The calculated carbon–sulfur stretching force constants are consistent with the above structures with F_{C-S} in bis(ethyl xanthato)nickel(II)[15a] equal to 3.7 mdyn/Å and in bis(dithiocarbamato)platinum(II)[20] equal to 3.00 mdyn/Å. [See also the calculations for bis(N,N-dimethyldithiocarbamato)nickel(II)[21] and the questions raised about this work by Jensen and Krishnan.[22]] These force constants are slightly larger than that of the pure carbon–sulfur single bond (2.50 mdyn/Å for diethyl thioether)[20] and smaller than that of the pure C–S double bond (7.8 mdyn/Å for CS₂).[23]

In an attempt to obtain an estimate of the strength of the metal–sulfur bonds in $M(CS_3)_2{}^{2-}$, a complete normal-coordinate analysis treatment was initiated. Preliminary calculations showed the existence of con-

siderable mixing of modes in the low-frequency region. From the results of normal-coordinate analyses of similar compounds,[15a,20,21,24] vibrational mixing of this type is recognized to be common. As a result a direct correlation of the metal–sulfur stretching frequencies with the metal–sulfur bond strengths cannot be made. Previous normal-coordinate analyses of metal–sulfur chelate compounds have not considered interligand interactions.[25]

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Cationic Organometallic Complexes with Unsaturated Systems. IV. Dimethylplatinum(IV) Cations. Chemical Reactivity and a Nuclear Magnetic Resonance Trans-Influence Series

BY H. C. CLARK* AND L. E. MANZER

Complexes of the type $[Pt(CH_3)_2Q_2L_2]^{2+}$ and $[Pt(CH_3)_2Q_2LI]^+$ have been prepared, where $Q = P(CH_3)_2(C_6H_5)$ and L is a ligand such as a phosphite, nitrile, isocyanide, phosphine, etc. $^2J(Pt(IV)-CH_3)$ is used to establish an nmr trans-influence series and the ratio of this coupling constant with $^2J(Pt(II)-CH_3)$ for an analogous series of complexes is discussed. The N≡C stretching frequencies for a series of cationic ethyl isocyanide complexes are discussed in terms of the electron density on platinum. The reactions of the dimethylplatinum(IV) cations with 1-butyn-4-ol and pentafluorobenzonitrile are compared with those of the corresponding methylplatinum(II) compounds.

Introduction

Trimethylplatinum(IV) iodide was the first organoplatinum complex to be prepared,[1] and most of the chemistry of organoplatinum(IV) has evolved from this compound.[2] Dimethylplatinum(IV) complexes have received much less attention due to their difficulty of preparation rather than to any inherent instability.[3]

While investigating the nature of the Pt–CF₃ bond in a series of CF₃–Pt(II) and CF₃–Pt(IV) complexes[4] we discovered that the iodide trans to CF₃ was quite labile to the extent that we were able to prepare several platinum(IV) cations including a carbene complex.[5] Consequently, the apparent stability of these platinum(IV) cations prompted us to extend our investigations to the synthesis of other organoplatinum(IV) cations.

We have recently been interested in the reactivity of unsaturated systems with methylplatinum(II) cations[6–10]

so it was also of interest to examine the reactivity of these ligands when present in organoplatinum(IV) cations. On oxidation from Pt(II) to Pt(IV), two electrons are removed from the metal resulting in a contraction of the metal orbitals and it is these orbitals that are used for π back-donation into ligand π^* orbitals. Therefore, any complexes with unsaturated ligands, that rely on M ($d\pi$) → L (π^*) bonding would be expected to be less stable for Pt(IV) compared with Pt(II).

In this paper we report the synthesis of a wide variety of dimethylplatinum(IV) cations and the reactions of these cations with acetylenes and pentafluorobenzonitrile. We also discuss the relationship between $^2J(^{195}Pt-CH_3)$ and the nmr trans influence of a neutral ligand trans to the methyl group in such dimethylplatinum(IV) cations.

Results and Discussion

I. Preparation of the Complexes.—One or both of the iodine atoms in dimethylbis(dimethylphenylphos-

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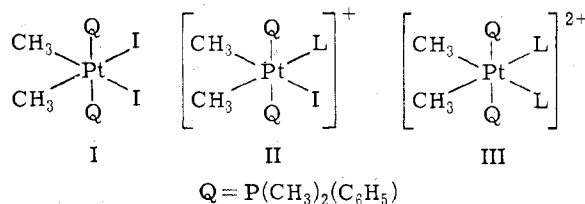
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Table I

Analytical, Physical, and Raman Data for Dimethylplatinum(IV) Cations[a]

Complex	Analysis, % calcd (% found) Carbon	Hydrogen	Mp, °C	Recrystallizn solvents	Raman data, cm⁻¹ ν_{Pt-CH_3}	Other	$\Delta\nu_{N\equiv C}$[c]
$[PtMe_2Q_2(NCC_6H_4OCH_3)_2](PF_6)_2$	38.61 (38.17)	4.00 (4.32)	150–153	CH_2Cl_2–CH_3OH–$(C_2H_5)_2O$	561	$\nu_{C\equiv N}$ 2261	48
$[PtMe_2Q_2(phen)](PF_6)_2$	36.41 (36.89)	3.67 (3.58)	309–311	CH_3COCH_3–CH_2Cl_2	560, 551		
$[PtMe_2Q_2(NH{=}C(OCH_3)C_6F_5)_2](PF_6)_2$	32.63 (32.58)	2.90 (3.15)	111–115	CH_3OH–$(C_2H_5)_2O$	586, 555	$\nu_{C\equiv N}$ 1663	
$[PtMe_2Q_2\{S_2CN(C_2H_5)_2\}](PF_5)$	34.91 (34.97)	4.78 (5.22)	174–176	CH_2Cl_2–$(C_2H_5)_2O$	b		
$[PtMe_2Q_2(terpy)](PF_6)_2$	38.68 (38.47)	3.84 (3.61)	242–248	CH_3COCH_3–CH_2Cl_2	553, 532, 523		
$[PtMe_2Q_2(bipy)](PF_6)_2$	35.49 (35.50)	3.83 (3.98)	304–306	CH_3COCH_3–CH_2Cl_2	562, 548		
$[PtMe_2Q_2(py)_2](PF_6)_2$	35.42 (35.37)	4.03 (3.72)	208–211	CH_3OH	546		
$[PtMe_2Q_2(diphos)](SbF_6)_2$	38.21 (38.01)	3.79 (3.64)	229–233	CH_2Cl_2–$(C_2H_5)_2O$	536, 517		
$[PtMe_2Q_2\{P(OMe)_3\}](PF_6)_2$	27.78 (27.71)	4.46 (4.32)	210–214	CH_3COCH_3–$(C_2H_5)_2O$	523		
$[PtMe_2Q_2(CNCH_3)_2](PF_6)_2$	30.25 (30.27)	3.92 (3.79)	162–166	CH_2Cl_2–CH_3OH–$(C_2H_5)_2O$	546, 535	$\nu_{N\equiv C}$ 2278	108
$[PtMe_2Q_2(CNC_6H_4CH_3)_2](PF_6)_2$	39.83 (39.59)	4.13 (4.09)	211–213	CH_3COCH_3–CH_2Cl_2	539	$\nu_{N\equiv C}$ 2227	111, 102
$[PtMe_2Q_2(CNC_6H_4OCH_3)_2](PF_6)_2$	38.61 (38.71)	4.00 (3.73)	209–211	CH_3COCH_3–$(C_2H_5)_2O$	540	$\nu_{N\equiv C}$ 2232, 2217	107, 92
$[PtMe_2Q_2(diars)](PF_6)_2$	31.21 (31.13)	4.17 (3.90)	211–214	CH_3COCH_3–$(C_2H_5)_2O$	513		
$[PtMe_2Q_2I(NC_5H_5)](PF_6)$	32.41 (32.29)	3.90 (3.94)	134–135	CH_3OH	555, 531		
$[PtMe_2Q_2I(CNC_6H_4OCH_3)][B(C_6H_5)_4]$	55.57 (56.23)	5.13 (5.39)	161–162	$CHCl_3$–$(C_2H_5)_2O$	544, 513	$\nu_{N\equiv C}$ 2216	91
$[PtMe_2Q_2I(CNC_6H_4CH_3)][B(C_6H_5)_4]$	56.40 (56.71)	5.21 (5.13)	168–169	CH_2Cl_2–CH_3OH–$(C_2H_5)_2O$	541, 518	$\nu_{N\equiv C}$ 2203	78
$[PtMe_2Q_2I(P(CH_3)_2C_6H_5)][B(C_6H_5)_4]$	55.31 (55.26)	5.48 (5.39)	158–159	CH_2Cl_2–CH_3OH	525, 503		
$[PtMe_2Q_2I(CNC_2H_5)](PF_6)$	30.45 (30.55)	4.02 (3.75)	148–149	CH_2Cl_2–$(C_2H_5)_2O$	546, 519	$\nu_{N\equiv C}$ 2243	92
$[PtMe_2Q_2(CNC_2H_5)_2](PF_6)_2$	31.97 (31.94)	4.25 (3.98)	178–179	CH_2Cl_2–$(C_2H_5)_2O$	550, 527	$\nu_{N\equiv C}$ 2246	95
$[PtMe_2Q_2\{B(pz)_4\}](PF_6)$	39.00 (38.75)	4.32 (4.19)	245–247	CH_2Cl_2–$(C_2H_5)_2O$	568, 559		

[a] Abbreviations are given at the bottom of Table II; all compounds are white except the diethyldithiocarbamate complex which is pale yellow. [b] Compound decomposed in the laser beam. [c] $\nu_{N\equiv C}$(complex) − $\nu_{N\equiv C}$(free ligand).
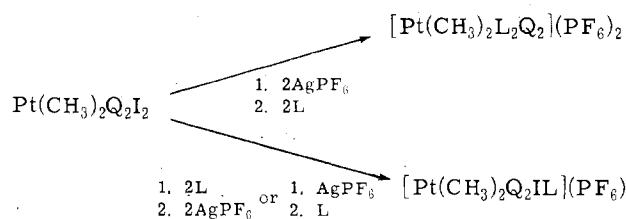
phine)platinum(IV) diiodide (I) may be removed by addition of the silver salt of a noncoordinating anion in the presence of a neutral ligand to give two types of cations (configurations II and III).

$$
\underset{\text{I}}{\begin{array}{c} CH_3\!-\!\overset{Q}{\underset{Q}{Pt}}\!-\!I \\ CH_3 \qquad I \end{array}} \qquad
\underset{\text{II}}{\left[\begin{array}{c} CH_3\!-\!\overset{Q}{\underset{Q}{Pt}}\!-\!L \\ CH_3 \qquad I \end{array}\right]^{+}} \qquad
\underset{\text{III}}{\left[\begin{array}{c} CH_3\!-\!\overset{Q}{\underset{Q}{Pt}}\!-\!L \\ CH_3 \qquad L \end{array}\right]^{2+}}
$$

$$Q = P(CH_3)_2(C_6H_5)$$

The dipositive cations (III) are prepared by the addition of 2 molar equiv of silver hexafluorophosphate to an acetone solution of I. Removal of the silver iodide gives a clear, colorless solution, presumably containing cation III (L = acetone). The addition of 2 molar equiv of a neutral ligand readily displaces acetone and the desired dipositive cations are obtained. Physical properties and recrystallization solvents are listed in Table I.

The monopositive cations may be prepared in two ways. The addition of 1 molar equiv of silver hexafluorophosphate to I in acetone followed by an equivalent amount of ligand (L) leads to the isolation of II in good yields. In an attempt to prepare the dipositive cations III by the addition of 2 molar equiv of silver hexafluorophosphate to an acetone solution containing I *and* the ligand (L) *only* the monopositive cations II are isolated (Scheme I), even though both iodine atoms

Scheme I

$$
Pt(CH_3)_2Q_2I_2
\begin{array}{c}
\overset{\text{1. 2AgPF}_6}{\underset{\text{2. 2L}}{\nearrow}} \quad [Pt(CH_3)_2L_2Q_2](PF_6)_2 \\[2ex]
\underset{\substack{\text{1. 2L} \\ \text{2. 2AgPF}_6}}{\overset{\text{1. AgPF}_6}{\underset{\text{2. L}}{\searrow}}} \text{ or } \quad [Pt(CH_3)_2Q_2IL](PF_6)
\end{array}
$$

can be readily removed in the absence of L. This is not expected nor can it easily be explained since methylplatinum(II) cations[11] are readily obtained by the use

of a silver salt and a neutral ligand regardless of the order of addition. Presumably the equilibrium (eq 1)

$$Ag^+ + L \rightleftharpoons AgL^+ \qquad (1)$$
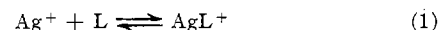
lies sufficiently far to the right to prevent removal of the second iodine atom, which would be expected to be more difficult than removal of the first iodide.

The acetone complex III (L = acetone) readily reacts with anionic bidentate ligands such as dialkyldithiocarbamates or tetrapyrazolylborates to form monopositive cations (configuration III with L = chelate).

The complexes are air-stable crystalline solids and melt without effervescence unlike trimethylplatinum-(IV) complexes[12,13] which melt with effervescence and loss of ethane. They are readily soluble in acetone and moderately soluble in dichloromethane or chloroform.

II. Nmr Spectra.—The phosphine–methyl resonances of complexes with configurations II and III (Tables II, III) appear as 1:2:1 triplets indicative of strong ³¹P–³¹P coupling of mutually trans phosphines[14] with coupling to ¹⁹⁵Pt ($I = \frac{1}{2}$, 34% natural abundance) giving rise to satellites of one-quarter total intensity. In several instances the absence of a plane of symmetry containing the P–Pt–P axis gives rise to inequivalent phosphine methyls and two sets of overlapping triplets are observed.[7]

The platinum methyl resonances appear as 1:2:1 triplets due to coupling with two equivalent ³¹P nuclei together with platinum satellites of one-quarter intensity. The magnitude of $^2J(^{195}Pt\text{–}C\text{–}^1H)$ is dependent on the nature of the ligand trans to the methyl group.

The ¹H nmr spectra of $[Pt(CH_3)_2Q_2(diphos)](SbF_6)_2$ (diphos = 1,2-bis(diphenylphosphino)ethane) is particularly interesting (Figure 1). The platinum methyl resonances appear as a doublet of triplets. The triplet pattern must arise from coupling to two equivalent ³¹P nuclei thus confirming the mutually trans configuration of the two dimethylphenylphosphines (configuration III). The fact that this resonance is split into a dou-

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(14) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

TABLE II
NMR DATA FOR DIMETHYLPLATINUM(IV) CATIONS $[PtMe_2Q_2L_2]^{2+}$

Complex[c]	Phosphine methyls			Platinum methyls			Other resonances
	δ_{CH_3}[a]	J_{P-H}[b]	J_{Pt-H}	δ_{CH_3}	J_{P-H}	J_{Pt-H}	
$[PtMe_2Q_2(NCC_6H_4OCH_3)_2](PF_6)_2$	2.17	8.1	20.2	1.18	6.5	70.2	δ_{OCH_3} 3.81
$[PtMe_2Q_2(phen)](PF_6)_2$	1.64	8.0	21.0	1.43	6.3	65.5	
$[PtMe_2Q_2(NH=C(OCH_3)C_6F_5)](PF_6)_2$	1.92	7.0	18.2	0.71	6.6	65.2	δ_{OCH_3} 3.97, δ_{NH} 8.80
$[PtMe_2Q_2\{S_2CN(C_2H_5)_2\}](PF_6)$	1.82	7.6	20.6	0.63	6.1	64.8	δ_{CH_3} 0.99, δ_{CH_2} 3.26, J_{H-H} = 7
$[PtMe_2Q_2(terpy)](PF_6)_2$	1.69	8.2	19.1	0.06	6.2	64.6	
	1.65	8.2	20.0				
$[PtMe_2Q_2(bipy)][PF_6)_2$	1.61	8.1	21.0	1.31	6.3	64.4	
$[PtMe_2Q_2\{B(pz)_4\}](PF_6)$	1.40	7.6	18.8	1.00	6.4	64.2	
$[PtMe_2Q_2(py)_2](PF_6)_2$	1.72	7.6	20.2	1.24	6.5	60.8	
$[PtMe_2Q_2(diphos)](SbF_6)_2$	1.50	10.0 d	31.0	0.43	6.5 t	60.6	
					8.1 d		
$[PtMe_2Q_2\{P(OCH_3)_3\}_2](PF_6)_2$	2.16	7.6	19.8	0.26	6.7	60.0	δ_{OCH_3} 4.09, J_{P-OCH_3} = 11
$[PtMe_2Q_2(CNCH_3)_2](PF_6)_2$	2.19	7.8	21.6	0.61	6.7	58.2	δ_{CH_3} 3.38, J_{Pt-H} = 8.3
$[PtMe_2Q_2(CNC_2H_5)_2](PF_6)_2$	2.22	7.6	20.4	0.78	6.8	58.2	δ_{CH_3} 1.28, δ_{CH_2} 3.79
$[PtMe_2Q_2(CNC_6H_4CH_3)_2](PF_6)_2$	2.32	8.0	21.2	0.90	6.6	58.0	δ_{CH_3} 2.26
$[PtMe_2Q_2(CNC_6H_4OCH_3)_2](PF_6)_2$	2.29	8.0	21.6	0.87	6.7	57.8	δ_{OCH_3} 3.71
$[PtMe_2Q_2(diars)](PF_6)_2$	1.99	7.4	21.6	1.34	7.5	56.0	δ_{AsCH_3} 1.34
	1.97	7.2	21.7				J_{Pt-H} = 7.0

[a] Chemical shifts are reported in ppm downfield from TMS using dichloromethane as solvent. [b] $^2J_{P-H}$ + $^4J_{P-H}$ is quoted (ref 14). [c] Q = $P(CH_3)_2(C_6H_5)$, phen = o-phenanthroline, terpy = 2,2',6',2''-terpyridine, bipy = 2,2'-bipyridyl, py = pyridine, diphos = 1,2-bis(diphenylphosphino)ethane, diars = o-phenylenebis(dimethylarsine), Me = CH_3, d = doublet, t = triplet.
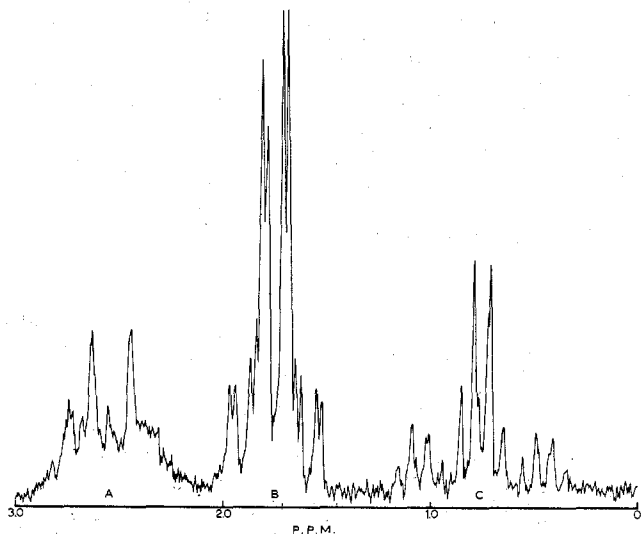

Figure 1.—¹H nuclear magnetic resonance spectrum of [Pt-$(CH_3)_2\{P(CH_3)_2C_6H_5\}_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}](SbF_6)_2$ in dichloromethane at 31°. Spectrum was recorded on a Varian HA100 spectrometer using a 500 Hz sweep width. A = $A_2A_2'XX'$ spin system of chelating diphosphine. B = phosphine methyl resonances showing two doublets $^2J_{P-H}$ with platinum satellites, and C = platinum methyl resonance as a doublet of triplets with platinum satellites.

blet indicates that coupling to the trans ³¹P nucleus of the chelating diphosphine is much greater than coupling to the cis phosphorus.[15]

The phosphine methyl resonance appearson ly as two overlapping doublets with platinum satellites. Such a pattern is usually associated with cis phosphines where the P–M–P bond angle is close to 90° and ³¹P–³¹P coupling is small. However, little is known of the magnitude of $^2J(^{31}P-^{31}P)$ when the angle P–M–P is between 180° (virtual coupling) and 90°. Since the phosphine methyl resonance appears only as a doublet the P–M–P bond angle in this complex must be less than 180° as a result of steric interaction with the chelating diphosphine IV as shown from molecular models.

(15) H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, **91**, 596 (1969).
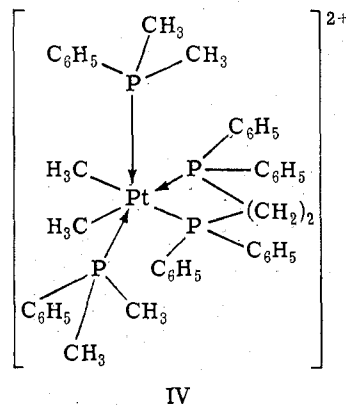
IV

Values of $^3J(Pt-H)$ for Pt(IV) complexes are generally about 20 Hz (Table II); however, for the diphos complex this value is 31 Hz. The coupling constant is dependent on the hybridization of phosphorus as well as the bond angles H–C–P and C–P–Pt which might all be affected by steric crowding and the molecular distortion from 180°.

The proton nmr spectrum of the cation V, [Pt(CH₃)₂-Q₃I](PF₆), is also very interesting (Figure 2).
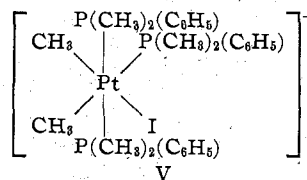
V

The resonances of the two mutually trans phosphines appear as two overlapping 1:2:1 triplets due to the lack of a plane of symmetry containing the P–Pt–P bonds and thus the P–Pt–P angle must be close to 180° with little of the distortion observed with the diphos complex. The platinum methyl group trans to the phosphine gives a 1:3:3:1 quartet due to an overlapping doublet of triplets with trans $^3J(P-H)$ equal to cis $^3J(P-H)$. It is interesting that cis $^3J(P-H)$ is greater than trans $^3J(P-H)$ for the platinum methyl resonance of the complex[11] *trans*-$[Pt(CH_3)Q_3]^+$ whereas cis $^3J(P-H)$ is less than trans $^2J(P-H)$ for the hydride

TABLE III
NMR DATA FOR DIMETHYLPLATINUM(IV) CATIONS [PtMe$_2$Q$_2$IL]$^+$

Ligand (L)	Phosphine methyls			Methyl trans to I			Methyl trans to L			Other resonances
	δ_{CH_3}	J_{P-H}	J_{Pt-H}	J_{CH_3}	J_{P-H}	J_{Pt-H}	δ_{CH_3}	J_{P-H}	J_{Pt-H}	
NC$_5$H$_5$	2.14	7.6	18.8	1.27	6.2	64.2	1.49	5.5	61.6	
	2.02	7.6	21.2							
CNC$_6$H$_4$OCH$_3$	2.32	8.0	18.8	0.88	5.6	64.9	0.88	6.0	58.3	δ_{OCH_3} 3.65
	2.01	8.2	20.6							
CNC$_6$H$_4$CH$_3$	2.43	7.3	20.0	1.02	5.5	62.5	1.09	7.1	57.0	δ_{CH_3} 2.46
	1.99	7.9	21.0							
P(CH$_3$)$_2$C$_6$H$_5$	2.08	6.5	18.4	0.95	5.3 t	62.6	1.18	6.8	50.5	
	1.98	7.6	19.5		8.1 d					
	1.64 d	9.6	15.6							
⌐ ¬ :CCH$_2$CH$_2$CH$_2$O	2.39	6.3	16.0	1.41	5.57	64.5	0.75	7.5	47.0	
	1.87	6.4	16.8							
CNC$_2$H$_5$	2.44	7.4	20.2	0.89	5.5	64.4	0.95	5.5	58.0	δ_{CH_3} 1.06
	2.11	7.8	21.0							δ_{CH_2} 3.40
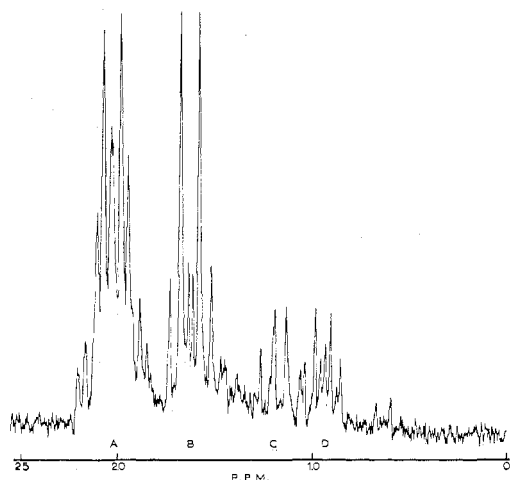
Figure 2.—^{1}H nuclear magnetic resonance spectrum of [Pt-(CH$_3$)$_2${P(CH$_3$)$_2$(C$_6$H$_5$)}$_3$I](PF$_6$) at 31°. Spectrum was recorded on a Varian HA100 spectrometer using dichloromethane as solvent and internal standard. A = resonance of the two trans phosphines, B = doublet resonance of the phosphine trans to the methyl, C = platinum methyl trans to phosphine, and D = platinum methyl trans to iodide. Each platinum methyl appears as a doublet of triplets with platinum satellites.

resonance[9] of *trans*-[PtH{P(C$_2$H$_5$)$_3$}$_3$]$^+$. The platinum methyl resonance for the methyl group trans to iodide appears as an overlapping doublet of triplets.

III. The Nmr Trans Influence.—The trans influence[16] is a static or ground-state effect and is defined as the ability of a ligand to weaken the bond trans to itself. This is often reflected by differences in bond lengths, obtained from X-ray crystallographic studies on platinum(II) compounds.[17-21]

The trans influence (from nmr coupling constants) is believed to arise from a rehybridization of platinum σ orbitals in response to changes in the orbitals on the ligand used in bonding.[16,22] Thus within a series[23] *trans* [PtHL{P(C$_2$H$_5$)$_3$}$_2$]$^+$ as the trans influence of the ligand L increases so the Pt–L bond gains in platinum

"s" and "d" character and loses "p" character, conversely the bond trans to L gains in platinum "p" and loses in "s" and "d" character. The coupling between two directly bound nuclei is believed to be dominated by the Fermi contact contribution[4,24,25] and in particular the α^2(Pt) term which is the amount of platinum 6s electron density in the hybrid orbital. Thus as the trans influence of L increases, the coupling constant ^1J(Pt–H) decreases.

Little is known about the mechanism of coupling between two nuclei that are separated by more than one bond. We have recently examined the ^{13}C nmr spectra[26] for a series of methylplatinum cations *trans*-[Pt-(CH$_3$)Q$_2$L]$^+$ (L = arsine or phosphine) and found an excellent linear correlation between ^1J(^{195}Pt–^{13}C) and ^2J(^{195}Pt–C–^{1}H) which suggests that the proton nmr spectrum may be used to evaluate the trans influence of a neutral ligand trans to the platinum methyl group. Therefore, by measuring the coupling constant ^2J(^{195}Pt–C–^{1}H) for a series of methylplatinum(IV) cations the ligands may be arranged as follows in order of their decreasing nmr trans influence (abbreviations are listed at the bottom of Table II): :CCH$_2$CH$_2$CH$_2$O > P(CH$_3$)$_2$(C$_6$H$_5$) > diars > CNC$_6$H$_4$OCH$_3$ ≳ CNC$_6$H$_4$CH$_3$ ≳ CN-CH$_3$ ≈ CNC$_2$H$_5$ > P(OCH$_3$)$_3$ > diphos > NC$_5$H$_5$ > B(pz)$_4^-$ > bipy ≳ terpy > S$_2$CN-(C$_2$H$_5$)$_2^-$ > NH=C(OCH$_3$)C$_6$F$_5$ > phen > NCC$_6$H$_4$-OCH$_3$.

Attempts to prepare cations of configuration III, with L = triphenylarsine, phosphine, or stibine, were unsuccessful and only very low yields of the methylplatinum(II) cations,[11] [Pt(CH$_3$)Q$_2$L]$^+$, were obtained. The reason for the instability of these platinum(IV) complexes is probably steric.

Carbon monoxide and triphenylstibine are high in the nmr trans-influence series for platinum(II) complexes;[11] however, this has been attributed to the synergic σ–π bonding mechanism,[4] *viz.*, strong π bonding resulting in a strong Pt–Sb and Pt–CO σ bond. Attempts to prepare [Pt(CH$_3$)$_2$Q$_2$(CO)$_2$]$^{2+}$ by bubbling carbon monoxide through a solution of [Pt(CH$_3$)$_2$Q$_2$-(CH$_3$COCH$_3$)$_2$]$^{2+}$ in acetone yielded only a small amount of the corresponding methylplatinum(II) cation [Pt(CH$_3$)Q$_2$(CO)]$^+$. The 5d orbitals of Pt(IV) would not be expected to be as effective for π back-bonding as those of Pt(II), and as a result the Pt(IV)–

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(22) S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6669 (1968).
(23) M. J. Church and M. J. Mays, *J. Chem. Soc. A*, 1938 (1970).

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CO bond would be very weak and reduction occurs, although the mechanism of this reduction remains obscure. A similar argument may also account for the instability of the complexes with triphenylphosphine, arsine, and stibine although as mentioned above the major reason is probably steric. Attempts to prepare the complex $[Pt(CH_3)_2Q_2I\{As(C_6H_5)_3\}]^+$ by the addition of 1 molar equiv of $As(C_6H_5)_3$ to a solution of $AgPF_6$ and $Pt(CH_3)_2Q_2I_2$ were unsuccessful. However, the platinum(II) cation $[Pt(CH_3)Q_2\{As(C_6H_5)_3\}]^+$ was obtained in good yield presumably due to the instability of the platinum(IV) cation and the ease by which methyl iodide is eliminated.

Trofimenko[27] has recently reviewed the coordination chemistry of polypyrazolylborates $[R_nB(pz)_{4-n}]^-$. The tetrapyrazolylborate ion reacts with III, L = acetone, to give the cation VI.

VI
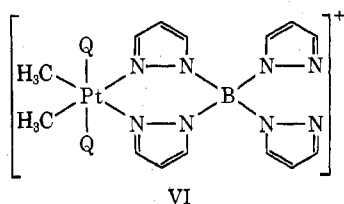
Attempts to prepare the bridged species $[(Pt(CH_3)_2-Q_2)_2\{B(pz)_4\}](PF_6)_3$ were unsuccessful and only the cation VI was isolated. The pyrazolylborate ion lies between pyridine and bipyridyl in the nmr trans-influence series and thus is typical of other nitrogen heterocycles.

For a related series of complexes of Pt(II) and Pt(IV) the ratio $^2J_{Pt(IV)-H}/^2J_{Pt(II)-H}$ would be expected to be 0.67[16] if the platinum 6s character was distributed equally over all bonds. This may be illustrated by the two complexes $[Pt(en)_2]Cl_2$[28] and $[Pt(en)_3]Cl_4$[29] (en = $NH_2CH_2CH_2NH_2$) where the ratio of the couplings $^3J_{Pt-N-CH_2}$ is 0.66. However we have shown that for methylplatinum complexes the methyl–platinum(IV) bond retains nearly 80% of the "s" character of the methyl–platinum(II) bond. A comparison between $^2J_{(Pt(IV)-CH_3)}$ and $^2J_{(Pt(II)-CH_3)}$ for the complexes prepared here (Figure 3) indicates that indeed the ratio is approximately 0.88. One interesting feature is that the methyl–platinum(IV) bond requires more platinum 6s orbital contribution relative to Pt(II) as the ligand trans to the methyl group rises in the nmr trans-influence series. Consider the cation $[Pt(CH_3)_2Q_2I(CNC_6H_4C-H_3)]^+$ where the ratio $^2J_{(Pt(IV)-CH_3)}/^2J_{(Pt(II)-CH_3)}$ is 0.92 for the methyl trans to isocyanide and 0.77 for methyl trans to iodide. Since the isocyanide is high in the nmr trans-influence series the methyl group trans to it requires more "s" character which is presumably obtained from the methyl trans to iodide.

The ratio of the coupling constants between the phosphine methyl protons and platinum for Pt(IV) and Pt(II) complexes is nearly theoretical at about 0.68.

IV. Raman and Infrared Spectroscopic Data.—All of the complexes show characteristic absorptions due to $P(CH_3)_2(C_6H_5)$.[30] The presence of the octahedral PF_6^- ion is easily detected due to $\nu_3(f_{1u})$ at 850 cm^{-1}
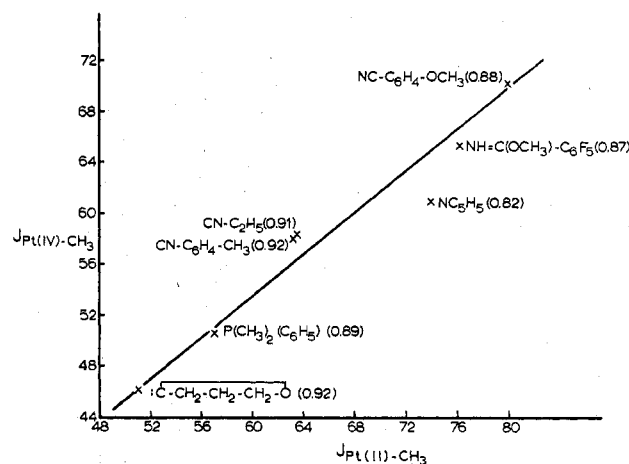

Figure 3.—A plot of $^2J_{Pt(IV)-CH_3}$ vs. $^2J_{Pt(II)-CH_3}$ for a variety of cations. The number in parentheses after the ligand gives the value of $^2J_{Pt(IV)-CH_3}/^2J_{Pt(II)-CH_3}$.

and $\nu_4(f_{1u})$ at 565 cm^{-1}, both of which appear as intense bands in the infrared spectra,[31] and $\nu_1(a_{1g})$ is observed in the Raman spectrum[32] at 741 cm^{-1}. The most intense peak in the Raman spectra occurs in the region 500–600 cm^{-1} and this has been assigned to the platinum–methyl stretching[33] vibration although it is unlikely to be a pure mode.

We would expect, in the Raman spectra, two platinum–methyl stretching bands for each configuration although ideally the symmetries of each would be different; complexes with configuration III belong to the C_{2v} point group and thus the bands $A_1 + B_1$ or B_2 are predicted from group theory and those with configuration II have lower symmetry (C_s) and two bands A_1 are predicted. In most cases the expected two bands are observed (Table I).

A very sharp and strong absorption, assigned to the $N{\equiv}C$ stretching vibration, is observed for the isocyanide complexes in both the infrared and Raman spectra. Within a series of platinum(II) isocyanide complexes[9,10] we have shown that $\Delta\nu_{N{\equiv}C}$ ($\nu_{N{\equiv}C}$(complex) $- \nu_{N{\equiv}C}$(free ligand)) increases as the electron density on the metal decreases. From Table IV it may be

TABLE IV

A COMPARISON OF THE ISOCYANIDE STRETCHING VIBRATIONS FOR SOME ORGANOPLATINUM ETHYL ISOCYANIDE CATIONS

Complex	$\nu_{N{\equiv}C}$, cm^{-1}	$\Delta\nu_{N{\equiv}C}$, cm^{-1}	Ref
trans-[Pt(CNC$_2$H$_5$)$_2$Q$_2$]$^{2+}$	2294	143	10
trans-[PtCl(CNC$_2$H$_5$)Q$_2$]$^+$	2267	116	10
trans- Pt(CNC$_2$H$_5$)Q$_2$-	2264	113	10
trans-[CF$_3$PtQ$_2$(CNC$_2$H$_5$)]$^+$	2256	105	4
trans-[Pt(CH$_3$)$_2$Q$_2$(CNC$_2$H$_5$)$_2$]$^{2+}$	2246	95	
trans-[Pt(CH$_3$)$_2$Q$_2$I(CNC$_2$H$_5$)]$^+$	2243	92	
trans-[Pt(CH$_3$)Q$_2$(CNC$_2$H$_5$)]$^+$	2234	83	10

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seen that $\Delta\nu_{N\equiv C}$ for the platinum(IV) complexes lies between the methyl- and trifluoromethylplatinum(II) cations. Thus it would appear that the electron density on platinum(IV) is similar to platinum(II) for these isocyanide cations. One must be careful when considering metals in different oxidation states; however, since the platinum–isocyanide bond is very similar (from nmr data) for Pt(II) and Pt(IV), we feel these considerations are valid.

The platinum electron density does not appear to be related entirely to the formal oxidation state but to some extent to the ligands surrounding the metal. Recent X-ray photoelectron studies[34] on some platinum complexes suggest that the electron density on a dimethylplatinum(II) complex is similar to platinum metal and in fact greater than several platinum acetylene complexes which are formally in a zerovalent oxidation state.

V. Ligand Reactivities.—Methylplatinum(II) cations react with monosubstituted acetylenes in alcohol to give carbene complexes[35]

$$Pt(CH_3)Q_2Cl + AgPF_6 + R'C\equiv CH \xrightarrow{ROH}$$
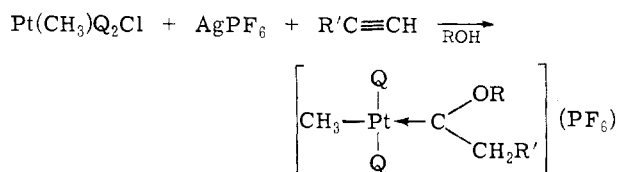
The reaction is believed to proceed *via* a π-bonded acetylene, delocalization of the positive charge from platinum onto the acetylene activating it toward nucleophilic attack by the alcohol.[36,37]
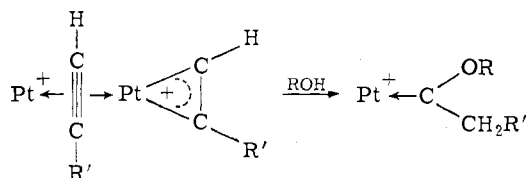

We have not been able to isolate dimethylplatinum(IV) carbene complexes by this method. Reaction of Pt(CH$_3$)$_2$Q$_2$I$_2$ with silver hexafluorophosphate and acetylenes in methanol led only to extensive polymerization and no platinum complex could be isolated. In contrast[5] Pt(CH$_3$)$_2$(CF$_3$)Q$_2$I reacts with 1-butyn-4-ol and AgPF$_6$ to give a platinum(IV) carbene (eq 2).
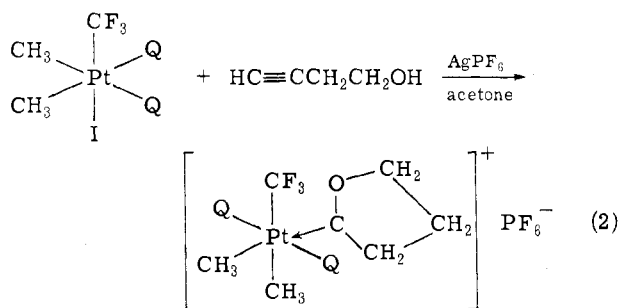
The activated π-bonded acetylene must have a sufficiently long lifetime for rearrangement[37] prior to car-

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bene formation. In the present case, since polymerization occurs there must be only a weak association, with a short lifetime, between the platinum and the acetylene.

Cationic methylplatinum(II) complexes are readily oxidized by methyl iodide,[38] and by this method we have been able to obtain a dimethylplatinum(IV) carbene cation[39] (eq 3). The configuration is confirmed by nmr data.
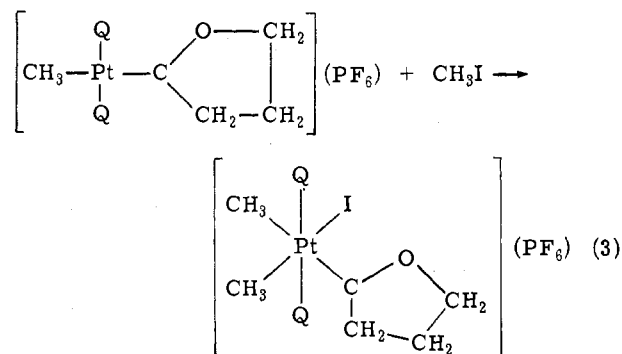
Perfluoroarylnitriles react with methylplatinum(II) cations in alcohol to give imino ether complexes.[6,7] Similarly with platinum(IV) a bis(imino ether) complex (configuration III) may be obtained (eq 4). Re-

$$Pt(CH_3)_2Q_2I_2 + 2AgPF_6 \xrightarrow{CH_3OH}$$

$$[Pt(CH_3)_2Q_2(CH_3OH)_2](PF_6)_2 \xrightarrow{2C_6F_5CN}$$
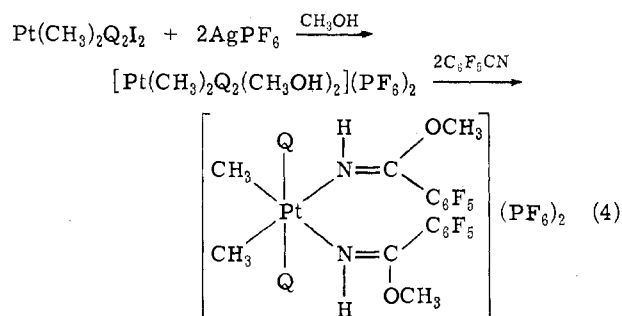
actions with alcohols to give imino ether complexes occur more readily for trifluoromethylplatinum(II) cations than for the corresponding methylplatinum cations. The proposed mechanism involves nucleophilic attack by the alcohol at a π-bonded nitrile.
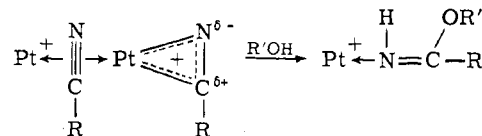
Since the π-bonded nitrile is higher in the nmr transinfluence series for platinum(II) than N-bonded nitrile,[7] the decreased electron density on the platinum in the trifluoromethyl complexes causes the preference for the π-bonded nitrile to be greater than for the methyl complexes. Since the electron density on the platinum atom in the dimethylplatinum(IV) cation is closer to that of the CF$_3$–Pt(II) cation than that of the CH$_3$–Pt(II) cation, the reactivity toward imino ether formation should be similar to the CF$_3$–Pt(II) case. This is indeed supported by the formation of the bis imino ether complex.

We have shown that dimethylplatinum(IV) cations

(38) T. G. Appleton, H. C. Clark, and L. E. Manzer, to be published.

(39) M. H. Chisholm and H. C. Clark, unpublished results.

are quite stable and in some cases more reactive than the corresponding methylplatinum(II) cations. In a future publication we will describe the preparation of trimethylplatinum(IV) cations as well as the relative ease by which these complexes reduce by elimination of ethane.

Experimental Section

p-Tolyl isocyanide was prepared by the phosgene method,[40] p-methoxyphenyl isocyanide by the method of Hertler and Corey,[41] and methyl isocyanide by the method of Casanova, Schuster, and Werner.[42] The other ligands were obtained commercially and were used without further purification. "Spectro" grade solvents were used for all reactions.

Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. Infrared spectra were recorded as 2% by weight KBr disks and were unchanged as Nujol mulls. Routine spectra were recorded on a Beckman IR-10 spectrophotometer and accurate values were obtained on a Beckman IR-7 spectrophotometer.

Raman spectra were recorded on a Cary 82 laser Raman spectrophotometer, the samples being prepared as crystalline solids in capillary tubes. The 5146 Å line of the argon laser was used as the exciting line; values are accurate to ± 2 cm^{-1}.

Many of the complexes were prepared by similar methods so only a few representative examples will be described.

Diiododimethylbis(dimethylphenylphosphine)platinum(IV) was prepared by the method of Ruddick and Shaw[43] with minor modifications. *trans*-Pt(CH$_3$)I{P(CH$_3$)$_2$C$_6$H$_5$}$_2$ was dissolved in methyl iodide and set aside for 6 hr. The methyl iodide was removed on a rotary evaporator to give, quantitatively, pure Pt(CH$_3$)$_2$I$_2${P(CH$_3$)$_2$C$_6$H$_5$}$_2$ (characterized by melting point and nmr spectroscopy[43]).

(a) **Preparation of [Pt(CH$_3$)$_2${P(CH$_3$)$_2$C$_6$H$_5$}$_2$(NH=C(OCH$_3$)-C$_6$F$_5$)$_2$](PF$_6$)$_2$.**—AgPF$_6$ (0.123 g, 0.488 mmol) was added to a magnetically stirred suspension of Pt(CH$_3$)$_2$I$_2${P(CH$_3$)$_2$C$_6$H$_5$}$_2$ (0.184 g, 0.244 mmol) in methanol. Silver iodide slowly precipitated over approximately a 5 min period and was then removed by centrifugation to give a clear colorless solution. Pentafluorobenzonitrile (0.095 g, 0.488 mmol) was added and after 5 min the solvent was removed to give white crystals which were recrystallized from methanol–ether to give the bis(imino ether) complex (0.110 g, 0.088 mmol).

(b) **Preparation of [Pt(CH$_3$)$_2${P(CH$_3$)$_2$C$_6$H$_5$}$_2$(NC$_5$H$_5$)$_2$](PF$_6$)$_2$.**—To a magnetically stirred solution of Pt(CH$_3$)$_2$I$_2${P(CH$_3$)$_2$C$_6$H$_5$}$_2$ (0.180 g, 0.239 mmol) in 10 ml of acetone was added AgPF$_6$ (0.121 g, 0.478 mmol). After 5 min the silver iodide was removed on the centrifuge to give a clear colorless solution. Pyridine (0.045 g, 0.478 mmol) was added and the solvent removed on a rotary evaporator to give a clear colorless oil. Methanol (2 ml) was added and the flask was warmed on a water bath, causing the oil to crystallize. The flask was cooled and the white crystals were filtered off and washed with ether, yield 0.187 g, 0.197 mmol (83%).

(c) **Preparation of [Pt(CH$_3$)$_2${P(CH$_3$)$_2$C$_6$H$_5$}$_2$(S$_2$CN(C$_2$H$_5$)$_2$)]-(PF$_6$).**—AgPF$_6$ (0.122 g, 0.482 mmol) was added to a solution of Pt(CH$_3$)$_2$I$_2${P(CH$_3$)$_2$C$_6$H$_5$}$_2$ (0.183 g, 0.243 mmol) in acetone. The AgI was removed by centrifugation and sodium diethyldithiocarbamate (0.055 g, 0.243 mmol) was added to give a yellow solution. The acetone was removed and the yellow solid was extracted from the NaPF$_6$ with dichloromethane. The addition of diethyl ether yielded pale yellow crystals which were filtered off and washed with ether, yield 0.142 g, 0.163 mmol (67%).

(d) **Preparation of [Pt(CH$_3$)$_2${P(CH$_3$)$_2$C$_6$H$_5$}$_2$(o-{As(CH$_3$)$_2$}$_2$-C$_6$H$_4$)](PF$_6$)$_2$.**—AgPF$_6$ (0.141 g, 0.558 mmol) was added to Pt(CH$_3$)$_2$I$_2${P(CH$_3$)$_2$C$_6$H$_5$}$_2$ (0.210 g, 0.278 mmol) in acetone and the AgI removed as above. o-Phenylenebis(dimethylarsine) (0.080 g, 0.278 mmol) was added and the volume reduced to 5 ml on a rotary evaporator. The addition of diethyl ether yielded white needles (0.180 g, 0.167 mmol, 61%).

(e) **Preparation of [Pt(CH$_3$)$_2${P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$(CNC$_6$H$_4$O-CH$_3$)I][B(C$_6$H$_5$)$_4$].**—To a solution of Pt(CH$_3$)$_2$I$_2${P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$ (0.211 g, 0.28 mmol) in acetone was added p-CH$_3$OC$_6$H$_4$NC (0.075 g, 0.56 mmol). The solution was stirred for 10 min and AgPF$_6$ (0.121 g, 0.56 mmol) was added. The dirty yellow precipitate of AgI was removed by centrifuge. The solvent was removed to give an oil that could not be crystallized so Na$^+$B-(C$_6$H$_5$)$^-$ (0.195 g, 0.56 mmol) in methanol (5 ml) was added. The solvent was removed and the complex extracted with dichloromethane and passed through a short Florisil column to remove traces of colloidal silver. The complex was eluted with dichloromethane. The volume was reduced and the addition of diethyl ether yielded white crystals (0.160 g, 0.142 mmol, 53%) which were filtered off and washed with ether.

A better yield of the iodoplatinum cations may be obtained by method (a) using 1 molar equiv of ligand and silver salt.

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