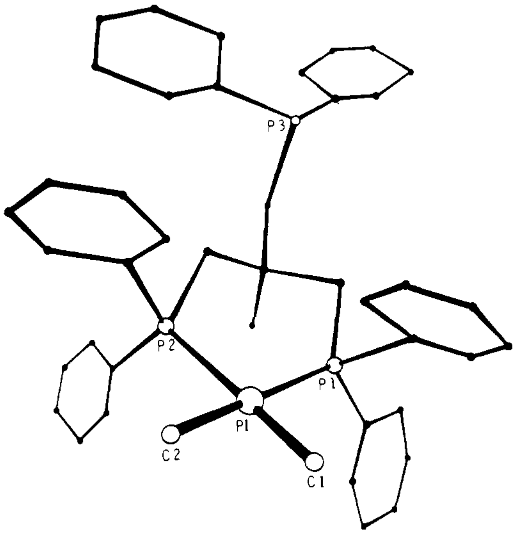


Figure 2. The inner coordination sphere of $Pt(CH_3)_2$(tripod): tripod = $CH_3C(CH_2PPh_2)_3$. Diagram from ref 8.

fluxional $Pt(CH_3)_2$(polyphosphine) complexes are all consistent with bidentate coordination of the potentially tri- and tetradentate ligands. In each case the central phosphorus atom and one of the chelate arms are attached to the metal while the remaining arm(s) dangle(s) freely in solution. The results of the ^{31}P NMR spectra are summarized in Table I.

An interesting feature of these compounds is the variability of the phosphorus-phosphorus coupling constants, which change with the chelate-chain length. When a ligand forms a six-member chelate ring, the P–P coupling increases relative to the value in the free ligand (for Cyttp, 19.0 vs. 0.0 Hz), whereas the phosphorus-phosphorus coupling observed for a chelating ligand that forms a five-member ring containing two phosphorus atoms decreases upon coordination to the metal as compared to the free ligands (for etp, 0.8 vs. 29.0 Hz).[5] Similar observations of this phenomenon have been made previously.[10,11] Grim et al.[12] have suggested that the phosphorus-phosphorus coupling within a chelate ring can be factored into "through-the-backbone" and "through-the-metal" contributions, i.e., $J_{P-P} = {}^BJ_{P-P} + {}^MJ_{P-P}$, where $^BJ_{P-P}$ is assumed to be equal to $^BJ_{P-P}$ in the free ligand. Thus, in five-member chelate rings the magnitudes of $^BJ_{P-P}$ and $^MJ_{P-P}$ are nearly equal but of opposite sign, which leads to the smaller observed J_{P-P} value. Within a six-member chelate ring, $^BJ_{P-P}$ is negligible;[12a] thus, the observed J_{P-P} can be attributed solely to coupling through the platinum, $^MJ_{P-P}$.

The possibility that exchange with the dangling phosphorus atom is in some manner affecting the J_{P-P} in these complexes can be ruled out by examination of the ^{31}P NMR spectra of $Pt(CH_3)_2$(diphos) complexes, where diphos is a bidentate ligand containing two different phosphorus groups. For the compound $Pt(CH_3)_2[Ph_2PCH_2CH_2P(CH_3)_2]$, the observed ^{31}P NMR spectrum consists of a well-defined AB pattern accompanied by satellites due to coupling to the platinum-195 nucleus. The phosphorus-phosphorus coupling in the five-member chelate ring is 3.6 Hz, which is reduced from 25.6 Hz in the free ligand. For the chiral diphosphine $Ph_2PCH_2CH_2P(Ph)neo\text{-}C_{10}H_{19}$, the P–P coupling constants for the two diastereomers decrease from 31.6 and 32.4 Hz in the free ligand to 4.4 and 7.3 Hz in their $Pt(CH_3)_2$ complexes. (No attempt was made to separate or identify the different diastereomers.) The fact that the J_{P-P} value within a five-member chelate ring in these $Pt(CH_3)_2$-polyphosphine compounds is reduced to near zero compared to the value in the free ligand appears to be a general phenomenon.

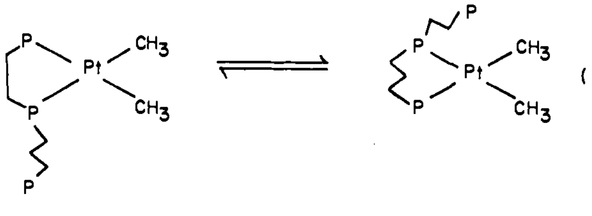
Coupling between a dangling phosphorus atom and the coordinated central phosphorus atom of a polydentate ligand ($J_{P_1-P_3}$ in **1**) must be transmitted via the carbon backbone since the phosphorus atoms are not *both* contained in the chelate ring. For the ttp and Cyttp ligands, which contain trimethylene backbones, P_1 and P_3 are not observed to couple in the $Pt(CH_3)_2$ complexes; similarly, $J_{P_1-P_3}$ = ~0 in the free ligands and their trioxide or trisulfide derivatives.[13] However, the ligands which have ethylene backbones show an increase in this P_1-P_3 coupling compared to the same coupling in the free ligands. For example, $^3J_{P_1-P_3}$ in etp is 29 Hz in the free ligand, but increases to 37.5 Hz in $Pt(CH_3)_2$(etp). Similar increases in $^3J_{P-P}$ through ethylene backbones were observed for complexes of the type $W(CO)_5(P\text{-}P')$ [P-P′ = $Ph_2PCH_2CH_2P(Ph)R$, R = CH_3, C_2H_5, $i\text{-}C_3H_7$], although the magnitude of the increases was smaller (1–7 Hz).[14] The dioxide derivatives of the P-P′ ligands exhibit J_{P-P} values of 49–51 Hz compared to 26–30 Hz in the free ligands. The increase in $J_{P_1-P_3}$ can be attributed to an increased partial positive charge on P_1 when complexed to a metal or oxygen as compared to the free ligand. The effect of the increased charge on phosphorus is apparently transmitted through the ethylene chain but not through the trimethylene chain.

The tripod ligand provides an interesting exception to the "insulating" effect of the trimethylene chain discussed above. Although the dangling phosphorus atom is separated from each coordinated phosphorus atom by four bonds (P-C-C-C-P) and would be expected to show a P-P coupling = ~0, the observed coupling constant, $J_{P_1-P_3}$, is 2.4 ± 0.5 Hz in $Pt(CH_3)_2$(tripod). (Of course, J_{P-P} is not observed in the free ligand where the phosphorus nuclei are magnetically equivalent.) In $Pt(CH_3)_2$(tripod), part of the backbone connecting the dangling and coordinated phosphorus atoms is also part of the six-member chelate ring (see Figure 2). Perhaps the more rigid nature of this arrangement enhances the coupling mechanism via the carbon chain compared to the flexible trimethylene backbones of ttp and Cyttp.

The downfield shift of a phosphorus resonance upon coordination to a metal is called the coordination chemical shift, Δ, and has been defined as $\Delta = \delta^{31}P_{\text{coordinated}} - \delta^{31}P_{\text{free ligand}}$.[10,12] The magnitude of Δ for chelated phosphines depends to a large extent on the size and number of the chelate rings containing the phosphorus atom; phosphorus atoms in five-member rings commonly exhibit a value for Δ that is much larger than in four- or six-member rings. Comparison of the chemical shifts of the bonded phosphorus atoms in $Pt(CH_3)_2$(etp) and $Pt(CH_3)_2$(ttp), which contain five- and six-member chelate rings, respectively, shows that the phosphorus atoms in the five-member chelate ring experience a much larger coordination shift (Δ = 66.0 and 61.3 ppm) than in the six-member chelate ring analogue (Δ = 24.5 and 21.6 ppm). These Δ values are in close agreement with those reported for the analogous four-, five-, and six-member chelate ring compounds $Pt(CH_3)_2[Ph_2P(CH_2)_nPPh_2]$ (n = 1, 2, 3) where Δ = −17.4, 59.7, and 20.5 ppm, respectively.[15] Ring strain has been invoked to explain the anomalous shifts of phosphorus resonances in the five-member ring chelates,[12] but, in view of the small *upfield* shift found in the four-member chelate rings where strain is expected to be greater, the ring-strain explanation is not completely satisfactory.[10b]

When the unsymmetrical triphosphine ligand eptp acts as a bidentate, it can form either a five- or a six-member chelate ring about the metal, with the remaining terminal phosphorus atom dangling. The ligand offers an ideal opportunity to study the relative preference for five- or six-member chelate rings containing phosphorus about Pt(II). The low-temperature limiting ^{31}P NMR spectrum of $Pt(CH_3)_2$(eptp) in toluene (Figure 3) shows an AB pattern accompanied by satellites due to platinum-phosphorus coupling and a single sharp resonance. The small P_1-P_2 coupling constant value of 3.7 Hz for the coordinated phosphorus nuclei and their large coordination chemical shifts (Δ = 66.6 and 60.6 ppm) indicate that they are contained in a five-member chelate ring. Also, no coupling to the dangling phosphorus atom is observed, consistent with assignment of the single resonance at −18.9 ppm to the uncoordinated $-CH_2CH_2CH_2PPh_2$ group. At this temperature, there is no evidence of an isomer containing a six-member chelate ring.

As the temperature of the solution is raised, *all* of the resonances start to broaden, indicating an exchange process which involves changes in the environments of all of the phosphorus atoms. An equilibrium between two isomers which would have different chelate chain lengths, such as those indicated in eq 1, would account for this behavior. Recooling the solution to −30 °C results in a ^{31}P NMR spectrum indistinguishable from the initial spectrum, indicating that the system is reversible and that the isomer containing a five-member chelate ring is *thermodynamically* favored.



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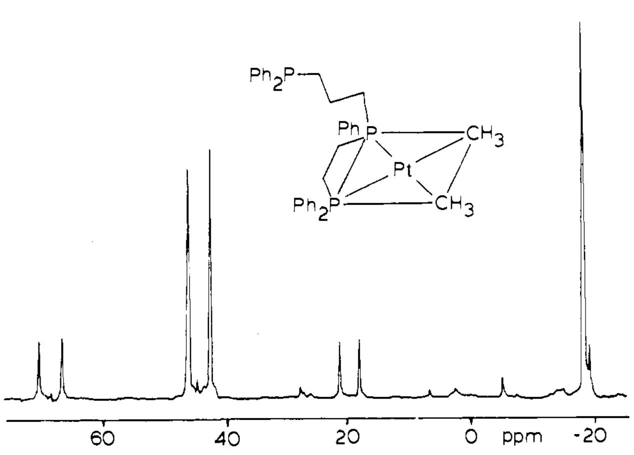


Figure 3. The $^{31}P\{^1H\}$ NMR spectrum of $Pt(CH_3)_2$(eptp) in toluene at −10 °C; eptp = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$.

Figure 4 shows the variable-temperature $^{31}P\{^1H\}$ NMR spectrum of $Pt(CH_3)_2$(ttp). The low-temperature limiting spectrum (0 °C) shows an AB pattern centered at −0.1 ppm with satellites due to ^{195}Pt coupling and a single sharp resonance at −18.9 ppm. The spectrum is consistent with two bonded phosphorus nuclei and one dangling, terminal phosphorus atom. As the temperature is increased, the peaks due to the two terminal phosphorus nuclei broaden and the coupling to platinum is lost. The central phosphorus atom retains its Pt-P coupling at the higher temperatures, but the P-P coupling decreases from 18 Hz at 0 °C to 9 Hz at 100 °C. The $^2J_{P-P}$ at the high temperature is the average of the two P-P coupling constants in the low-temperature spectrum, indicating that the terminal phosphino groups are undergoing rapid exchange on the NMR time scale.

The potentially tetradentate ligand $P(CH_2CH_2PPh_2)_3$, PP_3, also chelates in a bidentate manner to $Pt(CH_3)_2$ at low temperatures (−60 °C) as shown by ^{31}P NMR spectroscopy. A triplet centered at 31.5 ppm can be assigned to P_1 ($^3J_{P_1-P_3}$ = 32.8, $^1J_{P_1-Pt}$ = 1773 Hz), and a singlet at 32.4 ppm can be assigned to P_2 ($^1J_{P_2-Pt}$ = 1853 Hz), while the remaining doublet ($^3J_{P_1-P_3}$ = 32.8 Hz) at −35.0 ppm must be assigned to the two equivalent dangling phosphorus atoms owing to the absence of coupling to ^{195}Pt. The negligible coupling between the two coordinated phosphorus atoms ($J_{P_1-P_2} \simeq 0$ Hz) indicates that they are contained in a five-member chelate ring (vide supra). As the temperature is raised, the resonances due to P_2 and the two dangling phosphorus atoms broaden and collapse into the base line at 0 °C, while the P_1 resonance slowly changes from a triplet into a quartet with J_{P_1-P} = 22.0 Hz while maintaining coupling to ^{195}Pt. The phosphorus-phosphorus coupling constant at the high temperature (22.0 Hz at 30 °C) is thus an average of the three phosphorus-phosphorus couplings at low temperature (32.8, 32.8, and 0.0 Hz at −60 °C), indicating that all three terminal phosphorus atoms are undergoing rapid exchange.

Two schemes can be constructed to account for the exchange.[4] Scheme I involves association of the dangling phosphino group as a first step, followed by rearrangement of the five-coordinate intermediate to a structure in which the terminal phosphino groups are equivalent. Either terminal phosphorus is equally likely to dissociate from a short-lived, symmetric intermediate, making them equivalent on the NMR time scale. [Repetition of these steps will serve to equilibrate the remaining dangling phosphorus atom in $Pt(CH_3)_2(PP_3)$.]

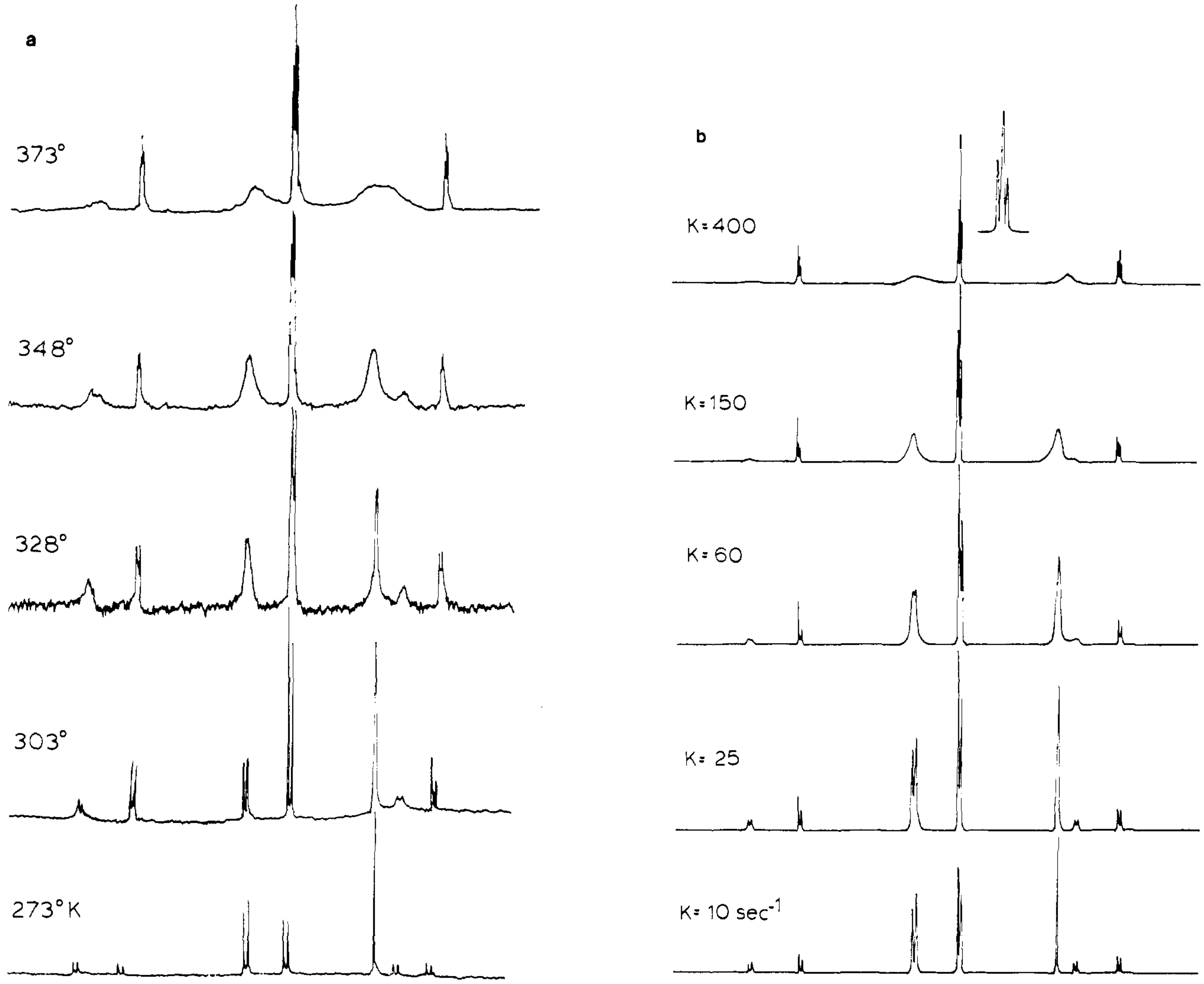
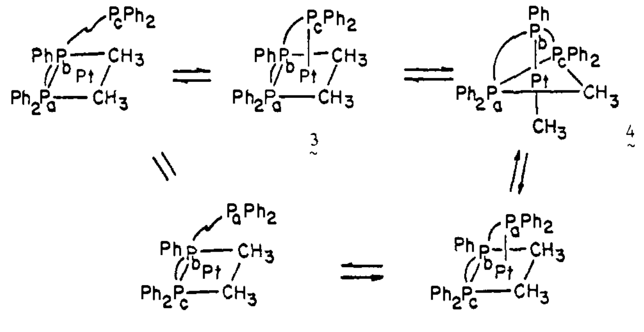


Figure 4. The variable-temperature $^{31}P\{^1H\}$ NMR spectrum of $Pt(CH_3)_2(ttp)$; ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$. (a) The experimental spectrum at the indicated temperatures in toluene. (b) The computer-simulated spectrum for the indicated exchange rates for P_2 and P_3.

Scheme I



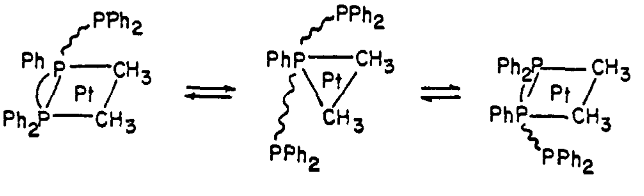
Five-coordinate Pt(II) intermediates have recently been observed in the reaction[16]

$$HPtP_3^+ + L \rightleftharpoons HPtP_3L^+$$

Scheme II requires Pt-P bond dissociation as the first step to form a three-coordinate Pt(II) species as the intermediate. Such a species may be possible, since three-coordinate platinum(II) intermediates have been suggested in the uncatalyzed cis $\rightleftharpoons$ trans isomerization of $PtRX(PEt_3)_3$ complexes,[17] in the thermal decomposition of $Pt(n\text{-}Bu)_2(PPh_3)_2$,[18] and in the mechanism of olefin insertion into a Pt-H bond.[19]

A detailed line-shape analysis of the NMR data was undertaken to provide more information about the exchange mechanism. A large negative value of the entropy of activation would suggest that the exchange involves association of the dangling phosphino group as the rate-limiting step, whereas a dissociation of the bonded terminal phosphino group should lead to a positive (or near zero) entropy of activation. The results of the line-shape analysis for $Pt(CH_3)_2(ttp)$ are presented in Figure 4 along with the experimental spectrum. An Arrhenius plot of the data yields $\Delta G^{\ddagger} = 7.1$ kcal/mol and $\Delta S^{\ddagger} = -30.4$ eu, indicating that the exchange of the terminal phosphino groups proceeds via an associative pathway. Similar analyses were performed for $Pt(CH_3)_2$ complexes of the ligands etp and PP_3; a summary of the data appears in Table II. In each case the large negative activation entropy suggests that an associative mechanism, involving a five-coordinate intermediate, is operative, i.e., Scheme I.

Scheme II



Additional support for the associative mechanism comes from a comparison of the $Pt(CH_3)_2$ complexes of two very similar ligands, ttp and Cyttp. The difference between the two

Table II. Thermodynamic Parameters for Phosphine Exchange in $Pt(CH_3)_2$(polyphosphine) complexes. Data Derived from Computer Line-Shape Analysis

complex	temp range studied, °C	$\Delta G^{\ddagger}$, kcal/mol[a]	$\Delta S^{\ddagger}$, eu[b]
$Pt(CH_3)_2$(ttp)	−80 to 100	7.1	−30.4
$Pt(CH_3)_2$(etp)	−100 to 55	7.1	−22.8
$Pt(CH_3)_2(PP_3)$	−90 to 55	10.3	−20.7

[a] The estimated standard deviation is 0.2 kcal/mol. [b] The estimated standard deviation is 2.5 eu.

ligands is the substitution on the terminal phosphorus atoms; ttp has phenyl substituents, whereas Cyttp has the more basic and more bulky cyclohexyl substituents. While $Pt(CH_3)_2$(ttp) undergoes exchange at room temperature, the ^{31}P NMR spectrum of $Pt(CH_3)_2$(Cyttp) shows no evidence of exchange up to 100 °C. The cyclohexyl groups increase the effective cone angle of each terminal phosphorus atom by 15° (142 vs. 127°), for a net increase of 30° over the ttp ligand.[13,20] Ligands of greater steric bulk generally dissociate more readily than smaller ligands; on this basis, Cyttp would be expected to exchange more rapidly via a dissociative mechanism such as that in Scheme II. On the other hand, the bulky dicyclohexylphosphino groups are required to be only 90° apart in the associative intermediate of Scheme I (i.e., **3**). The nonfluxionality of $Pt(CH_3)_2$(Cyttp) probably reflects an inability of the complex to form such a highly crowded intermediate.

The ^{31}P NMR spectrum of $Pt(CH_3)_2$(tripod) remains invariant up to 83 °C, the highest temperature studied. This behavior seems strange in view of the tendency of this ligand to chelate to various metals in a facial arrangement.[3,21] Examination of models shows that the formation of **3** does not require large deformations of the chelate backbone. However, formation of the trigonal-bipyramidal structure **4** requires the P-Pt-P angle to approach 120°. The largest P-M-P angle within the tripod ligand reported to date is only 97.0 (3)°.[9,21] Thus, we propose that the strain involved in the rearrangement **3** → **4** for $Pt(CH_3)_2$(tripod) prevents the exchange of dangling and coordinated phosphorus atoms. If a dissociative mechanism were operative, i.e., Scheme II, the tripod ligand would almost certainly show fluxional behavior in $Pt(CH_3)_2$(tripod).

We have already shown that a five-member chelate ring containing two phosphine groups is favored thermodynamically over a six-member ring in these platinum(II) complexes. However, comparison of the $Pt(CH_3)_2$ complexes of the ligands etp and ttp shows that it is $Pt(CH_3)_2$(etp) that more readily undergoes exchange. It seems likely that the increased rate of exchange is due to the favorable effect of formation of an additional five-member chelate ring, also lending support to the associative mechanism of Scheme I. The steric difference between the two ligands is slight (cone angles are 125° for $-CH_2CH_2PPh_2$ vs. 127° for $-CH_2CH_2CH_2PPh_2$)[20] and it would not be expected to produce a large difference in the rate of exchange.

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(5) (a) As a result of the complicated (and sometimes unusual) nature of these polyphosphine ligands, a glossary of formulas and corresponding abbreviations is given here for reference: ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$; Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$; PPH = $Ph_2PCH_2CH_2CH_2P(Ph)H$; dmetp = $PhP(CH_2CH_2PMe_2)_2$; eptp = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$; ppol = $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH{=}CH_2$; tripod = $CH_3C(CH_2PPh_2)_3$; PP_3 = $P(CH_2CH_2PPh_2)_3$; etp = $PhP(CH_2CH_2PPh_2)_2$; dppp = $Ph_2PCH_2CH_2CH_2PPh_2$; dppe = $Ph_2PCH_2CH_2PPh_2$. (b) R. Uriarte, T. J. Mazanec, K. D. Tau, and D. W. Meek, *Inorg. Chem.*, in press; (c) R. B. King and J. C. Cloyd, Jr., *J. Am. Chem. Soc.*, **97**, 53 (1975); (d) D. L. DuBois, W. H. Myers, and D. W. Meek, *J. Chem. Soc., Dalton Trans.*, 1011 (1975); (e) K. D. Tau, D. W. Meek, T. Sorrell, and J. A. Ibers, *Inorg. Chem.*, **17**, 3454 (1978).

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