pears at lower temperatures. Thus, the bound water molecules, whatever their environment, exchange at different rates. Although the relative areas of the bound water signals could not be accurately determined, they are all intense in the 6:1 water–Ce^{3+} solution, and in total they correspond to an average hydration number of ~4.5 for this ion. At higher water mole ratios, the bound water signal at lowest field decreases in intensity and the cation hydration number increases to almost 6. At higher water concentrations and when the solutions were acidified, the three-signal pattern for bound water was still present but broadening prevented accurate integrations. The value shown in Table I for the acidified solution may be somewhat in error but it does rule out the presence of extensive hydrolysis. The hydration number result in the 6:1 water–Ce^{3+} solution must reflect inner-shell complex formation and the multiple bound water pattern which also is present at higher water concentrations may indicate that this complexing process is still prevailing. At this point, one can only state that the Ce^{3+} hydration number is at least 6 by direct measurement and possibly greater if complex formation with ClO_4^- is occurring. Measurements with other anions are underway to resolve this matter.

The $Er(NO_3)_3$ solution spectrum of Figure 6 and the extremely low hydration number listed in Table I are only preliminary in nature but they demonstrate the strong complexing tendency of the NO_3^- anion. The bonding is probably bidentate to account for the hydration number but this conclusion must await the determination of the maximum value for Er^{3+}. This measurement may be possible with the ClO_4^- or halide salts of this cation. Although the upfield displacement of the bound water signal from that of the bulk may indicate a positive sign for the hyperfine coupling constant, the low signal intensity and excessive line width prevented a detailed temperature study at this point.

In addition to expanded studies of the species described here to elucidate their complexing properties and to resolve any ambiguities concerning maximum hydration numbers, attempts to extend this pmr technique to other diamagnetic and paramagnetic ions presently are underway. Considerations of effective magnetic moments for a variety of paramagnetic species and solvent-exchange rates for examples of both types of ions indicate that the list of cations lying within the scope of this method is extensive.[47]

Acknowledgments.—The authors are grateful for the support of Research Grant No. 14-01-0001-2162 from the Office of Saline Water and National Science Foundation Instrument Grant GP-8347, for the purchase of the Varian HA-100 MHz spectrometer. A. F. wishes to acknowledge a National Institutes of Health Research Career Development Award (5-K4-GM42334-03). The authors are indebted to Mr. R. Perrigan for his assistance in recording several of the spectra.

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(47) NOTE ADDED IN PROOF.—Recent measurements in our laboratories have indicated a maximum hydration number of 6–7 for Er^{3+}. Bound water signals also have been observed in aqueous Lu^{3+}, Pr^{3+}, and Yb^{3+} solutions. While this paper was in press a more refined oxygen-17 nmr hydration study of Fe^{2+} and Ni^{2+} was completed [A. M. Chmelnick and D. Fiat, *J. Amer. Chem. Soc.*, **93**, 2785 (1971)] confirming the results presented here.

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Cationic Acetylenic Platinum(II) Compounds and Their Derivatives. II. Acetylene and Vinyl Ether Complexes

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Cationic acetylenic complexes of platinum(II), *trans*-$[PtCH_3(RC\equiv CR')Q_2]^+PF_6^-$ (I), have been prepared by the reaction of *trans*-$PtClCH_3Q_2$ (II), where Q = dimethylphenylphosphine or trimethylarsine, with alkyl- or aryl-disubstituted acetylenes and silver hexafluorophosphate in the presence of methanol as solvent. The nature of the platinum–acetylene bond is discussed in view of nmr and vibrational spectra of I. In several instances it was not possible to isolate I and reaction proceeded with the ultimate formation of $[PtCH_3Q_3]^+PF_6^-$. Reactions involving $RC\equiv CR'$, where R and R′ are CF_3, $COOCH_3$, CH_2OH, and COOH, are also considered and evidence for vinyl ether formation is presented.

Introduction

Our interest in both acetylenic[1-3] and cationic[4-7] complexes of platinum initiated a study of reaction 1 with the hope of isolating I. We recently described[8,9] reactions involving monoalkyl- and -aryl-substituted acetylenes, $RC\equiv CH$, in methanol and ethanol which led to the formation of methoxy- and ethoxycarbene complexes, respectively. The reaction is believed[9a] to

$$\underset{\text{II}}{trans\text{-}PtClCH_3Q_2} + RC\equiv CR' + AgPF_6 \xrightarrow{CH_3OH} \underset{\text{I}}{trans\text{-}[PtCH_3(RC\equiv CR')Q_2]^+PF_6^-} + AgCl \quad (1)$$

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(1) H. C. Clark and R. J. Puddephatt, *Chem. Commun.*, 92 (1970).
(2) H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, **9**, 2670 (1970).
(3) H. C. Clark, and R. J. Puddephatt, *ibid.*, **10**, 18 (1971).
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(5) H. C. Clark and K. R. Dixon, *ibid.*, **91**, 596 (1969).
(6) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *ibid.*, **91**, 1346 (1969).
(7) H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, **9**, 1226 (1970).
(8) M. H. Chisholm and H. C. Clark, *Chem. Commun.*, 763 (1970).
(9) Part I: M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 1711 (1971).

(9a) NOTE ADDED IN PROOF.—Since the submission of this paper, we have been able to isolate stable cationic vinyl ether complexes and hence must discard this mechanism. A general mechanism involving platinum-stabilized carbonium ions has been proposed, and this readily accounts for all the reactions of cationic acetylenic platinum complexes [M. H. Chisholm, H. C. Clark, and D. H. Hunter, *Chem. Commun.*, 809 (1971)].

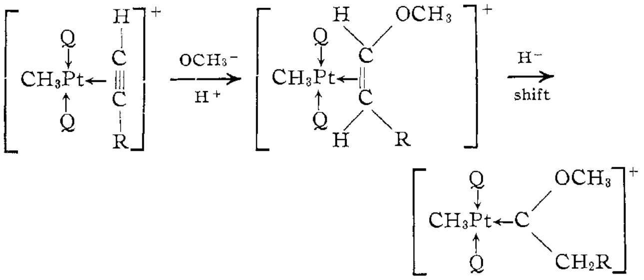
TABLE I

CHARACTERIZATION DATA FOR THE ACETYLENIC COMPLEXES *trans*-$[PtCH_3(L)Q_2]^+PF_6^-$

			Analysis, %				Vibrational spectra,[b] cm^{-1}		
			C		H				
L	Q	Mp,[a] °C	Calcd	Found	Calcd	Found	$\nu_{str}(PtC)$[c]	$\nu_{str}(C\equiv C)$	$\nu_{str}(C\equiv C)$[d]
$CH_3C\equiv CCH_3$	$P(CH_3)_2C_6H_5$	150	36.79	36.86	4.56	4.34	547	2114	2230 sh, 2237, 2314
$CH_3C\equiv CC_2H_5$	$P(CH_3)_2C_6H_5$	152–155	37.76	37.65	4.76	4.46	551	2116	2208, 2239, 2303
$C_2H_5C\equiv CC_2H_5$	$P(CH_3)_2C_6H_5$	150–153	38.71	38.57	4.95	4.91	547	2101	2212, 2247, 2298
$CH_3C\equiv CC_6H_5$	$P(CH_3)_2C_6H_5$	159	41.76	41.82	4.45	4.45	556	2087	2213, 2245
$C_6H_5C\equiv CC(C_6H_5)_2OH$	$As(CH_3)_3$	145	38.23	38.51	4.24	4.10	542	2040	2223
$C_6H_5C\equiv CC_6H_5$	$As(CH_3)_3$	157–159	32.60	32.48	4.01	4.02	549	2024	2223
$C_6H_5C\equiv CC(C_6H_5)_2OH$	$P(CH_3)_2C_6H_5$	136	49.60	51.38	4.47	4.56	547	2051	2223

[a] Accompanied by decomposition. [b] From Raman spectra ±3 cm^{-1}. [c] Platinum–methyl group. [d] Free acetylene; sh = shoulder.

proceed *via* nucleophilic attack of the initially formed cationic complex I to give a vinyl ether complex which then by hydride shift gives the alkoxycarbene complex III. A schematic route is



III

We now consider reactions involving alkyl, aryl, and other disubstituted acetylenes, $RC\equiv CR'$.

Results and Discussion

The acetylenic complexes *trans*-$[PtCH_3(RC\equiv CR')Q_2]^+PF_6^-$ (I), prepared in methanol as in reaction 1 above, are white, air-stable crystalline solids and are appreciably soluble in chlorinated solvents such as chloroform and dichloromethane but insoluble in nonpolar organic solvents. They are also extremely soluble in polar oxygen-containing solvents such as acetone. However, there is evidence (see later) that they react in such solvents liberating the acetylene. Analytical and other physical data are presented in Table I.

It was not possible to isolate I for Q = $As(CH_3)_3$ and $RC\equiv CR'$ = $CH_3C\equiv CCH_3$, $CH_3C\equiv CC_2H_5$, or $C_2H_5C\equiv CC_2H_5$, despite several attempts at their synthesis. It is tempting to relate this to electronic factors associated with tertiary phosphine and arsine ligands,[10,11] although it may be due to their differing solubilities in methanol. We believe methanolic solutions of I exist as an equilibrium as shown in

$$trans\text{-}PtCH_3(RC\equiv CR')Q_2^+ + CH_3OH \rightleftharpoons trans\text{-}PtCH_3(CH_3OH)Q_2^+ + RC\equiv CR' \quad (2)$$

If the solubility of I in methanol is low, then crystallization from solution may take place and this allows isolation of I where Q = $P(CH_3)_2C_6H_5$ and $RC\equiv CR'$ = $CH_3C\equiv CCH_3$, $CH_3C\equiv CC_2H_5$, and $C_2H_5C\equiv CC_2H_5$. Any attempt to concentrate the solution by the evaporation of solvent will also remove the acetylene, and for highly volatile acetylenes, *viz.*, those under consideration, such removal will occur preferentially. The complex formalized as *trans*-$[PtCH_3(CH_3OH)Q_2]^+PF_6^-$ (see Experimental Section) is only stable in excess methanol, and as this is removed *in vacuo*, decomposition occurs with the deposition of platinum and formation of $[PtCH_3Q_3]^+PF_6^-$. It is noteworthy that reactions involving the acetylenes $CH_3C\equiv CCH_3$, $CH_3C\equiv CC_2H_5$, and $C_2H_5C\equiv CC_2H_5$ when Q = $P(CH_3)_2C_6H_5$ did not yield I on evaporation of the mother liquor obtained from reaction 1; indeed decomposition occurred as for Q = $As(CH_3)_3$, and $[PtCH_3Q_3]^+PF_6^-$ was ultimately obtained.

Vibrational Spectra of I.—The acetylenic complexes I all showed $\nu_{str}(C\equiv C)$ in the range 2000–2125 cm^{-1} as an intense polarizable absorption in the Raman spectra; this absorption was not present in the infrared spectra. Polarization measurements on a dichloromethane solution of *trans*-$[PtCH_3(C_6H_5C\equiv CC_6H_5)(As(CH_3)_3)_2]^+PF_6^-$ showed this absorption to be *ca.* 90% polarizable which was a negligible reduction from that of $\nu_{str}(C\equiv C)$ in pure diphenylacetylene. [Solutions of I tended to boil (form bubbles) in the laser beam and so an accurate comparison of polarizability was not possible.] An absorption in the range 542–556 cm^{-1}, strong and polarizable (0.75*P*) in the Raman and weak in the infrared spectra, is assigned to $\nu_{str}(PtC)$ for the platinum–methyl group, although coupling to other vibrational modes is possible and it is unlikely to be a pure mode. At present, assignment of an absorption associated with a platinum–acetylene stretching mode is not possible; indeed examination of Raman spectra in the region 600–160 cm^{-1} for the entire series of I shows no evidence of any such characteristic absorption. We would expect a platinum–acetylene stretching mode to occur at a low frequency, since other evidence indicates a weak platinum–acetylene bond, and, furthermore, to be strongly coupled to other skeletal modes associated with the acetylene.

trans-$[PtCH_3(C_6H_5C\equiv CC(C_6H_5)_2OH)(P(CH_3)_2C_6H_5)_2]^+PF_6^-$ showed $\nu_{str}(OH)$ at 3535 ± 5 cm^{-1} consistent with that found for pure α,α,γ-triphenylpropargyl alcohol indicating little or no involvement of the hydroxyl group. This contrasts with the work of Chatt, *et al.*,[12] who found that the anionic complexes $acPtCl_3^-$, where ac was a disubstituted acetylene containing α-hydroxyl groups, showed $\nu_{str}(OH)$ reduced by 110–140 cm^{-1} from the frequency observed for the parent acetylene. However, they concluded from nmr studies that hydrogen bonding to chlorine was taking place and that there was no evidence for coordination to the platinum. The compounds I show infrared and Raman absorptions characteristic of $P(CH_3)_2C_6H_5$ and

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[10] P. J. D. Park and P. J. Hendra, *Spectrochim. Acta, Part A*, **25**, 227 (1969).

[11] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

[12] J. Chatt and R. G. Guy and (in part) L. A. Duncanson and D. T. Thompson, *ibid.*, 5170 (1963).

$As(CH_3)_3$,[13,14] and the presence of the octahedral PF_6^- ion is easily detected due to $\nu_3(f_{1u})$ at 850 cm^{-1} and $\nu_4(f_{1u})$ at 565 cm^{-1}, both of which appear as intense bands in the infrared spectra;[15] we also observed $\nu_1(a_{1g})$ at 741 cm^{-1} as a medium peak in the Raman spectra.[16]

Assignments of $\nu_{str}(C{\equiv}C)$ and $\nu_{str}(Pt{-}C)$ for a series of I are given in Table I.

^{1}H Nmr Spectra.—The phosphine methyl resonances of I, Q = $P(CH_3)_2C_6H_5$ and $RC{\equiv}CR'$ = $CH_3C{\equiv}CCH_3$, $CH_3C{\equiv}CC_2H_5$, and $C_2H_5C{\equiv}CC_2H_5$, appear as 1:2:1 triplets with platinum satellites (^{195}Pt 34% natural abundance, $I = {}^1/_2$), characteristic of mutually trans phosphine methyl groups in square-planar platinum(II) complexes.[17] When $RC{\equiv}CR'$ is $C_6H_5C{\equiv}CCH_3$, two sets of overlapping triplets appear due to inequivalent methyl protons. A similar splitting is observed[9] for alkoxycarbene complexes III, for $CH_3OCCH_2C_6H_5$ and $C_2H_5OCCH_2C_6H_5$. However, I for $C_6H_5C{\equiv}CCH_3$ shows a greater separation of the phosphine methyl resonances and some interesting patterns emerge. At 60 MHz (Figure 1A) the resonances appear as quartets with the downfield platinum satellite complicated by the methyl resonance of the acetylene. At 100 MHz (Figure 1B) a 1:2:2:2:5:8:8:8:5:2:2:2:1 "tredecet" appears due to a fortuitous overlapping of triplets. However, it is readily seen that the outer absorptions show irregularities in peak heights and some further splitting, which can only be attributed to differing values of J(PtPCH) for the two types of methyl protons, but it is not immediately obvious why this should arise. At 220 MHz (Figure 1C) the phosphine methyl resonances are clearly seen to arise from sets of overlapping triplets. The loss in resolution in going from 100 to 220 MHz precludes any further elucidation of the differing platinum–hydrogen coupling constants, but a lack of symmetry is still clearly present.

Previously[9] we considered that the splitting of the phosphine methyl resonances was entirely due to the absence of a σ plane of symmetry in the CH_3PtP_2 unit.[17] It may of course also be due to the containment of an unsymmetrical ligand within the CH_3PtP_2 plane, when a splitting would be expected due to inequivalent dimethylphenylphosphine groups, $P(CH_3)_2C_6H_5$ and $P'(CH_3)_2C_6H_5$. Thus, for all situations other than that where the unsymmetrical ligand is bound perpendicularly to the plane of the CH_3PtP_2 unit, one would expect *four* inequivalent methyl groups, $P(CH_3)(CH_3)'C_6H_5$ and $P'(CH_3)(CH_3)'C_6H_5$, which is not the case observed. It is hoped that ^{31}P nmr spectra will help to clarify the situation.

The platinum–methyl resonances of I are also characteristic of complexes of the form *trans*-$PtCH_3(L)Q_2^+$, *viz.*, when Q = $P(CH_3)_2C_6H_5$, a 1:2:1 triplet due to coupling with ^{31}P with further platinum satellites,[7] and when Q = $As(CH_3)_3$, a singlet with platinum satellites. In all our complexes I, J(PtCH) is in the range 74–78 Hz.

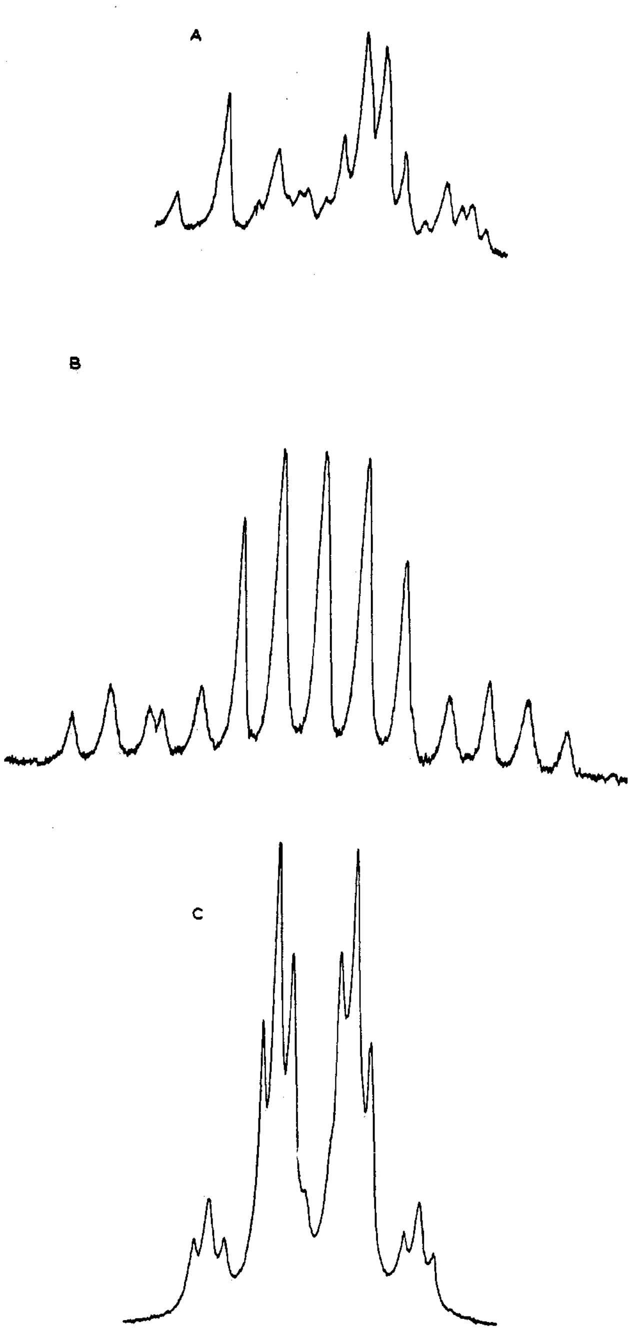

Figure 1.— ^{1}H nmr spectra of the phosphine–methyl proton resonances of *trans*-$[PtCH_3(C_6H_5C{\equiv}CCH_3)(P(CH_3)_2C_6H_5)_2]^+$-$PF_6^-$: A, at 60 MHz; B, at 100 MHz; C, at 220 MHz. Spectra recorded on CH_2Cl_2 solution at ~30°.

The methyl proton resonances of $CH_3C{\equiv}CCH_3$ and $C_6H_5C{\equiv}CCH_3$ appear as singlets with platinum satellites, J(PtH) = 18 Hz. The α methyl resonance of $CH_3C{\equiv}CC_2H_5$ also shows J(PtH) = 18 Hz but the resonance is further complicated due to coupling with the α acetylenic methylene group through the triple bond which gives a 1:2:1 triplet, $J(HH')$ = 1.4 Hz. The methylene protons of $CH_3CH_2C{\equiv}CCH_2CH_3$ appear as a quartet, $J(H^\alpha H^\beta)$ = 7.2 Hz, with further coupling to platinum, J(PtH) = 11.8 Hz. The methylene protons of $CH_3C{\equiv}CC_2H_5$ give extremely complicated resonances due to proton–proton coupling through the triple bond and with the adjacent methyl group, similar to those observed in the free acetylene. However, there is also coupling to platinum, but we have not been able to measure this. The hydroxyl proton of I, Q = $As(CH_3)_3$ and $RC{\equiv}CR'$ = $C_6H_5C{\equiv}$

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[13] R. J. Goodfellow, J. G. Evans, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc., A*, 1604 (1968).

[14] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Morton, and J. G. Smith, *ibid.*, 545 (1970).

[15] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1968.

[16] A. De Lettre, *J. Chem. Phys.*, **19**, 1610 (1951).

[17] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969).

TABLE II

PROTON NMR[a] FOR THE ACETYLENIC COMPLEXES *trans*-$[PtCH_3(L)Q_2]^+PF_6^-$

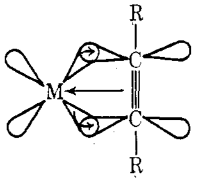
			Platinum-methyl			Q methyls				α acetylenic protons	
L	Q	Solvent	δ(CH_3)[b]	J(PtH)	J(PH)	δ(CH_3)[b]	J(PtH)	J(PH)[c]		δ(CH_2R)	J(PtH)
$CH_3C{\equiv}CCH_3$	$P(CH_3)_2C_6H_5$	CH_2Cl_2	−0.77	77.2	6.9	−1.76	29.7	7.1		−1.88	18.4
$CH_3C{\equiv}CC_2H_5$	$P(CH_3)_2C_6H_5$	CH_2Cl_2	−0.78	77.6	6.8	−1.77	30.1	7.0	CH_3 CH_2	−1.96 −2.16	18.4 e
$C_2H_5C{\equiv}CC_2H_5$	$P(CH_3)_2C_6H_5$	CH_2Cl_2	−0.76	76.0	6.9	−1.75	29.8	7.0		−2.21	11.8
$CH_3C{\equiv}CC_6H_5$	$P(CH_3)_2C_6H_5$	CH_2Cl_2	−0.97	76.3	6.8	−1.68 −1.74[d]	29.0	7.4		−2.15	17.8
$C_6H_5C{\equiv}CC(C_6H_5)_2OH$	$P(CH_3)_2C_6H_5$	CH_2Cl_2	−1.14	74.4	6.7	−1.62	29.6	6.9			
$C_6H_5C{\equiv}CC(C_6H_5)_2OH$	$As(CH_3)_3$	$CHCl_3$	−1.19	74.0		−1.22	21.5				
$C_6H_5C{\equiv}CC_6H_5$	$As(CH_3)_3$	$CHCl_3$	−1.23	73.5		−1.28	21.5				

[a] Chemical shifts (δ) in ppm from internal reference TMS; coupling constants (*J*) in Hz. All data recorded in CH_2Cl_2, at ~35° (probe temperature). All other expected resonances for phenyl protons were observed. [b] 1:2:1 triplets with platinum satellites unless otherwise stated. [c] $^2J(PH) + {}^4J(PH)$ is quoted: R. K. Harris, *Can. J. Chem.*, **42,** 2275 (1964). [d] See text and Figure 1. [e] Not observed; see text.

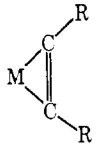
$CC(C_6H_5)_2OH$, appeared as a sharp resonance at δ −3.62 ppm in chloroform solution, and coupling to platinum was not observed.

The nmr spectra of I, Q = $P(CH_3)_2C_6H_5$ and $RC{\equiv}CR'$ = $CH_3C{\equiv}CCH_3$, $CH_3C{\equiv}CC_2H_5$, $C_2H_5C{=}CC_2H_5$, and $C_6H_5C{\equiv}CCH_3$, in acetone-d_6 are very complicated. Apart from relatively small changes in chemical shifts, the resonances of I obtained in dichloromethane were present with the same platinum–hydrogen coupling constants [most notable in this respect was J(PtH) = 18 Hz for the α acetylenic methyl protons]. However, free acetylene was present and a new platinum–methyl resonance appeared at δ −0.95 ppm with J(PtCH) = 90 Hz. Tentatively we assign this to the acetone complex *trans*-$[PtCH_3((CH_3)_2CO)(P(CH_3)_2C_6H_5)_2]^+PF_6^-$. The magnitude of J(PtCH) is of interest since it is appreciably larger than any reported earlier.[7] No new phosphine–methyl resonances were observed, although proton impurities in the acetone-d_6 partially obscured this region.

The Platinum–Acetylene Bond in I.—Much interest has been shown in developing models to describe the bonding in transition metal–acetylene complexes and this was enhanced by the emergency of two apparently different classes of compounds. Chatt, *et al.*,[18] suggested that the bonding might be described in two ways, IV and V. X-Ray structural determinations have



IV



V

allowed some complexes to be neatly labeled as type IV[19,20] or V,[21] although intermediate situations have been found.[22]

The complexes I may be classified under IV since (i) $\Delta\nu_{str}(C{\equiv}C) < 200\ cm^{-1}$ [$\Delta\nu_{str}(C{\equiv}C)$ is the difference in $\nu_{str}(C{\equiv}C)$ between the free and coordinated acetylene]; (ii) the near linearity of the acetylene is indicated by the absence of $\nu_{str}(C{\equiv}C)$ in the infrared spectra and the negligible change in polarizability of this band in the Raman spectra [relative to that of the free acetylene], (iii) the nmr of I where Q = $P(CH_3)_2C_6H_5$ and $RC{\equiv}CR'$ = $C_6H_5C{\equiv}CCH_3$ is consistent with the acetylene molecule perpendicular to the CH_3PtP_2 coordination plane [ignoring the slight variance of J(PtPCH) (Figure 1)], and (iv) the series I is isoeletronic with a series of complexes $(RC{\equiv}CR')PtCl_2L$[19,23] and $(RC{\equiv}CR')PtCl_2X$[12] already characterized as being of type IV.

Recently Maitlis, *et al.*,[24] suggested that the bonding in acetylene complexes could be considered as a function of the relative energies of the acetylenic π and π* orbitals and the metal valence electrons. They considered that five situations could reasonably be postulated to occur, A → E, in which the energy of the metal valence electrons decreases relative to the acetylenic π and π* orbitals. Their case D was compared to the classification under IV and they predicted weak interaction between the metal and the acetylene, the bonding orbital having mostly metal character and the antibonding orbital mostly acetylene. As a result the pair of electrons originally on the acetylene is transferred to the metal, with an effective positive charge residing on the acetylene. They predicted (i) that complexes of this type would be difficult to isolate since the bonding is only dative, (ii) that they should be stabilized by electron-donating substituents on the acetylene, and (iii) that they would be susceptible to nucleophilic attack at the acetylenic carbon atoms. It is interesting to note that we have only been able to isolate a series of I with specified Q [so that the metal orbital energies are fixed] when R and R′ are alkyl or aryl groups. When R and R′ = H or electron-withdrawing groups, products arising from nucleophilic attack at an acetylenic carbon atom are obtained, *viz.*, alkoxycarbene complexes III or vinyl ether complexes.

Our studies on I show $\nu_{str}(PtC)$ ~550 cm^{-1} (Table I) and J(PtCH) = ~76 Hz (Table II) for the platinum–methyl group which suggests that the acetylene ligand is exerting a weak trans influence.[25,26] [We assume that a correlation may be made between $\nu_{str}(PtC)$ and J(PtCH) for the platinum–methyl group and the trans influence of a ligand L in complexes of the form *trans*-

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(19) G. R. Davies, W. Hewertson, R. H. B. Mais, and P. G. Owston, *Chem. Commun.*, 423 (1967).

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(23) J. Chatt, R. G. Guy, and (in part) L. A. Duncanson, *J. Chem. Soc.*, 827 (1961).

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

(25) M. J. Church and M. J. Mays, *J. Chem. Soc. A*, 3074 (1968).

(26) A. Pidcock, R. E. Richards, and L. M. Venanzi, *ibid.*, *A*, 1707 (1966).

$PtCH_3(L)Q_2^+$ for reasons previously outlined.[9]] An interesting comparison may be made with the alkoxycarbene complexes III which show $\nu_{str}(PtC) \sim 518$ cm^{-1} and $J(PtCH) \sim 49$ Hz and where the carbene ligand is considered to exert a high trans influence. Acetylene and carbene ligands[27] can act as both σ donors and π acceptors and the Maitlis, *et al.*,[24] model for the bonding of acetylenic complexes may be extended to carbenes. Since, for complexes of the form *trans*-$[PtCH_3(L)Q_2]^+PF_6^-$, where L is an acetylene or carbene ligand, the symmetry requirements for both σ and π bonding are fulfilled, the strength of the bonds formed will be dependent on (i) the energies of the ligand orbitals involved in bonding and (ii) their overlap with the metal orbitals. We assume[28] that the relative energies of the orbitals concerned are in the order acetylene $\pi^* >$ carbene $p_z \sim$ acetylene $\pi >$ carbene $sp^2 \sim$ platinum(II) spd and that metal–ligand overlap is in the order carbene sp^2–platinum $dsp^2 >$ acetylene π–platinum dsp^2 and acetylene π^*–platinum d or dp $>$ carbene p_z–platinum d or dp. Consequently the platinum–carbene σ bond should be stronger from both "energy" and "overlap" considerations, with the bonding molecular orbital containing a considerable carbene sp^2 contribution. It is mostly this term which is reflected in $J(PtCH)$ and $\nu_{str}(PtC)$ of the *trans* platinum–methyl group and in the high trans influence of the carbene ligand.

Such naive arguments cannot readily be extended to the π bonding contribution since it is not obvious whether the "overlap" or the "relative energies" of the ligand and metal orbitals is the dominant factor. If π interaction makes a sizable contribution to the overall metal–ligand bond, the energy barrier to free rotation about the metal–acetylene or metal–carbene bond will be high. However, if this contribution to the bonding is weak, rotation will be possible and variable-temperature nmr studies might reveal this. We previously considered the situation for III and concluded that nmr studies were consistent with a rigid carbene ligand and that the phosphine methyl resonances were relatively insensitive to differing alkyl groups on the carbene. A similar situation is found for I since when $Q = P(CH_3)_2C_6H_5$ and $RC{\equiv}CR' = C_6H_5C{\equiv}CCH_3$ rotation is clearly absent (Figure 1), although for $CH_3C{\equiv}CC_2H_5$ the spectrum is consistent with free rotation. Furthermore, no temperature dependence is observed for these spectra in the range -60 to $+60°$. We expect a preferred conformation of I with the acetylene bound perpendicularly to the CH_3PtP_2 coordination plane and the equivalence of the phosphine methyl groups in the spectrum of I when $RC{\equiv}CR' = CH_3C{\equiv}C_2H_5$ probably arises from their accidental degeneracy.

The spectrum of I for $C_6H_5C{\equiv}CCH_3$ where $Q = P(CH_3)_2C_6H_5$, which is consistent with a rigid acetylene bound perpendicularly to the square plane of the CH_3PtP_2 unit, could arise from strong interaction or steric factors associated with the bulky acetylene or a combination of both these factors.

An indication of relative σ-donor, π-acceptor properties of a ligand, L, in a series *trans*-$PtCH_3(L)Q_2^+$ (VI) may be obtained from examination of $J(PtCH)$ for the platinum–methyl group and $J(PtPCH)$ for the phosphine methyl groups. $J(PtCH)$ and $J(PtPCH)$ for a series of VI are listed in Table III. If one accepts (i) that $J(PtCH)$ is dominated by σ-donor properties of L (as the σ-donor strength of L increases, the PtL bond gains s and d character and loses p character[29]) and (ii) that $J(PtPCH)$ reflects the total electron density on the platinum, then in addition to formulating a trans influence series we may also obtain an estimate of the relative π-acceptor properties of L. Thus alkoxycarbene and tertiary phosphine ligands show $J(PtCH) \approx 50$ and 57 Hz and $J(PtPCH) = 35$ and 29 Hz, respectively, which suggests that while both are strong σ donors, the phosphines are much better π acceptors. Similarly, a comparison between acetylenes and nitrogen donors, such as alkyl or aryl cyanides and pyridines, which show $J(PtCH) \approx 74$–80 Hz and $J(PtPCH) =$ 29 and 32 Hz, respectively, suggests that while they are all weak σ donors, the acetylenes are better π acceptors. Thus we conclude that $ROCR' \gg RC{\equiv}CR'$ in σ-donor strength and $RC{\equiv}CR' > ROCR'$ in π-acceptor strength. While this is derived for VI, the relationship should hold for other complexes. However, different metal valence orbital energies will alter the relative σ- and π-bonding contributions and so influence the formal oxidation state of the metal. Thus complexes of the form $PtQ_2(RC{\equiv}CR')$, where the π-bonding contribution is large, may be considered as formally platinum(II), type V. However, $(CO)_5M(ROCR')$ where M = Cr or W are still considered metal(0) complexes with the alkoxycarbene ligand acting as both a strong σ donor and a strong π acceptor—comparable to phosphines.[27] Changes in R and R′ may, however, alter this relationship and highly electron-withdrawing groups attached to acetylenes are known to increase its acceptor properties. An even more dramatic change would be expected in a metal–carbene bond in going from an alkoxycarbene to a dialkylcarbene. Although the latter are not known, one would predict a large increase in the acceptor properties of the carbene because of the absence of an adjacent p_π-donating atom.

TABLE III[a]

$J(PtCH)$ AND $J(PtPCH)$ FOR *trans*-$[PtCH_3(L)Q_2]^+PF_6^-$ ($Q = P(CH_3)_2C_6H_5$)

L	J(Pt-CH)	J(Pt-PCH)	L	J(Pt-CH)	J(Pt-PCH)
$CH_3OCCH_2C_6H_5$[b]	49	35.5	$As(C_6H_5)_3$	67	29
CH_3OCCH_3[b]	51	35.0	Pyridine	74	32
$Sb(C_6H_5)_3$	55	29	2,4,6-Trimethylpyridine	74	32
$P(CH_3)_2C_6H_5$	57	30	$CH_3C{\equiv}CCH_3$[c]	77	29
$P(OC_6H_5)_3$	58	31	CH_3CN	80	32
CO	63	33	$CH_2{\equiv}CHCN$	80	32

[a] Previously reported in ref 7 except where noted otherwise. Trans-influence, σ-donor strength decreases down the series $CH_3OCCH_2C_6H_5 \rightarrow CH_2{=}CHCN$. We suggest π-acceptor properties are in the order $Sb(C_6H_5)_3 > PR_3 \sim AsR_3 \sim CH_3C{\equiv}CCH_3 > P(OC_6H_5)_3 > CO \sim$ pyridines $\sim$ alkoxycarbenes. [b] Previously reported in ref 9. [c] Reported in this work.

Methyl Vinyl Ether Complexes.—Reactions based on (1) involving the disubstituted acetylenes $COOCH_3C{\equiv}CCOOCH_3$, $CH_2OHC{\equiv}CCH_2OH$, and $COOHC{\equiv}CCOOH$ led to noncrystalline products. Attempts to

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[27] M. Y. Darensbourg and D. J. Darensbourg, *Inorg. Chem.*, **9**, 32 (1970).

[28] By comparison with the Maitlis, *et al.*,[24] energy diagram for acetylene complexes of type IV (their case D).

[29] M. J. Church and M. J. Mays, *J. Chem. Soc. A*, 1938 (1970).

crystallize them from chloroform–ether or methanol–ether solutions gave oils which showed the presence of the oxygen-containing solvents in their nmr spectra. If these oils were dried under high vacuum at ~45°, pale yellow, light, fluffy solids were obtained. These did not melt sharply and showed signs of decomposition on heating. Their infrared spectra showed the presence of the PF_6^- ion, the ligand Q, and a strong absorption at *ca.* 1600 cm^{-1}. The nmr spectra of these solids in chloroform showed the absence of a platinum–methyl group, and gave complex phosphine methyl resonances and absorptions at ~−3.5 ppm. Reactions involving $CF_3C{\equiv}CCF_3$ led to the isolation of $[PtCH_3Q_3]^+PF_6^-$; even reaction of the known adduct[1−3] $(C_4F_6)PtClCH_3(As(CH_3)_3)_2$ with silver hexafluorophosphate gave this product. With a large excess of hexafluorobutyne in reaction 1, a product with similar properties to the above was also obtained. Initially we considered that the presence of the electron-withdrawing groups weakened the platinum–acetylene bond in I and that insertion to the platinum–methyl bond had subsequently occurred; this insertion had previously[1−3] been found in the reaction of fluoroolefins and -acetylenes with *trans*-$PtClCH_3Q_2$. This suggested that the products were cationic complexes of the form $[Pt(RC{=}CCH_3R')Q_2]^+PF_6^-$ and that the properties observed, *viz.*, the tendency to coordinate with donor solvents and the complex phosphine methyl resonance, were readily explained by the low formal coordination about the platinum. However, it was surprising that insertion to the platinum–methyl bond should take place so rapidly since reactions of II with fluoroolefins and -acetylenes indicated that this was a relatively slow process.[2,3] Consequently, we treated II with $COOCH_3C{\equiv}CCOOH_3$ (1 mol ratio) in methanol as solvent and isolated a white crystalline compound, mp 126–128°. The nmr spectrum in chloroform showed the absence of a platinum–methyl group, a complicated phosphine–methyl resonance pattern (similar to that shown in Figure 1), and three singlets at δ −3.32, −3.43, and −3.62 ppm. Integration showed these were equivalent to three methyl absorptions as would be expected for *trans*-$PtCl(COOCH_3C{=}CCH_3COOCH_3)(P(CH_3)_2C_6H_5)_2$. However, the absence of $J(PtC{=}CCH)$ and the chemical shift of the vinylic methyl group were inconsistent with that found[2] for *trans*-$PtCl(CF_3C{=}CCH_3CF_3)(P(CH_3)_2C_6H_5)_2$ where $J(PtC{=}CCH)$ = 15 Hz and $\delta(CH_3)$ is −1.95 ppm and suggested the possibility of methoxy insertion into the triple bond. Reaction of II with $COOCH_3C{\equiv}CCOOH_3$ in methanol-d_4 led to the isolation of a white crystalline compound, mp 126–128°, which gave no resonance at δ −3.32 ppm and so confirmed that methoxy insertion had occurred. This was also supported by the analytical data. We assign[30] the methoxy resonances in the group $PtC(COOCH_3{}^1){=}C(OCH_3{}^2)COOCH_3{}^3$: $\delta(CH_3{}^1)$ −3.43, $\delta(CH_3{}^2)$ −3.32, $\delta(CH_3{}^3)$ −3.62 ppm. Reaction of II with $CH_2OHC{\equiv}CCH_2OH$ in methanol was relatively slow and a pure compound has not been isolated from the reaction product, but nmr spectra indicated that reaction had proceeded in the same manner. This suggests that our reactions based on (1) are proceeding by the same mechanism and we should formulate the products as cationic methyl vinyl ether complexes; $[Pt(RC{=}C(OCH_3)R')Q_2]^+PF_6^-$.

Preliminary studies on reactions of II with acetylenes, $RC{\equiv}CH$, show that while reaction in benzene or chloroform solution does not take place, reaction in methanol proceeds quickly with the elimination of methane and loss of the platinum–methyl group. We believe these reactions proceed *via* cationic complexes in contrast to the previously established π-complex mechanism found in the reaction of II with fluoroolefins and -acetylenes in benzene and chloroform. The reaction may be represented by the equilibrium

$$\textit{trans}\text{-}PtClCH_3Q_2 + RC{\equiv}CR' \overset{CH_3OH}{\rightleftharpoons} \textit{trans}\text{-}[PtCH_3(RC{\equiv}CR')Q_2]^+Cl^- \quad (3)$$

While this equilibrium probably lies well to the left, the addition of silver hexafluorophosphate has allowed isolation of I and the stable alkoxycarbene complexes III depending on the nature of R and R′. It now appears that even in the absence of silver hexafluorophosphate the reaction can proceed to give neutral products which can be considered to be derived from the reaction of cationic acetylenic complexes with the solvent. A possible preparative route to vinyl ethers and other substituted olefins is also indicated, shown in (4), and is currently under investigation.

$$\begin{array}{c}\textit{trans}\text{-}PtClCH_3Q_2 + RC{\equiv}CR' \longrightarrow \textit{trans}\text{-}[PtCH_3(RC{\equiv}CR')Q_2]^+Cl^- \\ {\scriptstyle CH_3OH}\Big\downarrow \\ \textit{trans}\text{-}PtCl(RC{=}C(OCH_3)R')Q_2 + CH_4 \\ \Big\downarrow{\scriptstyle RC\equiv CR'} \\ \textit{trans}\text{-}[Pt(RC{=}C(OCH_3)R')(RC{\equiv}CR')Q_2]^+Cl^- \\ \Big\downarrow{\scriptstyle CH_3OH} \\ \textit{trans}\text{-}PtCl(RC{=}C(OCH_3)R')Q_2 + RCH{=}C(OCH_3)R' \end{array} \quad (4)$$

Experimental Section

The following chemicals were obtained commercially and were sufficiently pure for immediate use: K_2PtCl_4 from Johnson, Matthey and Mallory; $AgPF_6$ from Alfa Inorganics Inc.; $CH_3C{\equiv}CCH_3$, $CH_3C{\equiv}CC_2H_5$, $CH_3C{\equiv}CC_6H_5$, and $C_2H_5C{\equiv}CC_2H_5$ from Farchan Research Laboratories; $C_6H_5C{\equiv}CC_6H_5$, $C_6H_5C{\equiv}CC(C_6H_5)_2OH$, $COOHC{\equiv}CCOOH$, $CH_2OHC{\equiv}CCH_2OH$, and $COOCH_3C{\equiv}CCOOCH_3$ from Aldrich Chemical Co. *trans*-$PtClCH_3Q_2$, where Q = $P(CH_3)_2C_6H_5$ or $As(CH_3)_5$, was prepared by the method of Ruddick and Shaw.[17,31]

General methods have been described previously. The 220-MHz nmr spectra were obtained from the Canadian 220 MHz NMR Centre, Ontario Research Foundation, Sheridan Park, Ontario, Canada.

trans-**$[PtCH_3(RC{\equiv}CR')Q_2]^+PF_6^-$ (I)**.—Two general methods of preparation were adopted, depending on the volatility of the acetylene.

1. *trans*-**$[PtCH_3(CH_3C{\equiv}CCH_3)(P(CH_3)_2C_6H_5)_2{}^+PF_6^-$**.—The following method is similar for $RC{\equiv}CR'$ = $CH_3C{\equiv}CC_2H_5$ and $C_2H_5C{\equiv}CC_2H_5$. *trans*-$PtClCH_3(P(CH_3)_2C_6H_5)_2$ (0.3439 g) was dissolved in methanol (25 ml) at ~40°. To this solution under nitrogen was added $AgPF_6$ (0.166 g, 1 mol ratio) in methanol (5 ml) with stirring. A white precipitate of AgCl formed immediately. The solution was stirred vigorously for 5 min before filtering off the AgCl with a fine grade of filter paper. The colorless filtrate was collected and $CH_3C{\equiv}CCH_3$ (0.5 ml, ≫1 mol ratio) was added. The solution turned pale yellow and on cooling crystals formed. The solution was left in the refrigerator for 12 hr to promote further crystallization. The mother liquor was decanted and the crystals were washed with ether and dried *in vacuo*. Recrystallization from dichloromethane–ether gave

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(30) $\delta(CH_3{}^2)$ by reaction in methanol-d_4. $\delta(CH_3{}^1)$ and $\delta(CH_3{}^3)$ by a comparison of chemical shifts of other platinum–vinyl complexes. See ref 2 and H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, **89**, 533 (1967).

(31) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2964 (1969).

trans-$[PtCH_3(CH_3C{\equiv}CCH_3)(P(CH_3)_2C_6H_5)_2]^+PF_6^-$ (0.275 g, 61% theoretical yield) as a white crystalline solid, mp 150° dec.

2. *trans*-**$[PtCH_3(C_6H_5C{\equiv}CC(C_6H_5)_2OH)(As(CH_3)_3)_2]^+PF_6^-$.**—The following method is similar for $RC{\equiv}CR' = C_6H_5C{\equiv}C\text{-}C_6H_5$. *trans*-$PtClCH_3(As(CH_3)_3)_2$ (0.2447 g) was dissolved in methanol (15 ml) under nitrogen. To this solution $C_6H_5C{\equiv}CC(C_6H_5)_2OH$ (0.15 g, 1 mol ratio) was added followed by $AgPF_6$ (0.1269 g, 1 mol ratio) in methanol (15 ml) with stirring. A thick precipitate of AgCl formed instantaneously. After stirring the solution for 5 min to allow coagulation of the precipitate, the solution was filtered using a fine-grade filter paper, and the clear colorless filtrate was collected. Evaporation of the filtrate gave a yellow gum. This was dissolved in dichloromethane (1 ml) and passed through a short chromatography column (Florisil) eluting with dichloromethane. The pale yellow solution obtained was evaporated to a small volume (2 ml) and diethyl ether was slowly added dropwise with shaking. Pale yellow crystals formed and the solution was cooled in the refrigerator for 2 hr. The resulting fine yellow crystals were collected by filtration, washed with ether, and dried *in vacuo*. Recrystallization from chloroform–ether gave *trans*-$[PtCH_3(C_6H_5C{\equiv}CC(C_6H_5)_2OH(As(CH_3)_3]_2]^+PF_6^-$ (0.215 g, 60% theoretical yield) as pale yellow crystals, mp 145° dec.

trans-**$[PtCH_3(C_6H_5C{\equiv}CCH_3)(P(CH_3)_2C_6H_5)_2]^+PF_6^-$** was made by this method, but its low solubility in methanol allowed crystallization from the mother liquor and chromatography was not required.

$[PtCH_3(P(CH_3)_2C_6H_5)_3]^+PF_6^-$ from the Decomposition of $Pt\text{-}CH_3(CH_3OH)Q_2^+$.—*trans*-$PtClCH_3(P(CH_3)_2C_6H_5)_2$ (0.246 g) was dissolved in methanol (25 ml) at ~40° under nitrogen. To this solution $AgPF_6$ (0.1277 g, 1 mol ratio) in methanol (5 ml) was added with vigorous stirring. A white precipitate of AgCl formed instantaneously, and after stirring for 5 min this was removed by gravity filtration using a fine grade of filter paper. The clear colorless filtrate was collected and evaporated under reduced pressure. As the volume of solution was reduced (5 ml), the solution turned yellow and finally gave a brown gum. This was dissolved in dichloromethane (2 ml) and passed through a short chromatography column (Florisil) eluting with dichloromethane. This removed most of the color from the solution, but evaporation once more yielded a brown gum. The process was repeated until the solution was clear and showed no sign of further decomposition (colloidal platinum and organic decomposition products remained on the Florisil column from which they could not be removed). Addition of diethyl ether to a small volume of the dichloromethane solution allowed crystallization of $[PtCH_3(P(CH_3)_2C_6H_5)_3]^+PF_6^-$ (0.086 g) as a white crystalline solid, mp 153–155°. The compound was further characterized by nmr and ir which agreed with that previously reported.[7] **$[PtCH_3(As(CH_3)_2)_3]^+PF_6^-$** was obtained by an analogous reaction involving *trans*-$PtCH_3Cl(As(CH_3)_3)_2$ with $AgPF_6$ in methanol. This, however, was not previously reported. *Anal.* Calcd: C, 16.78; H, 4.22. Found: C, 17.02; H, 4.48. For the platinum–methyl group: $\nu_{str}(PtC)$ 526 cm^{-1} (Raman), $\delta(CH_3)$ −0.58 ppm, and $J(PtCH) = 63.0$ Hz. For the mutually trans $As(CH_3)_3$ ligands: $\delta(CH_3)$ −1.59 ppm and $J(PtAsCH) = 22.2$ Hz. For $As(CH_3)_3$ trans to methyl: $\delta(CH_3)$ −1.57 ppm and $J(PtAsCH) = 11.8$ Hz. The nmr data were obtained from a dichloromethane solution at 30°, 60 MHz.

Cationic Vinyl Ether Complexes. $[Pt(COOHC{=}C(OCH_3)\text{-}COOH)(P(CH_3)_2C_6H_5)_2]^+PF_6^-$.—This method is similar for complexes involving $COOCH_3CC{\equiv}COOCH_3$ and $CH_2OHC{\equiv}CCH_2OH$. *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ (0.345 g) was dissolved in methanol (25 ml) at ~45° under nitrogen. To this solution $COOHC{\equiv}CCOOH$ (0.0745 g, 1 mol ratio) was added, followed by $AgPF_6$ (0.167 g, 1 mol ratio) in methanol (5 ml). A thick precipitate of AgCl formed instantaneously. The solution was stirred for 10 min before removing the AgCl by gravity filtration using a fine-grade filter paper. The brown filtrate was collected and the solvent removed *in vacuo* to yield an orange gum. This was dissolved in dichloromethane (5 ml) and the solution was centrifuged to remove traces of platinum(0) and then passed through a Florisil column eluting with dichloromethane. This gave a yellow solution which deposited a yellow oil on adding ether or pentane. Similar attempts to crystallize from methanol–ether and chloroform–ether led to oils. On evaporation to dryness under high vacuum a pale yellow "fluffy" solid was obtained. This solid did not show a melting point but darkened above 90° and completely decomposed above 110°. *Anal.* Calcd for $[Pt(COOHC{=}C(OCH_3)COOH)(P(CH_3)_2\text{-}C_6H_5)_2]^+PF_6^-$: C, 33.11; H, 3.57. Found: C, 32.62; H, 3.50.

trans-**$PtCl(COOCH_3C{=}C(OCH_3)COOCH_3)(P(CH_3)_2C_6H_5)_2$.**—*trans*-$PtClCH_3(P(CH_3)_2C_6H_5)_2$ (0.402 g) was dissolved in methanol (30 ml) at ~40° under nitrogen, and to this solution $COOCH_3C{\equiv}CCOOCH_3$ (120 μl, 1 mol ratio) was added. The solution was magnetically stirred for 1 hr during which time it turned pale yellow. Evaporation of the solvent under reduced pressure gave an orange gum which was dried under high vacuum for 15 min at 30°. This was dissolved in benzene (1 ml) and passed through a short Florisil column eluting with benzene. The colorless solution obtained was evaporated *in vacuo* to give a colorless oil. The addition of diethyl ether to this oil initiated crystallization, and subsequent recrystallization from benzene–pentane and chloroform–ether–pentane solutions gave *trans*-$PtCl(COOCH_3C{=}C(OCH_3)COOCH_3)(P(CH_3)_2C_6H_5)_2$ (0.319 g, 60% theoretical yield) as a white crystalline solid, mp 126–128°. *Anal.* Calcd for $PtP_2C_{23}H_{31}O_4Cl$: C, 41.60; H, 4.71; Cl, 5.35. Found: C, 41.55; H, 4.56; Cl, 5.76.

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