

ΔG° values are 1.0 and 1.1 kcal mol⁻¹ for the chloro and bromo derivatives. The ΔH° and ΔS° values of 1.3 and 0.9 kcal mol⁻¹ and 7.2 and 6.7 eu, respectively, for chloro and bromo complexes have been calculated by the least-squares method. Since no sizable isotropic shifts have been observed for the iodo derivative, ΔG° will presumably be >2 kcal mol⁻¹.

These ΔG° values indicate that the planar form is favored in the order Cl < Br \ll I. This is consistent with the softness and π -bonding capacity of the halogens.²³ The ΔS° values, which again favor the planar form, are consistent with the entropy loss due to the attachment of a donor group which is already partially

(23) F. Basolo and R. G. Pearson in "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y. 1967, p 370; R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968).

hindered.²⁴ Finally, the values of ΔH° are so small also on account of the large increase in bond distances in passing from the planar to trigonal-bipyramidal or tetragonal-pyramidal structures.²⁵ These values account for the relatively narrow range for the existence of five-coordinate nickel complexes. In fact, by going from planar complexes to hexacoordinated adducts, five-coordinate intermediates generally are just barely detectable or not formed at all.^{24,26,27}

(24) L. Sacconi, G. Lombardo, and P. Paoletti, *J. Chem. Soc.*, 848 (1958); A. Chakravorty, J. P. Fennessey, and R. H. Holm, *Inorg. Chem.*, **4**, 26 (1965).

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(26) G. N. La Mar, *Inorg. Chim. Acta*, 183 (1969); A. Sgamellotti, C. Furlani, and F. Magrini, *J. Inorg. Nucl. Chem.*, **30**, 2655 (1968).

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Preparation and Proton Magnetic Resonance Spectra of Some Tetrakis(arylmethylphosphine)platinum(0) and -palladium(0) Compounds

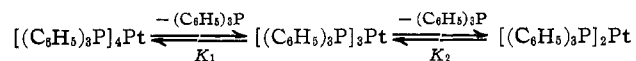
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Several new tertiary phosphine complexes of platinum(0), including tetrakis(methyldiphenylphosphine)platinum(0) (I), tetrakis(dimethyldiphenylphosphine)platinum(0) (II), and tetrakis(dimethylpentafluorophenylphosphine)platinum(0) (III), have been prepared. Low-temperature nmr spectroscopic studies of I show the loss of one phosphine molecule below -30° consistent with tris(methyldiphenylphosphine)platinum(0) being the most stable species at this temperature; above -30° rapid exchange of phosphine occurs. The spectra of II and III suggest no loss of phosphine; apparently the tetracoordinate species is the most stable. Tetrakis(methyldiphenylphosphine)palladium(0) did not show any evidence of dissociation. Reactions of I and III with perfluorobut-2-yne and of I with trimethyltin chloride are described.

Introduction

The chemistry of phosphine complexes of zerovalent platinum and palladium has attracted much attention since Malatesta's first report.¹ Most of the studies² have used triphenylphosphine as a ligand, although this is not appropriate for proton magnetic resonance spectroscopic studies. Molecular weight measurements³ of tetrakis(triphenylphosphine)platinum(0) have shown that the tetracoordinate species dissociates to tris- or bis-coordinate complexes by liberation of one or two molecules of triphenylphosphine, respectively



In particular, bis(triphenylphosphine)platinum(0) has been described as the reaction intermediate in a number of oxidative addition reactions. From a kinetic study of the reaction of tris(triphenylphosphine)platinum(0) with diphenylacetylene or triphenyltin chloride,^{3,4} the dissociation constant, K_2 , of tris(triphenylphosphine)platinum(0) into the corresponding bis-coordinate complex and triphenylphosphine was calculated as $(1.4-$

$1.8) \times 10^{-4} M$. This stability of the tris-coordinate complex which has a planar structure⁵ is thought to be due to strong platinum-phosphine bonding.

We have prepared tetrakis(methyldiphenylphosphine)platinum(0), tetrakis(dimethyldiphenylphosphine)platinum(0), tetrakis(dimethylpentafluorophenylphosphine)platinum(0), and tetrakis(methyldiphenylphosphine)palladium(0) and have studied their behavior with respect to phosphine exchange and dissociation by means of proton magnetic resonance spectroscopy at low temperatures. Some aspects of their chemical behavior are also described.

Experimental Section

Nmr measurements were made on a Varian HA-100 spectrometer with variable-temperature accessories. Samples were sealed under vacuum and measured in 8 wt % solutions in toluene-*d*₆ (Merck Sharp and Dohme Co. Ltd.). Analyses were carried out by Gygli Microanalysis Laboratory, Toronto. Tetrakis(methyldiphenylphosphine)palladium(0) was prepared by the method of Mukhedkar, *et al.*,⁶ from methyldiphenylphosphine and π -allyl- π -cyclopentadienylpalladium.

Preparation of Tetrakis(methyldiphenylphosphine)platinum(0) (I).—To *cis*-bis(methyldiphenylphosphine)dichloroplatinum (1.27 g), suspended in 30 ml of a 2:1 ethanol-water mixture, was added methyldiphenylphosphine (0.76 g) with stirring under nitrogen. The suspension turned to a clear bright yellow solu-

(1) (a) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958); (b) R. Ugo, F. Cariati, and G. LaMonica, *Inorg. Syn.*, **11**, 105 (1968).

(2) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968).

(3) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, **90**, 4491 (1968).

(4) J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, **7**, 2672 (1968).

(5) V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Commun.*, 507 (1966).

(6) A. J. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 3023 (1969).

tion. Sodium borohydride (0.2 g) in 10 ml of water was gradually added with rapid stirring and a yellow solid separated immediately. Stirring was continued for 30 min at room temperature. The yellow product was filtered under nitrogen and dried under vacuum. Recrystallization was performed by dissolving the solid in the minimum amount of dry benzene, adding *n*-pentane, and leaving in the refrigerator overnight. Tetrakis(methyldiphenylphosphine)platinum(0) (I) was obtained as a yellow powder in 80–85% yield; mp 152–154° (in an evacuated sealed tube). *Anal.* Calcd for $C_{52}H_{52}P_4Pt$: C, 62.71; H, 5.26. Calcd for $C_{35}H_{35}P_3Pt$: C, 58.86; H, 4.94. Found: C, 62.41; H, 5.08. Infrared spectrum (Nujol mull, cm^{-1}): 1585 (m), 1310 (w), 1288 (vw), 1094 (m), 1075 (sh), 1030 (w), 1005 (vw), 880 (vs), 750 (sh), 739 (sh), 720 (sh), 700 (vs), 510 (vs), 488 (w), 475 (sh), 440 (sh), 412 (s), 350 (w).

Rosevear and Stone⁷ prepared this compound by a direct method from potassium tetrachloroplatinate(II) and the phosphine in the presence of sodium borohydride; however, their method did not give high yields because approximately half of the platinum salt was reduced to platinum metal.

Preparation of Tetrakis(dimethylphenylphosphine)platinum(0) (II).—Dimethylphenylphosphine (1.5 g) was dissolved in 30 ml of deoxygenated ethanol and was added to potassium hydroxide (0.3 g) in 7 ml of a 6:1 ethanol–water mixture under nitrogen. An aqueous solution of potassium tetrachloroplatinate (1.4 g/10 ml) was added, with stirring, dropwise to give a yellow solution. Stirring was continued for 1 hr under nitrogen; then the solvent was evaporated under vacuum. Deoxygenated water (20 ml) was added to the residue and yellow-brown crystals were filtered under nitrogen. The product was washed with deoxygenated water (three 20-ml portions) and dried under vacuum. Tetrakis(dimethylphenylphosphine)platinum(0) (II) was isolated in 85% yield (1.6 g); mp 82–84° (in an evacuated sealed tube). *Anal.* Calcd for $C_{32}H_{40}P_4Pt$: C, 51.40; H, 5.93; P, 16.57; Pt, 26.09. Calcd for $C_{24}H_{32}P_3Pt$: C, 47.29; H, 5.44; P, 15.24; Pt, 32.01. Found: C, 51.26; H, 6.04; P, 16.46; Pt, 26.88. Infrared spectrum (Nujol mull, cm^{-1}): 1580 (vw) 1320 (vw), 1284 (vw), 1270 (w), 1152 (vs), 1091 (w), 1071 (vw), 1030 (vw), 934 (m), 929 (sh), 894 (vs), 839 (vw), 742 (s), 720 (sh), 700 (vs), 670 (s), 492 (s), 420 (s), 345 (vw), 326 (vw).

The preparation of II was attempted by reduction with sodium borohydride of *cis*-[(C_6H_5)(CH_3)₂P]₂PtCl₂ with (C_6H_5)(CH_3)₂P in the same manner as I. However, the product was a noncrystallizable brown oil, although its infrared spectrum was very similar to that reported above.

Preparation of Tetrakis(dimethylpentafluorophenylphosphine)platinum(0) (III).—*cis*-Bis(dimethylpentafluorophenylphosphine)dichloroplatinum, prepared from K_2PtCl_4 and (C_6F_5)(CH_3)₂P,⁸ was suspended in 30 ml of a 2:1 ethanol–water mixture and stirred under nitrogen. Addition of dimethylpentafluorophenylphosphine (0.61 g) produced a light yellow solution containing oily drops. Sodium borohydride (0.1 g) in 2 ml of water was gradually added. Reaction occurred immediately to give a yellow slurry. Stirring was continued for 2 hr under nitrogen and the mixture was then extracted with benzene (two 50-ml portions). The benzene layer was separated and dried over sodium sulfate. Benzene was evaporated under vacuum to give yellow crystals covered with oil. Extraction with 50 ml of petroleum ether (bp 30–60°) followed by evaporation of ether gave yellow crystals which were dried under vacuum; mp 111–112° (in evacuated tube) (0.35 g, 30% yield). *Anal.* Calcd for $C_{32}H_{24}F_{20}P_4Pt$: C, 34.79; H, 2.18; F, 34.30; P, 11.19. Found: C, 34.57; H, 2.05; F, 34.11; P, 11.00. Infrared spectrum (Nujol mull, cm^{-1}): 1632 (w), 1301 (sh), 1282 (w), 1260 (sh), 1089 (vs), 1020 (w), 981 (vs), 950 (m), 909 (s), 822 (w), 730 (sh), 713 (w), 690 (m), 630 (m), 505 (w), 410 (s).

Reaction of Tetrakis(methyldiphenylphosphine)platinum(0) with Perfluorobut-2-yne.—Tetrakis(methyldiphenylphosphine)platinum(0) (0.3755 g) dissolved in benzene (4 ml) was mixed with perfluorobut-2-yne (3 g) in a Pyrex tube cooled with liquid nitrogen. After the tube was sealed, the temperature was raised gradually. Reaction started at the melting point of benzene and a brown solid gradually precipitated. The mixture was kept for 3 days at room temperature and the brown powder was then separated by filtration and characterized as polyhexafluorobut-2-yne (0.1 g) by means of its infrared spectrum. The remaining liquid was concentrated under reduced pressure, giving a brown

oil, which was then purified by chromatography (Silica gel and benzene). All fractions were collected and solvent was evaporated *in vacuo*; *n*-pentane (5 ml) was then added to give colorless needles of bis(methyldiphenylphosphine)perfluorobut-2-yne-platinum, [(C_6H_5)₂(CH_3)P]₂Pt·C₄F₆ (0.2165 g, 76% yield), mp 131–132°. *Anal.* Calcd for $C_{20}H_{26}F_6P_2Pt$: C, 47.56; H, 3.46; F, 15.05. Found: C, 47.86; H, 3.50; F, 14.18. Infrared spectrum (Nujol mull, cm^{-1}): 1762 (s) ($\nu_{C=C}$), 1255 (s), 1220 (vs), 1121 (vs), 920 (w), 891 (s), 845 (w), 817 (m), 750 (s), 732 (m), 725 (m), 694 (s), 681 (sh), 650 (w), 510 (sh), 500 (s), 482 (m), 462 (w), 452 (w), 425 (w).

Reaction of Tetrakis(methyldiphenylphosphine)platinum(0) with Trimethyltin Chloride.—(a) To tetrakis(methyldiphenylphosphine)platinum(0) (0.3487 g) dissolved in benzene (4 ml), trimethyltin chloride (0.07 g) in benzene (1 ml) was added and the mixture was allowed to react in a sealed tube for 45 min at 80° to give a brown solution, which was kept at 5° for 10 days. Crystals, precipitated gradually, were filtered and washed with *n*-hexane and benzene to give a light brown powder (0.194 g), *trans*-[(C_6H_5)₂(CH_3)P]₂Pt[Sn(CH_3)₃]Cl·C₆H₆, mp 113–117° dec. *Anal.* Calcd for $C_{35}H_{44}ClP_2PtSn$: C, 48.21; H, 4.62. Found: C, 48.56; H, 4.53. Infrared spectrum (Nujol mull, cm^{-1}): 1235 (vw), 1180 (vw), 1160 (w), 1105 (s), 1075 (vw), 1030 (vw), 1000 (w), 890 (vs), 837 (m), 780 (m), 748 (vs), 735 (sh), 707 (sh), 695 (vs), 550 (m), 520 (sh), 505 (vs), 459 (m), 432 (w), 350 (w). Nmr spectrum (CH_2Cl_2): τ 9.42 (CH_3-Sn), τ 8.37 (CH_3-P), triplet with ¹⁹⁵Pt satellite which showed *trans* structure⁹ ($J_{H-P} = 3$ Hz, $J_{H-Pt} = 32$ Hz), τ 2.7 m (C_6H_5- and C_6H_6).

(b) A mixture of tetrakis(methyldiphenylphosphine)platinum(0) (0.642 g) and trimethyltin chloride (0.3605 g) in benzene (5 ml) was allowed to react at 81° for 55 min in a sealed tube. On cooling to room temperature, the mixture separated into two layers, which were then kept for 2 weeks at 5°. Block crystals precipitated slowly. The product was separated by filtration, washed carefully with three 2-ml portions of benzene, and dried under vacuum, giving *trans*-[(C_6H_5)₂(CH_3)P]₂Pt[Sn(CH_3)₃]Cl·2C₆H₆ (0.356 g) as white block crystals, mp 128–130°. *Anal.* Calcd for $C_{41}H_{47}ClP_2PtSn$: C, 51.78; H, 4.98; P, 6.51. Found: C, 51.99; H, 5.05; P, 6.69. Infrared and nmr spectra were similar to those of the monobenzene complex described in (a).

Reaction of Tetrakis(dimethylpentafluorophenylphosphine)platinum(0) with Perfluorobut-2-yne.—Tetrakis(dimethylpentafluorophenylphosphine)platinum(0)-hemibenzene (0.2243 g) was dissolved in benzene (5 ml) and mixed with perfluorobut-2-yne (1.8 g) in a Pyrex tube. After the tube was sealed, the mixture was warmed gradually to room temperature. The color of solution changed from yellow to light brown in a few minutes with the precipitation of polyperfluorobut-2-yne. The mixture was kept for 2 days at room temperature, and polyperfluorobut-2-yne (0.033 g) was then filtered off. The solution was evaporated under vacuum to give colorless crystals covered with red-brown oil. Purification was performed by means of chromatography (Florisil–benzene). Evaporation of benzene produced a light brown oil to which petroleum ether (bp 30–68°) was added,¹⁰ giving colorless crystals. The product was recrystallized from petroleum ether (bp 30–68°) and dried under vacuum; mp 100–101° (100 mg, 62% yield). *Anal.* Calcd for $C_{20}H_{12}F_{16}P_2Pt$: C, 29.78; H, 1.48. Found: C, 30.02; H, 1.72. Infrared spectrum (Nujol mull cm^{-1}): 1778 (s) ($\nu_{C=C}$), 1635 (m), 1263 (s), 1219 (s), 1118 (vs), 1090 (s), 981 (m), 960 (w), 920 (s), 889 (vw), 860 (vw), 840 (w), 809 (w), 830 (w), 702 (vw), 609 (vw), 655 (vw), 631 (vw), 510 (m), 440 (sh), 420 (m).

Results and Discussion

Tetrakis(methyldiphenylphosphine)platinum(0) (I) and tetrakis(dimethylpentafluorophenylphosphine)platinum(0) (III) were successfully prepared by reduction of the corresponding *cis*-bis(tertiary phosphine)dichloroplatinum(II) with sodium borohydride in the presence of excess phosphine. Tetrakis(dimethylphenylphosphine)platinum(0) (II) was prepared directly from potassium tetrachloroplatinate and dimethylphenylphosphine in the presence of potassium hydroxide. Complexes I–III were yellow powders which

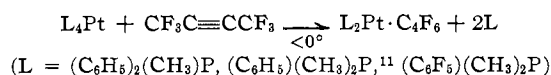
(7) D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc. A*, 164 (1968).

(8) M. Fild, O. Glemser, and I. Hollenberg, *Naturwissenschaften*, **52**, 590 (1965).

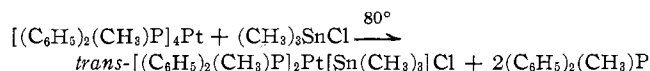
(9) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).

(10) M. Akhtar and H. C. Clark, *J. Organometal. Chem.*, **23**, 233 (1970), and references therein.

readily oxidized, particularly in solution, and were found to react oxidatively with perfluorobut-2-yne in benzene solution



Furthermore, tetrakis(methyldiphenylphosphine)platinum(0) (I) was found to give a tin-platinum compound, when treated with trimethyltin chloride; the structure of the product was assigned as *trans*-L₂Pt [Sn(CH₃)₃]₂·nC₆H₆ (n = 1-2; L = (C₆H₅)₂(CH₃)P) on the basis of the methyl proton nmr spectrum.⁹



These reactions are essentially identical with those of tetrakis(triphenylphosphine)platinum(0).^{2-4,10,11}

The proton magnetic resonance spectra of the methyl protons of I are shown in Table I and Figure 1. Above

TABLE I
NMR SPECTRA OF
TETRAKIS(METHYLDIPHENYLPHOSPHINE)PLATINUM(0)
AT VARIOUS TEMPERATURES^a

Temp, °C	Chem shift, ppm		J ¹⁹⁵ Pt-H, Hz	[Complexed L]/ [free L]
	(C ₆ H ₅) ₂ (CH ₃)PPt	(C ₆ H ₅) ₂ - (CH ₃)P		
35	1.68	b	b	c
10	1.75	b	b	c
0	1.75	1.34 ^d	e	c
-10	1.76	1.34 ^d	19.5	3.45
-30	1.75	1.30	20.0	3.16
-40	1.75	1.29	20.1	3.09
-60	1.78	1.30	20.0	3.02

^a Measured in toluene-*d*₈, chemical shifts were determined downfield from (CH₃)₄Si. ^b Cannot be observed because of rapid exchange. ^c All phosphines were complexed. ^d Observed as a broad singlet, indicative of exchange. ^e Separation of platinum satellite due to ¹⁹⁵Pt first observed at this temperature.

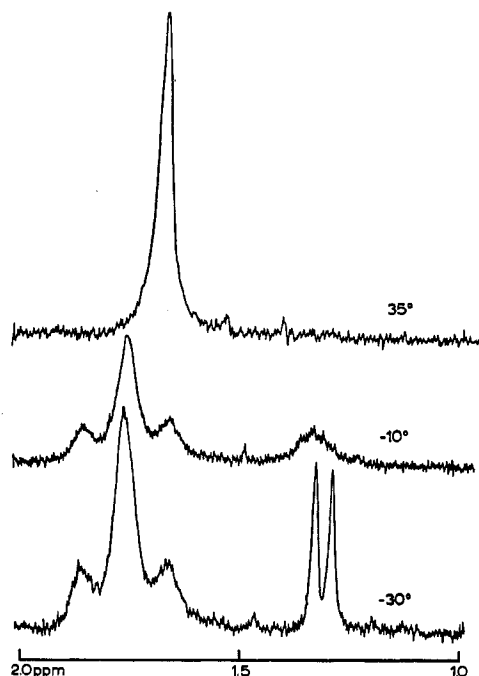
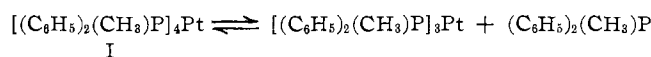


Figure 1.—Variable-temperature nmr spectra of [(C₆H₅)₂(CH₃)P]₄Pt in toluene-*d*₈.

(11) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

15°, the methyl proton signal showed neither satellite signals due to coupling to ¹⁹⁵Pt (33.8% natural abundance) nor splitting into a doublet or triplet by phosphorus, which is generally observed for a number of phosphine complexes of platinum.⁹ Furthermore, the signal for the ortho phenyl protons is observed as a broad singlet at δ 7.32 at room temperature. These findings suggest that, on the nmr time scale, a rapid exchange of methyldiphenylphosphine takes place above 15°. Lowering the temperature caused at first the appearance of typical platinum satellites with J¹⁹⁵Pt-H = 20 Hz. At -10°, a broad singlet (δ 1.34) due to free phosphine was observed. The absence of phosphorus-31 coupling (J_{H-P} = 4 Hz) and the slight downfield shift (Δδ = 0.04 ppm) of the free methyldiphenylphosphine signal suggest that exchange between free and complexed phosphine is still taking place rapidly on the nmr scale. Finally, below -30° the methyl proton signal of the free phosphine became a doublet (δ 1.30 and J_{H-P} = 4 Hz, values which were identical with those of pure methyldiphenylphosphine) and the exchange of the phosphine was actually frozen out. Moreover, the ratio of the signals from complexed and free methyldiphenylphosphine (δ 1.30) was 3.0. Accordingly, the predominant species, under these conditions, was tris(methyldiphenylphosphine)platinum(0), formed by the release of one molecule of methyldiphenylphosphine. The exchange process presumably involves the equilibrium between the tetra- and tricoordinate species which have tetrahedral and planar geometries, respectively



The methyl proton signal of tris(methyldiphenylphosphine)platinum(0) showed, even below -30°, a broad triplet (1:4:1), and no further splitting due to ³¹P could be resolved. The attempt to isolate tris(methyldiphenylphosphine)platinum(0) by refluxing the corresponding tetrakis complex in ethanol, which was reported to proceed successfully in the case of tris(triphenylphosphine)platinum(0),^{1b} was unsuccessful, and tetrakis(methyldiphenylphosphine)platinum(0) was recovered. Apparently the tetracoordinate complex in the case of methyldiphenylphosphine is more stable than that of triphenylphosphine in the solid state, so that the order of stability of L₄Pt is (C₆H₅)₃P < (C₆H₅)₂(CH₃)P.

The methyl proton signal of tetrakis(dimethylphenylphosphine)platinum(0) (II) also showed no platinum satellites, and the ortho phenyl proton signals (δ 7.1) were observed as broad multiplets. The dimethylphenylphosphine is therefore exchanging on the nmr time scale at 35°. The results of low temperature are summarized in Table II. Lowering the temperature to 25° caused splitting of the platinum satellites, which became more clear below 20°. Surprisingly, however, the signal for free dimethylphenylphosphine was never observed. The chemical shift for the methyl protons was shifted to higher field and coalesced at δ 1.41. These findings suggest that the tetracoordinate complex is more stable than the tris complex even in solution at -30°.

The methyl proton signal of tetrakis(dimethylpentafluorophenylphosphine)platinum(0) (III) was similar to that of II in that no sign of free dimethylpentafluoro-

phenylphosphine was observed although platinum satellites due to ^{195}Pt were observed below -10° . The results are shown in Table II and Figure 2; they sup-

TABLE II
NMR SPECTRA OF
TETRAKIS(DIMETHYLARYLPHOSPHINE)PLATINUM(0), L_4Pt ,
AT VARIOUS TEMPERATURES^a

Temp, °C	Chem shift, of $\text{CH}_3\text{-P}$, ppm	$J^{195}\text{Pt-H}$, Hz	$J_{\text{H-F}}$, Hz	Temp, °C	Chem shift, of $\text{CH}_3\text{-P}$, ppm	$J^{195}\text{Pt-H}$, Hz	$J_{\text{H-F}}$, Hz
$\text{L} = \text{C}_6\text{H}_5(\text{CH}_3)_2\text{P}$							
35	1.47	<i>b</i>	...	10	1.44	20.0	...
30	1.45	<i>b</i>	...	-10	1.42	20.3	...
25	1.44	<i>c</i>	...	-30	1.41	20.3	...
20	1.44	20.0	...				
$\text{L} = \text{C}_6\text{F}_5(\text{CH}_3)_2\text{P}$							
35	1.50	<i>b</i>	1.9	-30	1.43	19.0	<i>d</i>
10	1.49	<i>c</i>	1.5	-50	1.43	18.9	<i>d</i>
-10	1.45	17.8	<i>d</i>				

^a Measured in toluene- d_6 , chemical shifts were determined downfield from $(\text{CH}_3)_4\text{Si}$. ^b Cannot be observed because of rapid exchange. ^c Separation due to ^{195}Pt first observed. ^d Methyl proton signal showed no splitting due to ortho fluorine.

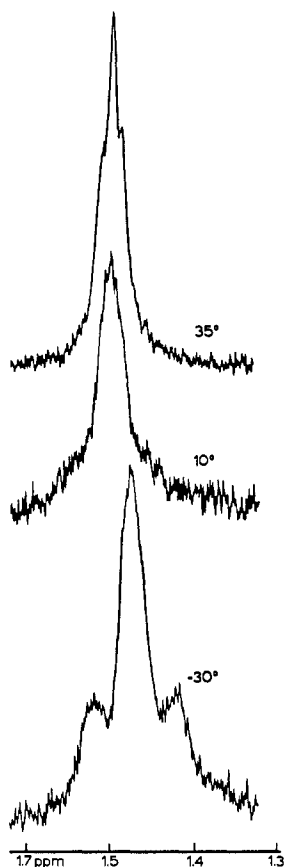


Figure 2.—Variable-temperature nmr spectra of $[\text{C}_6\text{F}_5(\text{CH}_3)_2\text{P}]_4\text{Pt}$ in toluene- d_6 .

port the view that the same sort of exchange reaction occurs in the case of II and III as in I above. The behavior of III is different from I or II in other respects. Firstly, the chemical shift for the methyl protons of complexed dimethylpentafluorophenylphosphines (δ 1.43) was higher than that for the phosphine itself (δ 1.56). Such an abnormal upfield shift of the methyl signal for II contrasts with the shift downfield pro-

duced by complex formation of other methylphosphines such as methylphenyl- or dimethylphenylphosphine. The introduction of the strongly electronegative C_6F_5 group on phosphorus apparently increases the delocalization of the d^{10} electrons on platinum to ligands. Recently, tetrakis-phosphine complexes with extremely electronegative phosphine ligands such as CF_2PF_2 and $(\text{CF}_3)_2\text{PF}$ have been prepared.¹² It was observed that these complexes did not react even with hydrogen chloride or methyl chloride, because the platinum electron density was sufficiently delocalized. In our case, complex III was found to exchange phosphine reversibly above -10° , although the most stable form was still the tetracoordinate complex. Perfluorobut-2-yne was found to react with III in the same manner as I or II, this also being consistent with reversible exchange of phosphine from III.

Second, the methyl proton signal of III showed coupling with the ortho fluorine atoms ($J_{\text{H-F}} = 1.9$ Hz) when exchange of phosphine occurs over the nmr time scale.

Although tetracoordinate species are more stable than tricoordinate complexes for both II and III, the temperatures at which platinum satellites due to ^{195}Pt start to be observed differ (at 25° for II and at 10° for III). This may indicate that the tetracoordinate complex of II is slightly more stable than that of III. It is concluded that the stability of tetrakis(tertiary phosphine)platinum(0), L_4Pt , in toluene solution decreases in the order $\text{L} = (\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{P} > (\text{C}_6\text{F}_5)(\text{CH}_3)_2\text{P} \gg (\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{P} > (\text{C}_6\text{H}_5)_3\text{P}$. This order of stability can probably best be explained in terms of the steric hindrance of the phosphines.¹³

Variable-temperature nmr spectra were similarly measured for tetrakis(methyldiphenylphosphine)palladium(0). The chemical shift of the methyl protons remained constant at δ 1.61 between -60 and $+35^\circ$ and no free methyldiphenylphosphine (δ 1.30; $J_{\text{H-P}} = 4$ Hz) was detected. The only change in the spectrum was the disappearance of phosphorus-proton coupling ($J_{\text{H-P}} = 1.4$ Hz at 10 – 35°) below 0° . Hence tetrakis(methyldiphenylphosphine)palladium(0) is thought to exist just as the tetracoordinate complex or as a complex which participates in an extremely rapid exchange which cannot be frozen even at -60° . The ortho phenyl proton signals showed hyperfine structures between δ 7.23 and 7.60 at room temperature, which were quite different from that of the corresponding platinum analog (I) for which only a broad singlet (δ 7.32) due to rapid exchange of phosphine was observed. Unfortunately, palladium does not have sufficient amounts of natural abundance isotopes with spin $1/2$ and less information is therefore available than for the platinum complex I. However, the possibility that a tris-coordinate complex is the most stable form is rejected, because no free methyldiphenylphosphine and no observable chemical shift change were observed.

It is interesting that for the tris(methyldiphenylphosphine)platinum(0) complex, for tetrakis(methyldiphenylphosphine)palladium(0), and for tetrakis(dimethylpentafluorophenylphosphine)platinum(0), the methyl proton- ^{31}P couplings were not resolved at low temperatures. Indeed, for the palladium compound, this coupling is observed at room temperature but lost

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as the temperature is lowered. This is most probably associated with the magnitudes of the P-P couplings in these complexes. The phenomenon of "virtual coupling" of phosphorus nuclei in square-planar trans complexes is well established,⁹ but less is known of the magnitude of P-P couplings in tetrahedral or trigonal metal complexes. In the absence of any theoretical treatment of this problem, it may be that the P-P couplings for such geometries are still large, although certainly less than for square-planar complexes where the P-M-P angle is 180°. If the P-P coupling is suf-

ficiently large¹⁴ in tris(methyldiphenylphosphine)platinum, this alone might explain the nonobservance of proton-³¹P coupling at low temperature. For the palladium compound, the loss of proton-³¹P coupling at low temperatures may similarly be due to a reasonably large P-P coupling, further complicated in this case by a reduction in the rate of phosphine exchange¹⁵ as the temperature is lowered.

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Cationic Acetylenic Platinum(II) Compounds and Their Derivatives. I. Alkoxy-carbene Complexes

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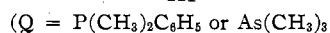
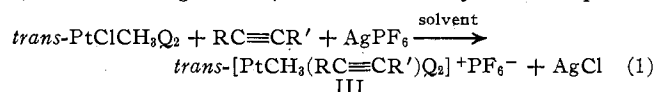
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Methoxy- and ethoxycarbene cationic platinum(II) complexes $trans-[PtCH_3(ROCCH_2R')Q_2]^+PF_6^-$ (I) have been prepared by the reaction of $trans-PtClCH_3Q_2$ (II), where Q = dimethylphenylphosphine or trimethylarsine, with $RC\equiv CH$ and silver hexafluorophosphate in the presence of methanol and ethanol, respectively. The nature of the platinum-carbene carbon bond is discussed in view of nmr and vibrational spectra of I. The formation of I is believed to be due to nucleophilic attack of the initially formed acetylenic complex $trans-PtCH_3(RC\equiv CH)Q_2^+$ (III).

Introduction

Several types of cationic platinum(II) complexes have been described recently.¹⁻⁵ A study of the hydride resonances of complexes $trans-PtHL\{P(C_2H_5)_3\}_2^+$ revealed² a correlation between $J(Pt-H)$ and the *trans* influence of the neutral ligand L. A similar trend of $J(Pt-C-H)$ for the platinum-methyl resonances was observed⁵ in a series $trans-PtCH_3L\{P(CH_3)_2C_6H_5\}_2^+$. The formation of the latter utilized the lability of the chloride ligand⁶ in II which allowed chloride to be displaced by a strongly σ -donating ligand in the presence of a polar solvent such as methanol or acetone. Addition of a large anion such as PF_6^- or $B(C_6H_5)_4^-$ caused precipitation of the cationic species so formed. In the case where L was a weak σ donor, complete abstraction of the chloride could be achieved by the addition of the silver salt of the large anion.

Although cationic acetylenic complexes of platinum(II) are not unknown⁷ $\{[PtX(en)(ac)]_n^+$ where $n = 1$ or 2, X = Cl, Br, or I, ac = $(CH_3)_2OHCC\equiv CC(C_6H_5)_2OH$, and en = ethylenediamine}, a study of the reaction shown in eq 1 was undertaken with the intention of isolating III. The cationic acetylenic complexes

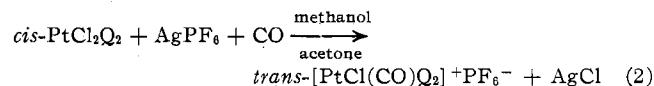


III are ideally suited for examination by nmr spectroscopy since the presence of the *trans* methyl group allows a comparison of $J(Pt-C-H)$ for various R and R' with the values found⁵ for the series $trans-PtCH_3LQ_2^+$.

We now consider reaction 1 for $RC\equiv CH$ where R = an alkyl or aryl group and the solvent is an alcohol.

Results and Discussion

Reaction Conditions. Isolation of I.—The reaction of II with $RC\equiv CR'$ and silver hexafluorophosphate in a solvent is complex. A variety of products may be obtained depending upon the nature of R and R', Q, and the solvent. Reactions involving II and some perfluoroacetylenes have already been described.⁸ The reaction of II with silver hexafluorophosphate in methanol leads to the isolation of $trans-[PtCH_3Q_2]^+PF_6^-$, while in the absence of chloride ions silver hexafluorophosphate reacts with many acetylenes yielding brown precipitates. Thus cationic complexes $trans-[PtCl(L)Q_2]^+PF_6^-$, where L = $RC\equiv CR'$ or RCH_2COCH_3 , cannot be prepared by a reaction analogous to eq 2 involving an acetylene instead of carbon monoxide.



Therefore our reactions were carried out by making the addition of the acetylene $RC\equiv CH$ (1 molar ratio) to a methanolic solution of II under nitrogen, followed by the immediate addition of silver hexafluorophosphate (<1 molar ratio) in methanol. A thick precipitate of silver chloride formed instantaneously. The solution was stirred for 5–10 min to allow completion of the reaction and coagulation of the precipitate. The silver

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