hedral nickel(II) complexes.[21] S-Alkylation reactions with the *o,o'*-xylyl dibromide of the nickel complex of the Schiff base of 2,3-pentanedione and β-mercaptoethylamine have been utilized to synthesize macrocyclic complexes.[50] An extension of these reactions[39] has recently been made to mercaptoaniline. S-Alkylation of the complexes[20] of the type $M(AsS)_2$ (M = Pd, Pt) has also been accomplished: $M(AsS)_2 + 2RX \rightarrow M(AsSR)X_2 + AsSR$ (M = Pd, RX = CH_3I, *n*-C_3H_7Br, $C_6H_5CH_2Cl$, *p*-$NO_2C_6H_4CH_2Br$; M = Pt, RX = CH_3I).

The demethylated complexes described in this article readily react with alkyl iodide, such as methyl iodide to regenerate the complexes $Pd(C_3)I_2$ and $Pd(C_3)I_2$.

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The identity of the S-alkylated products was established by elemental analyses, electronic spectra, and conductance measurements.

In several attempts to obtain a macrocyclic complex, the demethylated complex was allowed to react with *o,o'*-xylyl dibromide under varied conditions but a pure homogeneous product has not been isolated to date. This behavior is not inconsistent with the probable dimeric structure of the reactants (Figure 6).

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The Preparation and Nuclear Magnetic Resonance Spectra of Some Cationic Methylplatinum(II) Complexes

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Methods are described for the preparation of a wide range of cationic methylplatinum(II) complexes, *trans*-$Pt(CH_3)LQ_2^+$, where Q is dimethylphenylphosphine and L is a neutral ligand. Their nmr spectra are discussed and compared with those of other platinum(II) complexes. The nmr data for some platinum(II) complexes in liquid sulfur dioxide are interpreted in terms of octahedral solvate formation.

Introduction

Several types of cationic platinum(II) complexes have been described recently,[1–3] and some aspects of their chemistry have been explored.[4] These complexes are generally stabilized by tertiary phosphines or arsines, the other ligands about platinum(II) frequently being a halide and carbon monoxide. Methylplatinum(II) complexes show interesting chemical[5,6] and nmr spectroscopic[6] behavior; thus the nmr spectra of complexes of the type *cis*- or *trans*-$PtXCH_3\{P(C_2H_5)_3\}_2$ have recently been studied in detail,[7] and the methyl resonance patterns of some of the corresponding $P(CH_3)_2(C_6H_5)$ and $P(CH_3)(C_6H_5)_2$ complexes have also been reported.[6] A study of the hydride resonances of cationic complexes of the type *trans*-$PtHL\{P(C_2H_5)_3\}_2^+$ has shown[2] that there is a correlation between J(Pt–H) and the *trans* influence of the neutral ligand L, although such a relationship does not always hold[8] for neutral complexes $PtHX\{P(C_2H_5)_3\}_2$. We now describe the preparation and methyl resonance patterns of cationic complexes of the type *trans*-$PtCH_3LQ_2^+$ where Q = $P(CH_3)_2C_6H_5$ and L = neutral ligand.

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Results and Discussion

Preparation of the Complexes.—The chloride ligand in *trans*-$PtCl(CH_3)Q_2$ (I) is labile and can readily be replaced by another ligand L in a polar solvent such as methanol or acetone. Addition of 1 molar equivalent of a strongly bonding ligand L, such as a tertiary phosphine, to a suspension of I in methanol causes the solid to give a cationic species which can be precipitated out by addition of a large anion such as PF_6^- or $B(C_6H_5)_4^-$. If L is not strong enough to displace Cl, an alternative procedure may be used: the chloride ion is removed by addition of 1 molar equivalent of silver tetrafluoroborate, to give presumably $[PtCH_3(CH_3OH)Q_2]BF_4$. This reacts readily with L (or in some cases L can be used as reaction solvent in place of methanol) to give the required cationic complex, which can be precipitated out by addition of a large anion. However, addition of $B(C_6H_5)_4^-$ to solutions of $Pt(CH_3)(CH_3OH)Q_2^+$ or solutions presumably containing (by analogy with the above complexes) $Pt(CH_3)L'Q_2^+$ where L' is a very weakly held ligand, *e.g.*, an olefin, gives *trans*-

$Pt(C_6H_5)_2Q_2$. Thus, if trifluoroethylene is passed through a methanolic solution of I and the chloride is removed by addition of 1 molar equivalent of $AgBF_4$, addition of $NaB(C_6H_5)_4$ gives *trans*-$Pt(C_6H_5)_2Q_2$. Such ready transfer of a phenyl group from tetraphenylborate to platinum has been observed previously.[3]

The complexes thus obtained, whose nmr spectra are discussed below, are shown in Table I. Clearly, many other such derivatives could be obtained readily; some in which L is an acetylene will be described later, and other possibilities also exist. It is worth noting that the doubly charged PtQ_4^{2+} has been obtained and that several nitrile complex cations are included. Of particular interest is $[Pt(CH_3)(CH_2{=}CHCN)Q_2]$-$[B(C_6H_5)_4]$, for which the nmr spectrum shows that the acrylonitrile is bonded to the metal through the cyanide. Moreover, no band attributable to $\nu(C{\equiv}N)$ is observed in the infrared spectrum, but unfortunately $\nu(C{=}C)$ could not be identified because there are stronger bands due to the anion in the relevant region.

Nmr Data.—The methyl resonances of species of the type *trans*-$Pt(CH_3)LQ_2^+$, where L is not a tertiary phosphine, show the expected patterns. The methyl groups in Q give a 1:2:1 triplet, because of strong phosphorus–phosphorus coupling between the *trans* ^{31}P nuclei,[9] and there are triplet satellites of one-quarter intensity due to coupling with ^{195}Pt (33% abundance). The methyl group bonded to platinum gives a similar pattern but is found at higher field and has a larger coupling constant to platinum because of its closer proximity to the Pt nucleus.

$PtClQ_3^+$ gives a triplet for the mutually *trans* phosphines and a doublet for Q *trans* to Cl. The latter has J(Pt–H) = 40 Hz; in the corresponding methyl cation, $PtCH_3Q_3^+$, J(Pt–H) for the doublet is only 18 Hz. A similar large difference in the coupling constant to platinum between Q *trans* to Cl and Q *trans* to CH_3 is found[6] in *cis*-$PtCl(CH_3)Q_2$. The platinum-bonded methyl group in $Pt(CH_3)Q_3^+$ or $PtCH_3[P(C_6H_5)_3]Q_2^+$ gives for its main resonance two overlapping triplets: the *trans* ^{31}P nucleus splits the resonance into a doublet and the two *cis* ^{31}P nuclei split this into triplets. It is interesting that *cis* J(P–H) is greater than *trans* J(P–H), since in the hydride resonance[3] of $PtH\{P(C_2H_5)_3\}_3^+$ *cis* J(P–H) is much less than *trans* J(P–H). However, other work[6,7] has shown that *cis* and *trans* J(P–H) values for Pt(II) complexes are of the same order of magnitude.

Allen and Pidcock[7] have shown that the variation of J(Pt–H) for the platinum-bonded methyl group in *trans*-$PtX(CH_3)\{P(C_2H_5)_3\}_2$ (X = anionic ligand), as X is changed, parallels the changes in J(Pt–H) for the corresponding hydrido complexes. Church and Mays[2] have found that J(Pt–H) for the hydride in *trans*-$PtHL\{P(C_2H_5)_3\}_2^+$ varies with the changes in L in the order $C_5H_5N > CO > P(OC_6H_5)_3 \sim P(C_6H_5)_3$, and we find a similar variation for our methyl cations. We also observe that changing the coordinating atom from P to As causes J(Pt–H) for the methyl group to increase, as expected[2] since the *trans* influence of $P(C_6H_5)_3$ is greater than that of $As(C_6H_5)_3$. The corresponding antimony complex seems to have an anomalously low value, but little is known about the *trans* influence of $Sb(C_6H_5)_3$. The *trans* influence of CO (defined[10] as its ability to labilize the ligand *trans* to itself or weaken its bond to the metal) is lower than that of $P(C_6H_5)_3$, or Q, and hence J(Pt–H) for the *trans*-methyl group, which also depends largely on σ effects,[6,7,10] is greater in the carbonyl complex than in the tertiary phosphine complexes. The consistently high platinum coupling constant (79–80 Hz) shown by the methyl groups *trans* to the three nitrile ligands probably indicates that all three nitriles are coordinated end-on through the nitrogen atoms.

An unexpected product from some reactions which were intended to produce tetraphenylborate salts was *trans*-$Pt(C_6H_5)_2Q_2$. This complex is sparingly soluble in most solvents, but a good proton nmr spectrum was obtained in liquid sulfur dioxide. The methyl resonance pattern (Table II) consists of triplets indicating a *trans* configuration, and integration shows that there are four phenyl groups to four methyl groups. It is interesting that J(Pt–H) for the methyl groups in the phosphine is only 25 Hz in this solvent. For comparison, the spectrum of a saturated (40°) solution of the complex in pyridine was investigated and J(Pt–H) was found to be 34 Hz, which is normal for a *trans*-PtX_2Q_2 complex.[11] The nmr spectrum of the solution of *trans*-$Pt(C_6H_5)_2Q_2$ in sulfur dioxide had changed after 10 days to one which had a triplet methyl resonance pattern showing the more normal J(Pt–H) of 31 Hz. Evaporation of the solvent gave a solid which showed strong absorptions in the infrared spectrum at 1039 and 1162 cm^{-1}: these are probably ν_{sym}(S–O) and ν_{asym}(S–O) for an S-sulfinate complex[12,13] formed by insertion of sulfur dioxide into the platinum–phenyl bonds.

The explanation for the reduced coupling constant to platinum in the diphenyl complex may be that the sulfur dioxide coordinates weakly in the axial positions to give a distorted octahedral complex with long axial bonds. This would decrease the s character of the bonds to the equatorial ligands and hence decrease J(Pt–H):[7,10] the coupling constant to platinum in methylplatinum(IV) complexes containing mutually *trans* Q ligands[6] is 15–19 Hz.

Additional evidence in favor of the above explanation is provided by the methyl resonance patterns of some other complexes in liquid sulfur dioxide (Table II): (1) *trans*-$PtCl(CH_3)Q_2$, which will undergo oxidative addition reactions with, *e.g.*, chlorine, shows a reduced coupling constant to platinum (23.5 Hz in SO_2 compared with 31.5 Hz in $CHCl_3$[6]); (2) the octahedral complex $PtCl_2(CH_3)_2Q_2$, which has no room to expand its coordination shell, gives the same nmr spectrum in sulfur dioxide as in chloroform; (3) the cationic com-

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Table I

Nmr[a] and Other Data for Platinum(II) Cationic Complexes

Compound[b]	Method of prepn	% yield	Anal, % C Calcd	Anal, % C Found	Anal, % H Calcd	Anal, % H Found	Mp (dec), °C	Molar cond,[c] ohm^{-1} cm^2	Solvent[d]	Phosphine methyls $\delta(CH_3)$[e]	Phosphine methyls J(P–H)[f]	Phosphine methyls J(Pt–H)	Platinum methyls $\delta(CH_3)$[e]	Platinum methyls J(P–H)	Platinum methyls J(Pt–H)	Other resonances
$[PtClQ_3]PF_6$		90	36.55	36.07	4.21	4.10	153–155		C	1.42 d	10.7	40				
										1.90 t	7.8	23.5				
									A	1.64 d	11.0	40				
										1.93 t	8.0	24				
$[PtQ_4](PF_6)_2$		98	37.04	37.54	4.27[k]	4.75	278–281	54	A	1.68 (broad singlet)						
$[Pt(CH_3)Q_3]PF_6$	a	97	39.02	38.72	4.71	4.63	154–155		C	1.31 d	8.5	18.5	0.53 x	7.8[g]	57	
										1.67 t	7.0	30		6.5[h]		
									A	1.49 d	8.3	18.0	0.56 x	7.8[g]	57	
										1.74 t	7.0	30		6.4[h]		
$[Pt(CH_3)\{P(C_6H_5)_3\}Q_2]PF_6 \cdot CHCl_3$		85	42.68	42.71	4.08[l]	4.19	149–152		A	1.44 t	7.0	29	0.75 x	8.0[g]	60	
														6.0[h]		
$[Pt(CH_3)\{P(C_6H_5)_3\}Q_2]PF_6 \cdot CH_3COCH_3$		. . .	47.95	47.85	4.87	4.87	126–130									
$[Pt(CH_3)\{As(C_6H_5)_3\}Q_2]PF_6$	a	87	44.84	44.90	4.30	4.16	139–142	26	C	1.46 t	6.8	29	0.82 t	8.0	67	
$[Pt(CH_3)\{As(C_6H_5)_3\}Q_2]PF_6 \cdot CHCl_3$		. . .	40.91	40.71	3.91[m]	3.63	132–142									
$[Pt(CH_3)\{Sb(C_6H_5)\}Q_2]PF_6$	a	97	42.70	43.00	4.10	4.25	77–87	25	C	1.68 t	6.6	29	0.96 t	7.8	55	
$[Pt(CH_3)\{P(OC_6H_5)_3\}Q_2]ClO_4$		80	46.91	47.22	4.50	4.61	170–173	29	C	1.84 t	7.2	31	0.50 x	8.6[g]	58	
														8.8[h]		
$[Pt(CH_3)COQ_2]PF_6$	b	88	32.79	33.28	3.82	4.04	116–118	29	C	2.08 t	7.8	33	0.46 t	8.8	63	
$[Pt(CH_3)(py)Q_2]PF_6$	a	86	37.19	37.60	4.25[n]	4.32	109–111		C	1.57 t	6.8	32	0.44 t	7.4	74	
$[Pt(CH_3)(A)Q_2]B(C_6H_5)_4$		54	63.50	62.95	6.09	5.93	170–172	20	C	1.34 t	6.6	32	0.40 t	7.5	74	*i*
$[Pt(CH_3)(CH_3CN)Q_2]B(C_6H_5)_4$	c	73	61.10	61.66	5.71	6.03	100–102		C	1.53 t	6.8	32	0.32 t	7.7	80	*j*
$[Pt(CH_3)(C_6H_5CN)Q_2]B(C_6H_5)_4$	c	77	63.44	63.60	5.55	5.84	116–117		C	1.63 t	7.0	32	0.47 t	7.7	79	
$[Pt(CH_3)(CH_2{=}CHCN)Q_2]B(C_6H_5)_4$	c	55	61.54	61.20	5.65	5.75	108–109	15	C	1.61 t	7.0	32	0.40 t	7.8	80	

[a] Chemical shifts (δ) in ppm below internal TMS. Coupling constants (J) in hertz. [b] All compounds are white. Q = $P(CH_3)_2C_6H_5$; A = 2,4,6-trimethylpyridine. [c] Measured on 10^{-3} *M* solutions in nitrobenzene at 25°. [d] C = chloroform; A = deuterioacetone. [e] d = doublet; t = triplet; x = pair of triplets. [f] ^2J(P–H) + ^4J(P–H) is quoted (see ref 9). [g] *cis* coupling constant. [h] *trans* coupling constant. [i] $\delta(p\text{-}CH_3)$ 2.12 ppm (singlet); $\delta(o\text{-}CH_3)$ 2.49 ppm; J(Pt–H) = 6.4 Hz. [j] $\delta(CH_3CN)$ 0.65 ppm; J(P–H) = 0.9 Hz; J(Pt–H) = 7 Hz. [k] F: calcd, 21.97; found, 22.32. [l] Cl: calcd, 10.50; found, 10.71. [m] Cl: calcd, 10.06; found, 10.46. [n] N: calcd, 1.51; found, 1.46.

Table II

Methyl Resonance Patterns in Liquid Sulfur Dioxide[a]

Compound[b]	δ_Q	J(P–H)[c]	J(Pt–H)	δ_{PtCH_3}	J(P–H)	J(Pt–H)
trans-$PtCl(CH_3)Q_2$	1.35 t	7.8	23.5	0.14 t	6.4	83
trans-$Pt(C_6H_5)_2Q_2$[d]	0.83 t	8.0	25	. . .	. . .	. . .
$PtCl_2(CH_3)_2Q_2$	1.35 t	8.0	17.5	0.12 t	5.7	68
$[Pt(CH_3)Q_3]PF_6$	0.76 d	8.6	18	0.06 x	7.9 (*cis*)	57
	0.15 t	7.0	30		6.2 (*trans*)	
$[PtCH_3\{P(C_6H_5)_3\}Q_2]PF_6$	1.22 t	7.0	29	0.07 x	8.0 (*cis*)	60
					6.2 (*trans*)	

[a] Chemical shifts, δ, in ppm below external TMS in ethanol. Coupling constants, J, in hertz. d = doublet; t = triplet; x = doublet of triplets. [b] Q = $P(CH_3)_2C_6H_5$. [c] ^2J(PCH) + ^4J(P′PtPCH). See ref 9. [d] In pyridine: δ_Q 1.29 ppm; J(P–H) = 7.0 Hz; J(Pt–H) = 34 Hz.

plexes $[Pt(CH_3)Q_3]PF_6$ and $[Pt(CH_3)\{P(C_6H_5)_3\}Q_2]PF_6$ which do not undergo oxidative addition reactions, presumably because the positive charge causes contraction of the orbitals, also show the same nmr spectrum in sulfur dioxide as in chloroform.

The changes in chemical shift of the platinum-bonded methyl group in $Pt(CH_3)LQ_2^+$ as L is changed vary in the order $CH_3CN < (CH_3)_3C_5H_2N < C_5H_5N < C_6H_5CN \sim CO < P(OC_6H_5)_3 < P(CH_3)_2C_6H_5 < P(C_6H_5)_3 < As(C_6H_5)_3 < Sb(C_6H_5)_3$. A similar, but more limited, series was observed[2] for the cationic hydrides.

Experimental Section

In the procedures described below $Q = P(CH_3)_2(C_6H_5)$. Percentage yields and analytical data are shown in Table I. The general instrumentation and methods have been described previously. Nmr spectra were recorded on a Varian A-60 spectrometer.

$[PtClQ_3]PF_6$.—To a suspension of *cis*-$PtCl_2Q_2$ (0.60 g) in methanol (15 ml) under nitrogen was added dimethylphenylphosphine (0.16 g) to give a clear solution. A saturated solution of KPF_6 in water was added to give a precipitate which was washed with water and recrystallized from methanol.

$[PtQ_4](PF_6)_2$.—To a suspension of *cis*-$PtCl_2Q_2$ (0.51 g) in methanol (15 ml) under nitrogen was added dimethylphenylphosphine (0.50 g) to give a yellow solution. A solution of KPF_6 (0.5 g) in water (5 ml) was added and the precipitate was washed with water then with cold methanol.

Preparation of $[Pt(CH_3)LQ_2]Z$ {L = neutral ligand; Z = PF_6 or $B(C_6H_5)_4$}. Procedure a.—To a suspension of *trans*-$PtCl(CH_3)Q_2$[6a] (*ca.* 0.15 g) in methanol (10 ml) under nitrogen was added 1 molar equivalent of L to give a clear solution. A saturated solution of KPF_6 in water was then added and the precipitate was filtered off, washed with cold water, and dried.

Procedure b.—A saturated solution of *trans*-$PtCl(CH_3)Q_2$ (*ca.* 0.15 g) in methanol under an atmosphere of the ligand L was treated with a solution of 1 molar equivalent of $AgBF_4$ in methanol (1 ml). The precipitate of silver chloride was filtered off and to the filtrate was added a saturated solution of KPF_6 in water. The resulting precipitate was washed well with cold water and dried.

Procedure c.—To a solution of *trans*-$PtCl(CH_3)Q_2$ (*ca.* 0.15 g) in the ligand L (8 ml) was added a solution of 1 molar equivalent of $AgBF_4$ in methanol (1 ml). The precipitate of silver chloride was filtered off and the filtrate was reduced to an oil which was dissolved in methanol (2 ml). A solution of $NaB(C_6H_5)_4$ (1 molar equivalent) in methanol (2 ml) was added and the resultant precipitate was washed with cold methanol.

Solvates of $[P(CH_3)\{P(C_6H_5)_3\}Q_2]PF_6$ (I).—Compound I was not obtained pure. The crude product from procedure a was dissolved in chloroform (0.5 ml), and after a few minutes the monosolvate crystallized out. A solution of the chloroform solvate in acetone was allowed to evaporate at room temperature and gave the monoacetone solvate. The chloroform solvate of the corresponding $As(C_6H_5)_3$ complex was obtained similarly. The nmr solution of $[PtQ_4](PF_6)_2$ in CD_3COCD_3 deposited crystals of a solvate after 5 min.

$[Pt(CH_3)AQ_2]B(C_6H_5)_4$ (A = 2,4,6-Trimethylpyridine).—A suspension of *trans*-$PtCl(CH_3)Q_2$ (0.195 g) in methanol (8 ml) containing A (0.200 ml) was warmed to give a clear solution. A solution of $NaB(C_6H_5)_4$ (0.128 g) in methanol (4 ml) was added and the mixture was set aside at room temperature for 20 hr. The resultant precipitate was recrystallized from chloroform–methanol.

***trans*-$[Pt(C_6H_5)_2Q_2]$.**—Attempts to prepare tetraphenylborate salts of cationic complexes containing a weakly coordinating ligand L, using procedures a, b, or c [substituting $NaB(C_6H_5)_4$ for KPF_6] gave *ca.* 80% yields of *trans*-$Pt(C_6H_5)_2Q_2$. The complex was also prepared (50% yield) from *cis*-$PtCl_2Q_2$ and phenyllithium. It formed colorless prisms, mp 220–222° dec, from pyridine. *Anal.* Calcd for $C_{28}H_{32}P_2Pt$: C, 53.76; H, 5.15. Found: C, 53.59; H, 5.16.

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Chemistry of Metal Hydrides. VIII. The Hydrolysis of Transition Metal Alkoxycarbonyls and a Kinetic Study of the Hydrolysis of *trans*-$[PtCl(CO)(R_3P)_2]BF_4$

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A kinetic study of the reaction of *trans*-$[PtCl(CO)\{P(C_2H_5)_3\}_2]BF_4$ with water to give the hydride $PtHCl\{P(C_2H_5)_3\}_2$ is consistent with a mechanism based on the reversible acid dissociation of the carbonyl cation to give a carboxylate species which undergoes further direct reaction with water to give the hydride. The transition metal alkoxycarbonyls $Fe(\pi\text{-}C_5H_5)(CO)_2(COOCH_3)$ and $Mn(CO)_5(COOC_2H_5)$ react with water under mild conditions to give the corresponding hydrido complexes $Fe(\pi\text{-}C_5H_5)H(CO)_2$ and $MnH(CO)_5$ or decomposition products of the latter.

Introduction

Transition metal hydrides have been prepared by a variety of methods most of which require vigorous forcing conditions.[1] Direct hydrogenation at high pressure, reduction with hydride complexes of group III metals or hydrazine, and reductions with alkaline refluxing alcohols are all widely used. However, with the exception of protonation reactions in acidic aqueous media, few metal hydrides have been synthesized in aqueous media with water as the source of the hydride ligand. We previously reported[2,3] the reaction of the

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