

yield of *cis*-propenyl methyl ether and a trace amount of *trans*-propenyl methyl ether.

Registry No. IVa, 36608-66-9; IVb, 36608-67-0; IVc, 36608-68-1; Va, 37036-01-4; Vb, 37383-70-3; VIa, 36484-04-5; VIe, 36484-05-6; Vif, 37036-84-3; VIg, 37036-86-5; VIII, 37036-85-4; X, 37036-81-0; [Pt(2-methylallyl)-(PPh₂Me)₂]NO₃, 37036-83-2; *trans*-[PtH(PPh₂Me)₂(CH₃)₂-CO]BF₄, 37036-02-5; *trans*-[PtH(ClO₄)(PPh₃)₂], 32109-29-8; *trans*-[PtH(NO₃)(PPh₂Me)₂], 36464-75-2; *trans*-[PtH-

(PPh₃)₂(CH₃)₂CO]BF₄, 37036-05-8; allyl acetate, 591-87-7; 2-methylallyl acetate, 820-71-3; *N*-allylacetamide, 692-33-1; 2-methylallyl alcohol, 513-42-8; 2-methylallyl ether, 628-56-8; allyl alcohol, 107-18-6; allyl ether, 557-40-4; *trans*-crotyl alcohol, 504-61-0; *trans*-crotyl ether, 7023-45-2; allyl phenyl ether, 1746-13-0; allyl methyl ether, 627-40-7.

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Cationic Organometallic Complexes with Unsaturated Systems. V. Trimethylplatinum(IV) Complexes and Reductive Elimination Reactions

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A series of platinum(IV) cations of the type *fac*-[Pt(CH₃)₃Q₂L]⁺, where Q = P(CH₃)₂C₆H₅, NC₅H₅, As(CH₃)₃, or *p*-CNC₆H₄CH₃ and L is a variety of neutral ligands including a carbene, have been prepared, although in some cases the preparative reactions lead to elimination of ethane and formation of *trans*-[Pt(CH₃)Q₂L]⁺. Factors governing the stability of the platinum(IV) cations are discussed. The oxidative addition of CD₃I to *cis*-Pt(CH₃)₂Q₂, where Q = P(CH₃)₂C₆H₅ and As(CH₃)₃, gives exclusively the *trans* adduct. Pyrolysis and reductive elimination reactions of the CD₃Pt^{IV} compounds show that the CD₃-Pt bond is more resistant to cleavage than the CH₃-Pt bond. Isomerization occurs during the preparation of [Pt(CH₃)₂CD₃Q₂L]⁺ supporting a dissociative mechanism for octahedral substitution. The Raman spectra of the trimethylplatinum(IV) complexes have been examined and $\nu(\text{Pt}-\text{CH}_3)$ is shown to vary with the *trans* influence of L.

Introduction

Many neutral, anionic, and cationic platinum(IV) complexes¹ have been prepared from the first organoplatinum(IV) compound, trimethylplatinum(IV) iodide.² In contrast to the methyl-platinum(II) bond, which is readily cleaved,³ the methyl-platinum(IV) bond in the complexes [Pt(CH₃)₃X]₄ is quite stable and may be cleaved only under vigorous conditions.⁴ However, complexes of the type Pt(CH₃)₃L₂I, where L = phosphine or arsine, have been found to pyrolyze⁵ smoothly at temperatures >100° with loss of ethane.

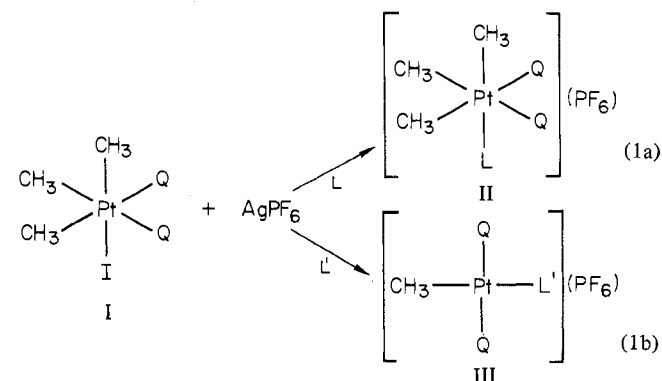
In the previous paper of this series⁶ we discussed the preparation and reactivity of a wide variety of cationic dimethylplatinum(IV) complexes of the type [Pt(CH₃)₂Q₂L₂]²⁺ or [Pt(CH₃)₂Q₂LI]⁺, where Q is dimethylphenylphosphine and L is a neutral or anionic ligand. These complexes were found to be quite stable; reduction occurred only when the L was a large and bulky ligand such as triphenylphosphine, -arsine, and -stibine or when the platinum-ligand bond required much Pt d π → L π^* back-bonding for its stability (*i.e.*, CO, olefins, and acetylenes).

In this paper we discuss the preparation and stability, with respect to reductive elimination, of the complexes *fac*-[Pt(CH₃)₃Q₂L]⁺, where Q = P(CH₃)₂(C₆H₅), CNC₆H₄CH₃, As(CH₃)₃, or NC₅H₅ and L is a variety of neutral ligands. The

oxidative addition of CD₃I to *cis*-Pt(CH₃)₂Q₂ (Q = P(CH₃)₂C₆H₅ and As(CH₃)₃) and the stereochemistry of the CD₃Pt^{IV} compounds are discussed.

Results and Discussion

(i) **Preparation.** The iodide in *fac*-Pt(CH₃)₃Q₂I (I), where Q is dimethylphenylphosphine, may be removed easily in solution, as silver iodide, by the addition of AgX where X is a noncoordinating anion, *e.g.*, AgPF₆. In the presence of a neutral ligand L, a variety of platinum(IV) cations, II, are obtained although, for L', reductive elimination occurs to give the corresponding methylplatinum(II) cations, III, as shown in (1), where L = NC₅H₅, P(CH₃)₂C₆H₅, P(OCH₃)₃, CNC₆H₄-



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CH₃, CNC₆H₄OCH₃, CNCH₃, CNC₂H₅, or Sb(CH₃)₃ and L' = CH₃COCH₃, CH₃OH, NCCH=CH₂, NCC₆H₄OCH₃, Sb⁻(C₆H₅)₃, P(C₆H₅)₃, As(C₆H₅)₃, CO, or HC≡CCH₂CH₂OH.

Thus, addition of silver hexafluorophosphate to a solution of I in acetone or methanol readily causes discoloration with

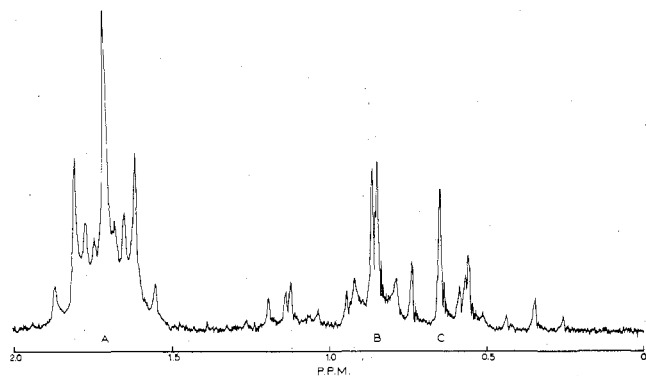


Figure 1. ^1H nmr spectrum of $[\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{OCH}_3)[\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)]_2(\text{PF}_6)$ recorded on a Varian HA-100 spectrometer. Key: A, phosphine methyl region appearing as a 1:2:1 triplet due to overlapping 1:1 doublets; B, $A_3A'_3XX'$ pattern for the two cis methyl groups trans to phosphine; C, triplet for the methyl group trans to isocyanide. Resonances A, B, and C also show platinum satellites of $1/4$ intensity.

effervescence. However, if the solution contains a ligand L, the iodide is removed cleanly. In the absence of a silver salt no displacement of iodide by L occurs; a solution of *p*-tolyl isocyanide and I in dichloromethane showed no evidence of reaction after 1 week.

The trimethylplatinum(IV) cations II give stable salts (usually as the hexafluorophosphate) which melt sharply with effervescence.

(ii) **Nmr Spectra.** The phosphine methyl resonances of the Pt(IV) complexes, II, appear as doublets due to coupling with the ^{31}P nucleus and are flanked by ^{195}Pt satellites ($I = 1/2$, 34% natural abundance) of $1/4$ intensity. Such a pattern is associated with cis phosphines⁷ where $^2J(^{31}\text{P}-^{31}\text{P})$ is small. For many of the complexes two overlapping doublets are observed (Figure 1) due to nonequivalent phosphine methyls $\text{P}(\text{CH}_3)(\text{CH}_3)(\text{C}_6\text{H}_5)$, the nonequivalence being attributable to restricted rotation of the phosphine about the Pt←P bond.

Two distinct resonances may be assigned to the platinum methyl groups. The resonance for the two methyl groups trans to phosphine appears as a complicated pattern (Figure 1B) quite typical of the A part of the $A_3A'_3XX'$ spectrum.⁸ A recent spectral analysis⁹ for *cis*- $\text{Pt}(\text{CH}_3)_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2$ showed that $\text{trans } ^3J(^{31}\text{P}-^1\text{H})$ is only slightly greater than $\text{cis } ^3J(^{31}\text{P}-^1\text{H})$ and that the coupling constants have opposite signs.

The platinum methyl group trans to L appears as a triplet (Figure 1C) due to equal coupling with the two cis phosphines and is accompanied by ^{195}Pt satellites. Each platinum methyl resonance in the spectrum of $[\text{Pt}(\text{CH}_3)_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2[\text{P}(\text{OCH}_3)_3]]^+$ is further split into a doublet by the ^{31}P nucleus of trimethyl phosphite.

The nmr spectrum of the complex $[\text{Pt}(\text{CH}_3)_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2(\text{PF}_6)]$ shows a very complicated resonance in the platinum methyl region (Figure 2) due to an $A_3A'_3A''_3XX'X''$ spin system. The proton spectrum is not easily analyzed; however the ^{13}C nmr spectrum with protons decoupled is quite suitable for spectral analysis and those results will be reported shortly.¹⁰

The coupling constant $^1J(^{195}\text{Pt}-^{13}\text{C})$ and hence $^2J(^{195}\text{Pt}-\text{C}-^1\text{H})$ for the platinum methyl groups may be used^{6,11,12} as a

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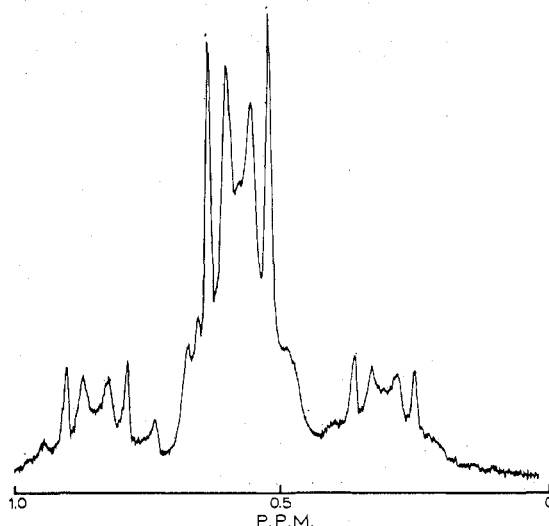


Figure 2. Platinum methyl region in the nmr spectrum of *fac*- $[\text{Pt}(\text{CH}_3)_3[\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)]_3(\text{PF}_6)$.

measure of the nmr trans influence of a ligand trans to the platinum methyl group. The latter coupling constant gives a relative measure of the amount of Pt(6s) orbital contribution¹³ to the Pt-L bond and consequently is a measure of the bond strength.¹⁴ In previous papers,^{6,13} we have shown that triphenylstibine bonds to platinum(II) by a synergic mechanism similar to carbon monoxide and acetylenes. However, for platinum(IV) the reduced size of the d orbitals results in less effective overlap with the ligand π^* orbitals and consequently a much weaker $\text{Pt}^{\text{IV}}-\text{CO}$ or $\text{Pt}^{\text{IV}}-\text{Sb}(\text{C}_6\text{H}_5)_3$ bond would be expected. We have been unable to prepare these Pt(IV) cations. The apparent nonexistence of the triphenylstibine cation may well be attributed to steric factors since the triphenylphosphine- and -arsineplatinum(IV) cations also reduce readily to Pt(II) complexes. We have been able to prepare a Pt(IV) cation with $\text{Sb}(\text{CH}_3)_3$ and from the nmr coupling constant $^2J(\text{Pt}-\text{C}-\text{H})$ it is clear that the Pt-Sb(CH_3)₃ bond is strong and comparable to a platinum(IV)-isocyanide bond.

(iii) **Stability and Reductive Elimination.** We have recently established an nmr trans-influence series⁶ for Pt(IV) (Table I) and from eq 1 it may be seen that stable platinum(IV) cations (II, Q = $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$) are obtained only for ligands L with a trans influence equal to or greater than that of pyridine. The pyridine complex, although quite stable in the solid state, slowly decomposes in solution to give *trans*- $[\text{Pt}(\text{CH}_3)_2\text{Q}_2(\text{NC}_5\text{H}_5)](\text{PF}_6)$ while the complex $[\text{Pt}(\text{CH}_3)_3\text{Q}_3](\text{PF}_6)$ is stable for weeks in acetone solution. It is tempting to postulate that reduction will occur if any one of the three ligands has a relatively low trans influence; yet the complexes $[\text{Pt}(\text{CH}_3)_3(\text{OH}_2)]^+$ ¹⁵ and $[\text{Pt}(\text{CH}_3)_3(\text{NC}_5\text{H}_5)]^+$ ¹⁶ are quite stable and exhibit no tendency toward reductive decomposition. Since the reason for this resistance to reduction is not obvious, we have investigated the importance of the nature of the ligand Q in determining the stability of the cations.

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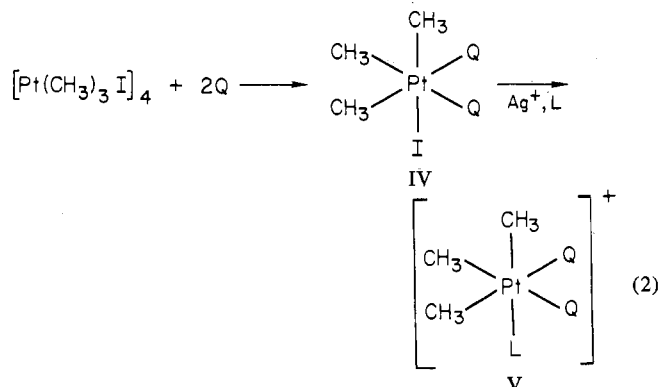
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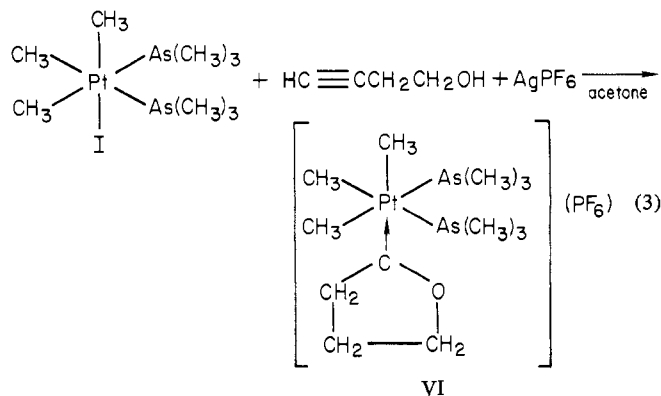
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Trimethylplatinum(IV) iodide reacts smoothly with 2 molar equiv of isocyanide, pyridine, or trimethylarsine as shown in (2), where Q = As(CH₃)₃, CNC₆H₄CH₃, or NC₅H₅.



For each of the compounds of IV, we attempted to prepare trimethylplatinum(IV) cations, V, with ligands L of high and low trans influence. With Q = CNC₆H₄CH₃ the cations, V, were stable for L having a *high* trans influence while reduction occurred for L = nitrile, a ligand of *low* trans influence. For the arsine and pyridine compounds all platinum(IV) cations were stable and exhibited no tendency to reduce. The stability of the arsine cation of V (Q = As(CH₃)₃ and L = NC-C₆F₅) prompted us to prepare a platinum(IV)-carbene cation, VI, by the use of the acetylene 1-butyn-4-ol (eq 3). Such a



reaction apparently involves a weakly coordinated π -bonded acetylene as the reaction intermediate.¹⁷

The nmr spectrum of the carbene cation VI supports the cyclic structure of the carbene, *viz.*, the α -alkoxy (OCH₂-) and α -carbene (CCH₂-) protons appear as triplets at δ 3.35 and 1.56, respectively, and the β -alkoxy protons (OCCH₂) appear as a quintet at δ 2.10.

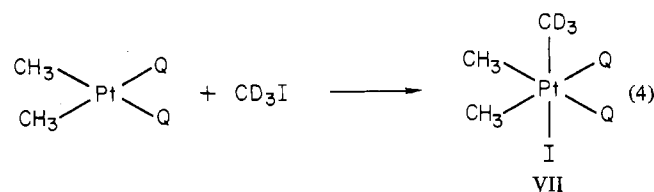
The series of cations V, L = P(CH₃)₂(C₆H₅) and Q = CNC₆H₄CH₃, As(CH₃)₃, or NC₅H₅, also provide interesting nmr spectroscopic data. For the isocyanide and pyridine cations *cis* ³J(¹H-C-Pt-³¹P) is slightly greater than *trans* ³J(¹H-C-Pt-³¹P) (Table II) while for the arsine cation there is no apparent coupling *cis* ³J(¹H-C-Pt-³¹P) yet there is a substantial *trans* coupling, ³J(¹H-C-Pt-³¹P) = 8.2 Hz. The nmr spectrum of [Pt(CH₃)₃[As(CH₃)₃]₂[P(CH₃)₂(C₆H₅)]]⁺ also shows two resonances which may be attributed to the arsine methyls. The separation between these two peaks is field dependent (17.5 Hz at 100 MHz and 10.5 Hz at 60 MHz) and is thus not due to coupling with phosphorus but to asymmetry of the arsines. This must arise from restricted rotation of the phosphine and

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a preferred orientation of the phenyl group near one of the arsines.

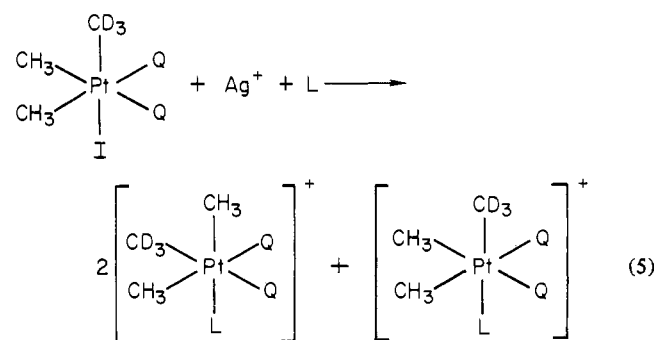
The results of the above reductive eliminations may be summarized as follows. The platinum(IV) cations reduce by elimination of ethane (identified by ir and mass spectrometry) *only* if there is a *disparity* in the platinum methyl groups and *two* of three ligands L are of high trans influence, *e.g.*, [Pt(CH₃)₃[P(CH₃)₂C₆H₅]₂(NC₅H₅)]⁺ is reduced (in solution) while [Pt(CH₃)₃[P(CH₃)₂C₆H₅](NC₅H₅)₂]⁺ is quite stable. The two equivalent platinum methyls must be labilized by the ligand Q of high trans influence and it is these two methyl groups that might be expected to couple in the formation of ethane. We have attempted to prove this by isotopically labeling one of the platinum methyl groups. Unfortunately the results are inconclusive, in that while they indicate a preference for Pt-CH₃ rather than Pt-CD₃ cleavage, they cannot readily be related to the relative trans influence of the ligands Q and L.

Thus, iodomethane-*d*₃ oxidizes *cis*-Pt(CH₃)₂Q₂, where Q = P(CH₃)₂C₆H₅ or As(CH₃)₃, giving exclusively *trans* addition (eq 4).



A similar stereospecific oxidative addition is also observed in the addition of bromomethane to *trans*-Ir(CO)Cl[P-(C₆H₅)₃]₂ and is believed to entail an S_N2 type attack involving an unsymmetrical transition state.¹⁸

The nmr spectra of the stable Pt(IV) cations [Pt(CH₃)₂(CD₃)Q₂L]⁺ (where Q = P(CH₃)₂C₆H₅ with L = CNC₆H₄CH₃, NC₅H₅, or P(OCH₃)₃; and Q = As(CH₃)₃ with L = NCC₆F₅) show the presence in solution of two geometrical isomers in the ratio of 2:1 as shown in (5).



Many octahedral substitution reactions proceed by a dissociative pathway¹⁹⁻²² involving a five-coordinate intermediate and this is probably the reason for the scrambling of the methyl groups during the preparation of the Pt(IV) cations (eq 6). Once formed, there is no evidence of intramolecular

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Table I. Nmr Trans-Influence Series for the Complexes
 $[\text{Pt}(\text{CH}_3)_2\text{Q}_2\text{L}_2]^{2+}$ and $[\text{Pt}(\text{CH}_3)_2\text{Q}_2\text{L}]^+$, $\text{Q} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$

L	$^2J(\text{Pt-H})$, Hz	L	$^2J(\text{Pt-H})$, Hz
$\text{NCC}_6\text{H}_4\text{OCH}_3$	70.2	CNC_2H_5	58.2
1,10-Phenanthroline	65.5	$\text{CNC}_6\text{H}_4\text{CH}_3$	58.0
$\text{NH}=\text{C}(\text{OCH}_3)_2\text{C}_6\text{F}_5$	65.2	$\text{CNC}_6\text{H}_4\text{OCH}_3$	57.0
NC_2H_5	60.8	$\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$	50.5
$\text{P}(\text{OCH}_3)_3$	60.0	$:\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}$	47.0
CNCH_3	58.2		

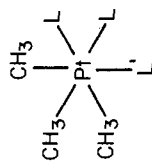
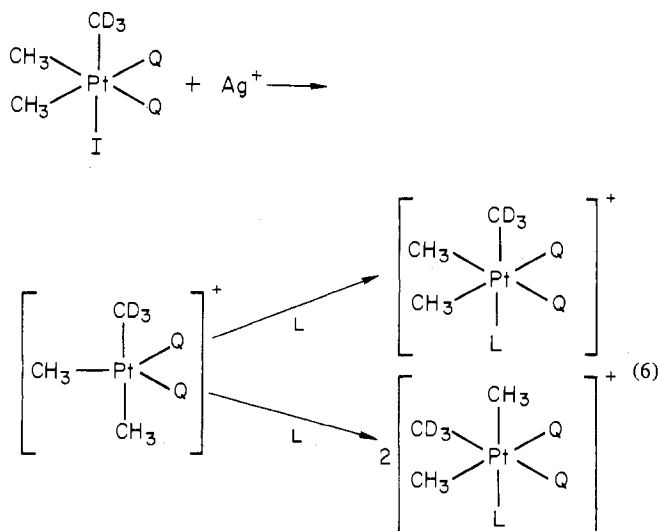


Table II. ^1H Nmr Data^c for Trimethylplatinum(IV) Complexes

Complex ^a	Phosphine methyls			Methyls trans to L			Methyls trans to L'			Other resonances
	$\delta(\text{CH}_3)$	$J(\text{P-H})$	$J(\text{Pt-H})$	$\delta(\text{CH}_3)$	$J(\text{P-H})$	$J(\text{Pt-H})$	$\delta(\text{CH}_3)$	$J(\text{P-H})$	$J(\text{Pt-H})$	
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{NC}_2\text{H}_5)](\text{PF}_6)$	1.54	8.5	14.0	0.94	<i>b</i>	53.0	0.65	8.5	68.0	
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_2\text{H}_5)](\text{PF}_6)$	1.49	9.0	14.0	0.71	<i>b</i>	53.6	0.52	9.2	61.2	$\delta(\text{CH}_3)$ 1.35, $\delta(\text{CH}_2)$ 3.72
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_6\text{H}_4\text{OCH}_3)](\text{PF}_6)$	1.60	10.0	16.0	0.84	<i>b</i>	54.4	0.68	9.1	61.2	$\delta(\text{OCH}_3)$ 3.90
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_6\text{H}_5)](\text{PF}_6)$	1.63	9.9	16.0	0.85	<i>b</i>	55.6	0.64	8.9	60.8	$\delta(\text{CH}_3)$ 2.73
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_6\text{H}_4\text{CH}_3)](\text{PF}_6)$	1.65	9.4	15.6	0.87	<i>b</i>	55.0	0.66	9.0	60.0	$\delta(\text{CH}_3)$ 2.49
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{Sb}(\text{CH}_3)_3)](\text{PF}_6)$	1.54	9.4	15.6	0.75	<i>b</i>	54.4	1.02	8.2	60.0	$\delta(\text{CH}_3)$ 0.98
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{NCC}_6\text{F}_5)](\text{PF}_6)$	1.77	9.6	15.6	0.58	<i>b</i>	54.5	0.58	54.5	54.5	$\delta(\text{OCH}_3)$ 3.78, $J(\text{P-H}) = 10.8$
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{P}(\text{OCH}_3)_3)](\text{PF}_6)$	1.68	9.4	15.6	0.69	8.4 d	54.2	0.42	9.5	53.8	$\delta(\text{As-CH}_3)$ 1.50, $J(\text{Pt-H}) = 7.0$
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{P}(\text{C}_6\text{H}_5)_2)](\text{PF}_6)$	1.87	8.8	15.2	0.78	<i>b</i>	60.2	0.79	8.2 d	60.8	$\delta(\text{As-CH}_3)$ 1.49, 1.32, $J(\text{Pt-H}) = 6.8$
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{P}(\text{C}_6\text{H}_5)_2)](\text{PF}_6)$	1.81	8.7	14.6	0.83	<i>b</i>	61.8	0.20		49.0	$\delta(\text{OCH}_2)$ 3.35 t, $\delta(\text{OCCH}_2)$ 2.10 q, $\delta(\text{CCH}_3)$ 1.56 t
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{P}(\text{C}_6\text{H}_5)_2)](\text{PF}_6)$	1.98	8.5	14.0	1.02	8.0 d	14.6			77.4	$\delta(\text{As-CH}_3)$ 1.38, $J(\text{Pt-H}) = 7.0$
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{P}(\text{C}_6\text{H}_5)_2)](\text{PF}_6)$	1.69	9.4	15.0	1.16		63.6	1.16		63.6	$\delta(\text{CH}_3)$ 2.48
$[\text{Pt}(\text{CH}_3)_3\text{A}_2(\text{NCC}_6\text{F}_5)](\text{PF}_6)$	1.88	8.0 d	14.6	0.79	8.8 d	62.8	1.02		55.6	$\delta(\text{CH}_3)$ 2.40
$[\text{Pt}(\text{CH}_3)_3\text{A}_2(\text{P}(\text{C}_6\text{H}_5)_2)](\text{PF}_6)$	1.98	10.0 d	16.2	1.02	8.4 d	67.2	0.95		54.5	$\delta(\text{As-CH}_3)$ 1.44, $J(\text{Pt-H}) = 7.0$
$[\text{Pt}(\text{CH}_3)_3\text{A}_2(\text{P}(\text{C}_6\text{H}_5)_2)](\text{PF}_6)$	1.63	8.6 d	13.6	1.23		63.6	0.91		72.8	$\delta(\text{CH}_3)$ 2.44
$[\text{Pt}(\text{CH}_3)_3\text{A}_2(\text{P}(\text{C}_6\text{H}_5)_2)](\text{PF}_6)$	1.63	8.6 d	13.6	1.34		64.0	1.44		73.3	

^a Q = $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$, A = $\text{As}(\text{CH}_3)_2$. ^b Coupling cannot be directly obtained. ^c Key: d, doublet; t, triplet; q, quintet.



exchange of the methyl groups in solution.

Since the isotopic scrambling occurs much quicker than the rate of reduction, it is *not* possible to observe reductive elimination from a stereospecifically labeled Pt(IV) cation. After reduction the ratio of Pt^{II}CH₃ to Pt^{II}CD₃ should be 2:1 regardless of the trans influences of the other three ligands. However, the addition of AgPF₆ and *p*-NCC₆H₄OCH₃ to an acetone solution of Pt(CH₃)₂(CD₃)[P(CH₃)₂C₆H₅]₂I gave a mixture of Pt(II) cations containing 55% PtCH₃ and 45% PtCD₃. At this time we are unable to explain why the Pt-CD₃ bond is more resistant to cleavage than the Pt-CH₃ bond.

Pyrolysis of Pt(CH₃)₃[P(CH₃)₂C₆H₅]₂I at 165° proceeds very smoothly with concomitant loss of ethane.⁵ A similar pyrolysis of VII gave a mixture of 54% *trans*-Pt(CH₃)[P(CH₃)₂C₆H₅]₂I and CD₃-CH₃ and 46% *trans*-Pt(CD₃)[P(CH₃)₂C₆H₅]₂I and CH₃-CH₃. The relative proportions of each Pt(II) complex were determined by integration of the platinum methyl-*h*₃ resonance against the phosphine methyl resonances and are believed to be accurate to about 5%. The percentages of Pt^{II}CH₃ and Pt^{II}CD₃ are very close to the values obtained by reduction of the platinum(IV) cations suggesting that the mechanisms of reductive elimination are similar. Since the solids melt before effervescence occurs, we believe that isomerization probably takes place before reductive elimination and again the greater amount of Pt^{II}CD₃ (46%) supports the observation that the Pt-CD₃ bond is more resistant to cleavage than the Pt-CH₃ bond.

(iv) **Infrared and Raman Spectroscopic Data.** The platinum-methyl stretching vibration appears as a very strong, sharp band in the Raman spectrum and is very weak in the infrared spectrum. Clegg and Hall²³ have examined the vibrational spectra for the trimethyl cations [Pt(CH₃)₃L₃]⁺, where L = OH₂ or NH₃. For such cations of C_{3v} symmetry, two platinum-methyl vibrations are expected, an A₁ and E mode. Since most of the present cations contain large and bulky phosphines, the symmetry of the molecule is reduced to C_s, thus splitting the degenerate E modes in C_{3v} symmetry into an A' and A'' mode. Thus three Raman-active bands are expected in the 500–600-cm⁻¹ region ascribable to the Pt-CH₃ stretching vibrations, and in most cases (Table III) three are observed.

The Raman spectra of Pt(CH₃)₃[P(CH₃)₂C₆H₅]₂I and Pt(CH₃)₂(CD₃)[P(CH₃)₂C₆H₅]₂I show three very strong bands (Figure 3) at 544, 531, and 521 cm⁻¹, respectively. On deu-

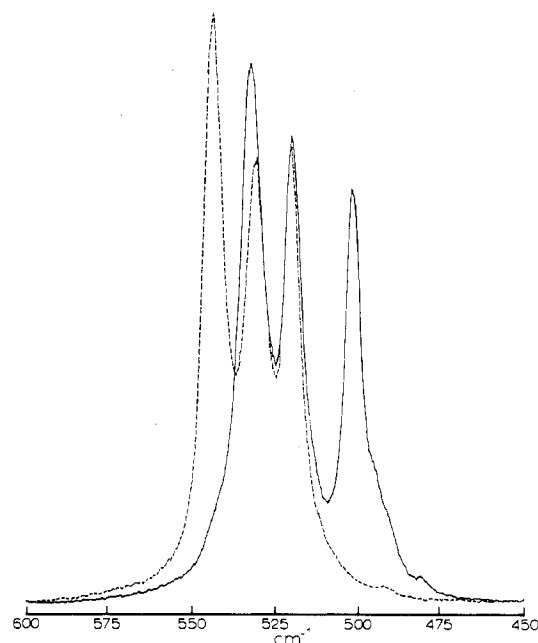


Figure 3. Raman spectra of Pt(CH₃)₃[P(CH₃)₂(C₆H₅)₂]₂I (---) and Pt(CH₃)₂(CD₃)[P(CH₃)₂(C₆H₅)₂]₂I (—) showing the effect of deuteration on the platinum methyl vibrations. Spectrometer settings: spectral bandwidth 2.0 cm⁻¹; sensitivity 20,000 counts/sec; scan speed 0.5 cm⁻¹/sec.

teration the highest frequency band is lowered in frequency by a factor of (15/18)^{1/2} indicating that the platinum-methyl group *trans* to I moves as a unit²⁴ and is not coupled to any extent to other vibrations. Therefore, within a series of trimethylplatinum(IV) cations the highest frequency platinum-methyl stretching vibration should decrease as the *trans* influence of the ligand L increases. Although the series is limited, the trend does hold as shown in Table IV for the cations [Pt(CH₃)₃[P(CH₃)₂C₆H₅]₂L]⁺. However, the occurrence of such a trend may be largely fortuitous since no account of possible coupling effects has been taken; when all three ligands are similar in *trans* influence (e.g., with Sb(CH₃)₃), the extent of coupling will differ from other cases where the ligands differ in *trans* influence.

We have recently shown^{6,25} that for isocyanide complexes an increase in the N≡C stretching frequency on coordination, Δν(N≡C) [ν(N≡C)(complex) - ν(N≡C)(free ligand)], varies with the electron density on platinum. The large values of Δν(N≡C) for the trimethylplatinum(IV) cations (Table I) are consistent with a considerable positive charge on the platinum.

Experimental Section

Experimental conditions have been previously described.⁶ Microanalyses were performed by Chemalytics Inc., Tempe, Ariz.

Raman spectra were recorded on crystalline samples in capillary tubes using a Cary 82 laser Raman spectrometer. The 5145-Å line of the argon laser was used as the exciting line and values are accurate to ±2 cm⁻¹. Only representative preparations will be described. Raman and nmr spectra were recorded at 31°.

Iodotrimethylbis(dimethylphenylphosphine)platinum(IV) was prepared by the method of Ruddick and Shaw²⁶ with minor modifications. *trans*-Pt(CH₃)₂Q₂ (Q = dimethylphenylphosphine) was dissolved in methyl iodide. The solution became quite warm and white crystals of Pt(CH₃)₃Q₂I precipitated from solution. The flask was allowed to cool, the ether was decanted, and the crystals were washed with diethyl ether. The yield was quantitative and the product was obtained pure (ir, nmr).

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Table III. Analytical, Physical, and Raman Data for Trimethylplatinum(IV) Complexes

Complex ^a	Carbon, %		Hydrogen, %		Mp, b °C	Recrystn solvents ^c	Raman data, cm ⁻¹		
	Calcd	Found	Calcd	Found			$\nu(\text{Pt-CH}_3)$	$\nu(\text{N}\equiv\text{C})$	$\nu(\text{N}\equiv\text{C})$
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{NC}_5\text{H}_9)](\text{PF}_6)$	38.92	39.01	4.90	4.69	99-100	A	569, 561, 524		
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2](\text{PF}_6)$	40.56	40.50	5.29	5.27	155-156	A	530, 525, 510		
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2[\text{P}(\text{OCH}_2)_3]][\text{B}(\text{C}_6\text{H}_5)_4]$	57.56	57.55	6.30	6.09	141-142	B	515		
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2[\text{Sb}(\text{CH}_3)_3]](\text{PF}_6)$	31.89	32.05	4.87	4.65	135-136	C	539, 523, 516		$\nu(\text{Sb-CH}_3)$ 531
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CN-C}_6\text{H}_4\text{CH}_3)](\text{PF}_6)$	41.65	41.68	4.92	4.79	180-182	A	541, 521, 511	2210	85
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_6\text{H}_4\text{OCH}_3)](\text{PF}_6)$	40.81	40.78	4.82	4.81	171-172	A	544, 520, 512	2210	85
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNCH}_3)][\text{B}(\text{C}_6\text{H}_5)_4]$	61.65	61.89	6.25	6.48	144-146	D	548, 522, 514	2243	73
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_2\text{H}_5)](\text{PF}_6)$	36.88	36.90	5.06	4.73	103-108	A	546	2260	109
$[\text{Pt}(\text{CH}_3)_3\text{A}_2(\text{NC-C}_6\text{H}_5)](\text{PF}_6)$	23.49	23.40	3.33	2.95	125-128	A	540, 531	2280	
$[\text{Pt}(\text{CH}_3)_3\text{A}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]](\text{PF}_6)$	26.75	26.42	5.02	4.72	145-150	A	e		
$[\text{Pt}(\text{CH}_3)_3\text{A}_2(\text{CCH}_2\text{CH}_2\text{O})](\text{PF}_6)$					90-92	A	e		
$[\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)](\text{PF}_6)$	44.02	43.92	4.11	3.90	170-173	A	555	2236, 2211	111, 86
$[\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)](\text{PF}_6)$	42.80	42.65	4.52	4.39	161-162	A	551, 542, 520	2220, 2207	95, 82
$[\text{Pt}(\text{CH}_3)_3(\text{NC}_5\text{H}_9)_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]](\text{PF}_6)$	37.01	36.90	4.44	4.34	108-110	E	580, 572, 538		
$[\text{Pt}(\text{CH}_3)_3\text{A}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]](\text{PF}_6)$	17.81	17.67	4.45	4.31	177-180	E	546, 532		$\nu(\text{As-CH}_3)$ 591
$[\text{Pt}(\text{CH}_3)_3\text{Q}_2\text{I}^d$						E	544, 531, 521		
$[\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{A}_2\text{I}^d$						E	547, 533, 507		$\nu(\text{As-CH}_3)$ 591
$[\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{Q}_2\text{I}^d$						E	532, 520, 502		
$[\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)_2\text{I}^d$	37.94	37.95	3.85	3.60	143-146	E	563, 536	2208, 2198	83, 73

^a Q = $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$, A = $\text{As}(\text{CH}_3)_3$; all complexes are colorless. ^b Melting points are uncorrected. ^c A = CH_2Cl_2 - $(\text{C}_2\text{H}_5)_2\text{O}$, B = CH_3OH , C = CHCl_3 - $(\text{C}_2\text{H}_5)_2\text{O}$, D = CH_3OH - $(\text{C}_2\text{H}_5)_2\text{O}$, E = CH_2Cl_2 - $n\text{-C}_3\text{H}_7$. ^d Not analyzed. ^e Decomposed in the laser beam. ^f Not analyzed due to instability.

Table IV. A Comparison of $^2J(\text{Pt-H})$ and $\nu(\text{Pt-CH}_3)$ for the Cations $[\text{Pt}(\text{CH}_3)_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{L}]^+$

L	$^2J(^{195}\text{Pt-H})$, Hz	$\nu(\text{Pt-CH}_3)$, cm ⁻¹
NC_5H_9	68.0	569
CNC_2H_5	61.2	546
$\text{CNC}_6\text{H}_4\text{CH}_3$	60.0	541
$\text{Sb}(\text{CH}_3)_3$	60.0	539
$\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$	54.5	530

$\text{Pt}(\text{CH}_3)_3\text{I}$ was prepared by the method of Clegg and Hall.²⁷

(a) Preparation of $\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{Q}_2\text{I}$. As above only the CD_3I was distilled, under vacuum into a flask containing $\text{Pt}(\text{CH}_3)_2\text{Q}_2$ at liquid nitrogen temperature. The flask was allowed to warm up to room temperature at which time the $\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{Q}_2\text{I}$ crystallized from solution. The excess CD_3I was distilled into an ampoule and sealed under vacuum.

(b) Preparation of $\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)_2\text{I}$. To a benzene solution of $\text{Pt}(\text{CH}_3)_3\text{I}$ (0.173 g, 0.470 mmol) was added *p*- $\text{CNC}_6\text{H}_4\text{CH}_3$ (0.110 g, 0.940 mmol). The solution was stirred for 10 min and the volume of the benzene was reduced. The addition of diethyl ether yielded pale yellow crystals of $\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)_2\text{I}$ (0.260 g, 0.434 mmol).

(c) Preparation of $\text{Pt}(\text{CH}_3)_3[\text{As}(\text{CH}_3)_3]_2\text{I}$. *cis*- $\text{Pt}(\text{CH}_3)_2[\text{As}(\text{CH}_3)_3]_2$ was dissolved in methyl iodide and the solution became bright yellow. After 10 min the methyl iodide was removed on a rotary evaporator to give a yellow solid which was recrystallized from dichloromethane and pentane. The yield was quantitative.

(d) Preparation of $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{NC}_5\text{H}_9)](\text{PF}_6)$. Pyridine (0.027 g, 0.342 mmol) was added to a solution of $\text{Pt}(\text{CH}_3)_3\text{Q}_2\text{I}$ (0.215 g, 0.336 mmol) in 10 ml of acetone. AgPF_6 (0.084 g, 0.336 mmol) in 2 ml of acetone was added dropwise and AgI precipitated immediately from solution. The solution was stirred for 10 min and the AgI was removed by centrifuge to give a clear colorless solution. The acetone was removed on a rotary evaporator and the oil was taken up in 2 ml of dichloromethane. Ether was added and the flask was placed in a refrigerator at 0° for 30 min to give white needles of $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{NC}_5\text{H}_9)](\text{PF}_6)$ (0.231 g, 0.312 mmol). The crystals were filtered, washed with ether, and recrystallized from dichloromethane and ether.

(e) Preparation of $[\text{Pt}(\text{CH}_3)_3\text{Q}_3](\text{PF}_6)$. To a solution of $\text{Pt}(\text{CH}_3)_3\text{Q}_2\text{I}$ (0.495 g, 0.780 mmol) in 30 ml of acetone was added $\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$ (0.106 g, 0.790 mmol). AgPF_6 (0.195 g, 0.780 mmol) was added; silver iodide precipitated immediately from solution and was removed by centrifuge to give a dark solution. The acetone was removed on a rotary evaporator and the black oil was taken up in dichloromethane and passed through a 3-in. Florisil column, eluting with dichloromethane, to remove colloidal silver and platinum. A clear colorless solution was obtained. The volume of solvent was reduced, diethyl ether was added until the solution became cloudy, and the flask was cooled at 0° for 2 hr to give white needles. The crystals (0.460 g, 0.575 mmol) were filtered, washed with ether, and recrystallized from dichloromethane and diethyl ether.

(f) Preparation of $[\text{Pt}(\text{CH}_3)_3\text{Q}_2[\text{P}(\text{OCH}_2)_3]][\text{B}(\text{C}_6\text{H}_5)_4]$. The complex was prepared by method e except that a crystalline product could not be obtained with PF_6 as the anion. Consequently the oil was dissolved in a small volume of methanol and an equivalent amount of $\text{NaB}(\text{C}_6\text{H}_5)_4$ was added. The white precipitate which formed immediately was filtered and washed with methanol then recrystallized from methanol to give white needles; 75% yield.

(g) Attempted Preparation of $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CO})](\text{PF}_6)$. Carbon monoxide was bubbled through a solution of $\text{Pt}(\text{CH}_3)_3\text{Q}_2\text{I}$ (0.130 g, 0.202 mmol) and an equivalent amount of AgPF_6 was added. The precipitated silver iodide was removed by centrifuge to give a clear, colorless solution. The acetone was removed and the oil was dissolved in methanol. $\text{NaB}(\text{C}_6\text{H}_5)_4$ (0.070 g, 0.202 mmol) was added and a white precipitate of $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CO})][\text{B}(\text{C}_6\text{H}_5)_4]$ (0.082 g, 0.10 mmol) formed. The solid was filtered and recrystallized from dichloromethane-ether.

(h) Preparation of $[\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)_3](\text{PF}_6)$. To a solution of $\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)_2\text{I}$ (0.144 g, 0.240 mmol) in acetone was added 1 molar equiv of AgPF_6 (0.061 g). Silver iodide precipitated rapidly and was removed by centrifuge to give a colorless solution; *p*- $\text{CNC}_6\text{H}_4\text{CH}_3$ (0.028 g, 0.240 mmol) was added, the solvent was removed on a rotary evaporator, and the oil was dissolved in dichloromethane. The addition of diethyl ether gave white crystals of $[\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)_3](\text{PF}_6)$ (0.147 g, 0.200 mmol).

(i) **Preparation of $[\text{Pt}(\text{CH}_3)_3[\text{As}(\text{CH}_3)_3]_2(\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O})]-(\text{PF}_6)$.** AgPF_6 (0.079 g, 0.312 mmol) was added to a solution of $\text{Pt}(\text{CH}_3)_3[\text{As}(\text{CH}_3)_3]_2\text{I}$ (0.190 g, 0.312 mmol) in 10 ml of acetone. The AgI was removed by centrifuge to give a clear colorless solution. 1-Butyn-4-ol (0.312 mmol) was added, the solution was stirred for 10 min, and the solvent was removed on a rotary evaporator to give a white solid that was recrystallized from dichloromethane and ether to give white needles; 85% yield. The crystals slowly darkened and decomposed over a period of a few hours even when stored under nitrogen.

(j) **Pyrolysis of $\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{Q}_2\text{I}$.** A 0.100-g amount of $\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{Q}_2\text{I}$ was placed in the bottom of a 25-ml round-bottom flask. The flask was evacuated and the bottom was placed in the preheated oil bath at 165°. Effervescence immediately occurred leaving a white solid. The evolved gases were analyzed by mass spectrometry and infrared spectroscopy. The solid residue was then recrystallized from methanol to give white needles. The nmr spectrum was recorded and the platinum methyl peak was integrated against those of the phosphine methyls.

Registry No. *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{NC}_5\text{H}_5)](\text{PF}_6)$, 37081-49-5; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_3](\text{PF}_6)$, 37081-50-8; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2\text{-P}(\text{OCH}_3)_3](\text{PF}_6)$, 37035-91-9; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2\{\text{Sb}(\text{CH}_3)_3\}](\text{PF}_6)$, 37035-92-0; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_6\text{H}_4\text{CH}_3)](\text{PF}_6)$, 37081-51-9; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_6\text{H}_4\text{OCH}_3)](\text{PF}_6)$, 37035-93-1; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNCH}_3)](\text{B}(\text{Ph})_4)$, 37035-94-2; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_2\text{H}_5)](\text{PF}_6)$, 37035-95-3; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{A}_2(\text{NCC}_6\text{F}_5)](\text{PF}_6)$, 37035-96-4; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{A}_2\text{Q}](\text{PF}_6)$, 37035-97-5; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{A}_2(\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O})](\text{PF}_6)$, 37035-82-8; *fac*- $[\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)_3](\text{PF}_6)$, 37408-40-5; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}(\text{CNC}_6\text{H}_4\text{CH}_3)_2](\text{PF}_6)$, 37036-88-7; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}(\text{NC}_5\text{H}_5)_2](\text{PF}_6)$, 37036-89-8; *fac*- $\text{Pt}(\text{CH}_3)_3\text{A}_2\text{I}$, 36604-67-8; *fac*- $\text{Pt}(\text{CH}_3)_3\text{Q}_2\text{I}$, 24833-69-0; $\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{A}_2\text{I}$, 37036-92-3; $\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{Q}_2\text{I}$, 37036-93-4; *fac*- $\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)_2\text{I}$, 37036-94-5; *trans*- $[\text{Pt}(\text{CH}_3)_2\text{Q}_2(\text{CO})](\text{B}(\text{Ph})_4)$, 37036-95-6; *cis*- $\text{Pt}(\text{CH}_3)_2\text{Q}_2$, 24917-48-4; *cis*- $\text{Pt}(\text{CH}_3)_2\text{A}_2$, 15413-98-6; CD_3I , 865-50-9.

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Studies on Coordination Complexes of Silver(II). VII.¹ A Comparative Study of the X-Ray Photoelectron Spectra of Complexes of Silver(II) and Silver(I) Containing Nitrogen Donor Molecules. Silver 3d and Nitrogen 1s Binding Energies

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The X-ray photoelectron spectra of twenty-five coordination complexes of silver(I) and silver(II) have been investigated and the silver 3d_{3/2} and 3d_{5/2} binding energies measured. While these binding energies show little variation with changes in formal oxidation state, their peak widths are usually broader by at least 0.8 eV for the paramagnetic silver(II) species, a feature which may be due in part to the occurrence of "multiplet splittings." Within the series of silver(II) complexes, there is some evidence for the dependence of silver 3d binding energies upon coordination number. Nitrogen 1s binding energies have been recorded for several of the complexes, with the object of assisting in the characterization of "silver(I) picolinate," a compound of ill-defined stoichiometry. The preparations of the new complexes bis(isoquinoline-1-carboxylato)silver(II) and pyridine-2,6-dicarboxylatodisilver(I) monohydrate are described.

Introduction

The technique of X-ray photoelectron spectroscopy (ESCA³) has recently been applied to a study of compounds of the heavier transition elements with the principal object of establishing whether correlations exist between electron binding energies and the formal charge at the metal center. To date, most detailed studies have been carried out on coordination complexes of platinum and palladium, where fairly extensive series of complexes are available for study.⁴⁻⁷

The results generally bear out the expected trends: (a) a decrease in the binding energies of metal core electrons with decrease in oxidation state; (b) a dependence of these binding energies upon ligand electronegativities and π -acceptor ability. Unfortunately, for the heavier transition elements, there is often unlikely to be a clear correlation between a "characteristic" range of binding energies and a particular oxidation state. This is illustrated by the similar molybdenum 3d_{3/2} and 3d_{5/2} binding energies of $\text{MoCl}_4 \cdot 2\text{py}$ and $\text{MoO}_2(\text{acac})_2$, derivatives of molybdenum(IV) and -(VI), respectively,⁸ and the similar iridium 4f_{5/2} and 4f_{7/2} binding energies of $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Me}_3\text{N}]_2\text{IrCl}_6$.⁹ However, generally it seems that the higher the oxidation states, the greater is the binding energy difference, provided comparisons are made within related series of compounds.

Many of the chemical problems of current interest to us involve a study of low oxidation state transition metal complexes and we have consequently been interested in the X-ray photoelectron spectra of such species. Specifically we have

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