as the temperature is lowered. This is most probably associated with the magnitudes of the P–P couplings in these complexes. The phenomenon of "virtual coupling" of phosphorus nuclei in square-planar trans complexes is well established,[9] but less is known of the magnitude of P–P couplings in tetrahedral or trigonal metal complexes. In the absence of any theoretical treatment of this problem, it may be that the P–P couplings for such geometries are still large, although certainly less than for square-planar complexes where the P–M–P angle is 180°. If the P–P coupling is sufficiently large[14] in tris(methyldiphenylphosphine)platinum, this alone might explain the nonobservance of proton–^{31}P coupling at low temperature. For the palladium compound, the loss of proton–^{31}P coupling at low temperatures may similarly be due to a reasonably large P–P coupling, further complicated in this case by a reduction in the rate of phosphine exchange[15] as the temperature is lowered.

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Cationic Acetylenic Platinum(II) Compounds and Their Derivatives. I. Alkoxycarbene Complexes

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

Introduction

Several types of cationic platinum(II) complexes have been described recently.[1–5] A study of the hydride resonances of complexes *trans*-$PtHL\{P(C_2H_5)_3\}_2^+$ revealed[2] a correlation between J(Pt–H) and the *trans* influence of the neutral ligand L. A similar trend of J(Pt–C–H) for the platinum–methyl resonances was observed[5] in a series *trans*-$PtCH_3L\{P(CH_3)_2C_6H_5\}_2^+$. The formation of the latter utilized the lability of the chloride ligand[6] in II which allowed chloride to be displaced by a strongly σ-donating ligand in the presence of a polar solvent such as methanol or acetone. Addition of a large anion such as PF_6^- or $B(C_6H_5)_4^-$ caused precipitation of the cationic species so formed. In the case where L was a weak σ donor, complete abstraction of the chloride could be achieved by the addition of the silver salt of the large anion.

Although cationic acetylenic complexes of platinum(II) are not unknown[7] $\{[PtX(en)(ac)]_n{}^+$ where $n = 1$ or 2, X = Cl, Br, or I, ac = $(CH_3)_2OHCC{\equiv}CC(CH_3)_2OH$, and en = ethylenediamine$\}$, a study of the reaction shown in eq 1 was undertaken with the intention of isolating III. The cationic acetylenic complexes III are ideally suited for examination by nmr spectroscopy since the presence of the trans methyl group allows a comparison of J(Pt–C–H) for various R and R′ with the values found[5] for the series *trans*-$PtCH_3LQ_2^+$.

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

$$(Q = P(CH_3)_2C_6H_5 \text{ or } As(CH_3)_3)$$

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

Results and Discussion

Reaction Conditions. Isolation of I.—The reaction of II with $RC{\equiv}CR'$ and silver hexafluorophosphate in a solvent is complex. A variety of products may be obtained depending upon the nature of R and R′, Q, and the solvent. Reactions involving II and some perfluoroacetylenes have already been described.[8] The reaction of II with silver hexafluorophosphate in methanol leads to the isolation of *trans*-$[PtCH_3Q_3]^+PF_6^-$, while in the absence of chloride ions silver hexafluorophosphate reacts with many acetylenes yielding brown precipitates. Thus cationic complexes *trans*-$[PtCl(L)Q_2]^+PF_6^-$, where L = $RC{\equiv}CR'$ or RCH_2COCH_3, cannot be prepared by a reaction analogous to eq 2 involving an acetylene instead of carbon monoxide.

$$cis\text{-}PtCl_2Q_2 + AgPF_6 + CO \xrightarrow[\text{acetone}]{\text{methanol}} trans\text{-}[PtCl(CO)Q_2]^+PF_6^- + AgCl \quad (2)$$

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

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TABLE I

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE ALKOXYCARBENE COMPLEXES *trans*-$[PtCH_3(L)Q_2]^+PF_6^-$

L	Q	Mp,[a] °C	Analysis, %				Solubilities[b]			Vibrational spectra, cm^{-1}	
			C		H					Platinum methyl	Carbene
			Calcd	Found	Calcd	Found	$(CH_3)_2CO$	$CHCl_3$	$(C_2H_5)_2O$	$\nu_{str}(Pt–C)$[c]	$\nu_{str}(C–O)$[d]
CH_3OCCH_3	$P(CH_3)_2C_6H_5$	148–150	34.83	34.39	4.49	4.22	VS	S	I	514	1305
CH_3OCCH_3	$As(CH_3)_3$	170–172	18.38	18.33	4.17	4.18	VS	VS	I	514	1315
$C_2H_5OCCH_3$	$P(CH_3)_2C_6H_5$	152–154	35.85	35.80	4.73	4.81	VS	S	I	519	1310
$C_2H_5OCCH_3$	$As(CH_3)_3$	170–172	19.79	19.65	4.38	4.52	VS	VS	I	523	1315
$CH_3OCC_2H_5$	$P(CH_3)_2C_6H_5$	155	35.85	36.01	4.73	4.60	VS	S	I	521	1300
$CH_3OCC_2H_5$	$As(CH_3)_3$	140	19.79	19.76	4.38	4.23	VS	VS	I	516	1310
$CH_3OC\text{-}n\text{-}C_3H_7$	$P(CH_3)_2C_6H_5$	148–149	36.82	36.84	4.92	4.81	VS	S	I	516	1300
$CH_3OC\text{-}n\text{-}C_3H_7$	$As(CH_3)_3$	150	21.14	21.42	4.59	4.46	VS	VS	I	519	1310
$CH_3OC\text{-}n\text{-}C_4H_9$	$P(CH_3)_2C_6H_5$	136	37.75	37.91	5.10	5.02	VS	VS	I	523	1305
$CH_3OC\text{-}n\text{-}C_4H_9$	$As(CH_3)_3$	125–126	22.45	22.57	4.78	4.64	VS	VS	I	516	1310
$CH_3OC\text{-}n\text{-}C_5H_{11}$	$P(CH_3)_2C_6H_{11}$	120–122	38.65	38.55	5.27	5.28	VS	VS	SS	514	1290
$CH_3OC\text{-}n\text{-}C_5H_{11}$	$As(CH_3)_3$	100	23.70	23.91	4.94	5.29	VS	VS	SS	514	1310
$CH_3OCCH_2\text{-}c\text{-}C_6H_{11}$	$P(CH_3)_2C_6H_{11}$	114	40.46	41.15	5.36	5.24	VS	VS	I	514	1300
$CH_3OCCH_2\text{-}c\text{-}C_6H_{11}$	$As(CH_3)_3$	152	26.12	26.16	5.07	5.20	VS	VS	SS	516	1320
$CH_3OCCH_2C_6H_5$	$P(CH_3)_2C_6H_5$	150	40.79	41.29	4.57	4.36	VS	S	I	526	1290
$C_2H_5OCCH_2C_6H_5$	$P(CH_3)_2C_6H_5$	185–190	41.59	41.72	4.79	4.81	S	SS	I	516	1290
$\overline{CH_2CH_2COCH_2}$	$P(CH_3)_2C_6H_5$	155	35.94	35.97	4.41	4.31	VS	S	I	523	1260
$\overline{CH_2CH_2COCH_2}$	$As(CH_3)_3$	153–155	19.84	19.60	4.06	4.08	VS	S	I	514	1255

[a] Accompanied by decomposition. [b] Abbreviations: VS, very soluble, >100 mg ml^{-1}; S, soluble, >50 mg ml^{-1}; SS, slightly soluble, >5 mg ml^{-1}; I, insoluble, <5 mg ml^{-1}. All compounds are insoluble in nonpolar organic solvents. [c] Raman values ±2 cm^{-1}. [d] Infrared values ±5 cm^{-1}.

TABLE II

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

L	Q	Solvent[b]	Platinum methyls			Q Methyls			α-Alkoxy protons		α-Carbene protons	
			δ(CH_3)[c]	J(Pt–H)	J(P–H)	δ(CH_3)[c]	J(Pt–H)	J(P–H)[e]	δ(OCH_2R)[f]	J(Pt–H)	δ(CH_2R)[f]	J(Pt–H)
CH_3OCCH_3	$P(CH_3)_2C_6H_5$	D	−0.12	51.0	9.0	−1.90	35.0	7.5	−4.94 s	7.0	−2.48 s	6.0
CH_3OCCH_3	$As(CH_3)_3$	C	−0.11	48.5	...	−1.51	25.5	...	−4.86 s	6.0	−2.55 s	6.0
$C_2H_5OCCH_3$	$P(CH_3)_2C_6H_5$	C	−0.18	48.5	8.5	−1.80	34.0	7.0	−5.15 q	7.5	−2.48 s	6.0
$C_2H_5OCCH_3$	$As(CH_3)_3$	C	−0.12	48.0	...	−1.52	25.0	...	−5.20 q	7.0	−2.55 s	6.0
$CH_3OCC_2H_5$	$P(CH_3)_2C_6H_5$	C	−0.16	49.0	8.7	−1.79	35.5	7.0	−4.75 s	7.0	−2.40 q	(5?)
$CH_3OCC_2H_5$	$As(CH_3)_3$	C	−0.14	48.0	...	−1.52	25.5	...	−4.80 s	7.0	−2.68 q	7.0
$CH_3OC\text{-}n\text{-}C_3H_7$	$P(CH_3)_2C_6H_5$	C	−0.15	48.5	8.5	−1.80	35.0	7.5	−4.80 s	7.0	−2.28 t, br	(5?)
$CH_3OC\text{-}n\text{-}C_3H_7$	$As(CH_3)_3$	C	−0.14	47.5	...	−1.50	25.5	...	−4.78 s	6.0	−2.78 t	g
$CH_3OC\text{-}n\text{-}C_4H_9$	$P(CH_3)_2C_6H_5$	C	−0.18	49.0	8.8	−1.78	35.0	7.0	−4.78 s	7.0	−2.28 t	g
$CH_3OC\text{-}n\text{-}C_4H_9$	$As(CH_3)_3$	C	−0.16	47.0	...	−1.55	25.5	...	−4.79 s	6.5	−2.48 t	7.0
$CH_3OC\text{-}n\text{-}C_5H_{11}$	$P(CH_3)_2C_6H_5$	C	−0.16	48.5	8.7	−1.82	35.0	7.0	−4.81 s	7.0	−2.30 t, br	g
$CH_3OC\text{-}n\text{-}C_5H_{11}$	$As(CH_3)_3$	C	−0.10	48.0	...	−1.50	25.5	...	−4.82 s	7.0	−2.50 br	g
$CH_3OCCH_2\text{-}c\text{-}C_6H_{11}$	$P(CH_3)_2C_6H_5$	D	−0.14	48.5	8.5	−1.90	35.0	7.5	−5.00 s	7.0	−2.60 d	g
$CH_3OCCH_2\text{-}c\text{-}C_6H_{11}$	$As(CH_3)_3$	C	−0.11	47.5	...	−1.50	25.5	...	−4.80 s	6.0	−2.50 d	(6?)
$CH_3OCCH_2C_6H_5$	$P(CH_3)_2C_6H_5$	D	−0.12	49.0	8.7	−1.80	35.5[d]	7.5	−4.04 s	7.0	−4.02 br	g
$C_2H_5OCCH_2C_6H_5$	$P(CH_3)_2C_6H_5$	D	−0.10	49.0	9.0	−1.78	36.0[d]	7.0	−5.18 q	7.0	−4.05 br	g
$\overline{CH_2CH_2COCH_2}$	$P(CH_3)_2C_6H_5$	D	−0.10	51.0	8.5	−1.86	34.0	7.0	−4.86 t	8.0	−2.90 t	g
$\overline{CH_2CH_2COCH_2}$	$As(CH_3)_3$	D	−0.18	49.0	...	−1.55	24.5	...	−5.25 t	g	−3.25 t	g

[a] Chemical shifts (δ) in ppm from internal reference TMS coupling constants (J) in Hz. All data recorded at ∼35° (probe temperature). All other expected resonances for phenyl and alkyl protons were observed. [b] C, chloroform; D, deuterioacetone. [c] 1:2:1 triplets with platinum satellites unless otherwise stated. [d] Pseudo quartets; see text and Figure 2. [e] $^2J(P–H) + {}^4J(P–H)$: R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964). [f] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. All resonances also show platinum coupling. [g] Not clearly resolved.

chloride was removed by filtration and the filtrate was evaporated under reduced pressure. In several instances a reduction in volume led to the precipitation of I, and addition of diethyl ether further enhanced this. In certain cases, however, evaporation led to the formation of yellow oils or gums. Subsequent short-column chromatography (Florisil–methylene dichloride) removed organic tars and/or colloidal platinum, thus allowing crystallization from chloroform–ether or dichloromethane–ether solutions. Purification by recrystallization from methanol–ether or dichloromethane–ether solutions gave the carbene complexes (I) as white crystalline solids. They are relatively stable to the atmosphere: melting points of I where Q = $P(CH_3)_2C_6H_5$ and $As(CH_3)_3$ remain constant for periods of 4 and 1 weeks, respectively. Slow decomposition of I occurred in chloroform and dichloromethane, although this was not found to invalidate their use as solvents for nmr spectroscopy. Analytical data and other characterization data are presented in Table I.

Spectroscopic Characterization of I.—The complexes I show neither an infrared nor a Raman absorption assignable to $\nu_{str}(C{\equiv}C)$ in the region 2100–1600 cm^{-1}, in marked contrast to the acetylenic complexes III which show[9] a strong polarizable band in the Raman spectra in the region 2000–2150 cm^{-1}. Reactions undertaken in methanol led to an absorption in the ^1H nmr spectrum in the region δ −4.70 to −5.00 ppm (from TMS internal reference). This absorption appeared as a singlet (equivalent to three protons) with satellites due to coupling with ^{195}Pt ($I = {}^1/_2$, natural

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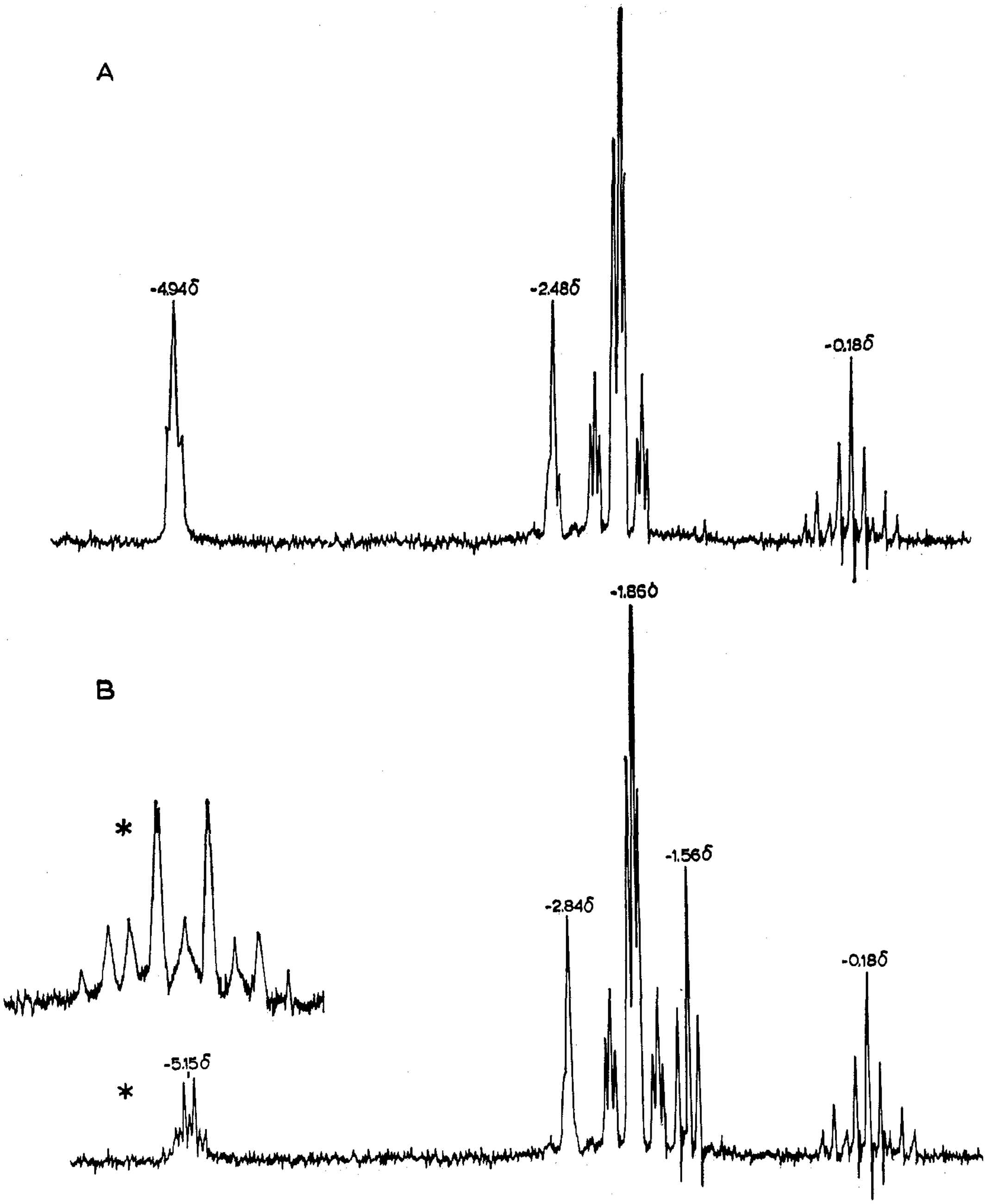

Figure 1.—The ^{1}H nmr spectra recorded in perdeuterioacetone at 30° on an HA-100 spectrometer: A, *trans*-[PtCH$_3$(CH$_3$OCCH$_3$){P(CH$_3$)$_2$C$_6$H$_5$}$_2$]$^+$PF$_6^-$; B, *trans*-[PtCH$_3$(C$_2$H$_5$OCCH$_3$){P(CH$_3$)$_2$C$_6$H$_5$}$_2$]$^+$PF$_6^-$; *, sweep width $\times \sim 5$.

abundance 34%), J(PtH) = 7 Hz (see Figure 1). Reactions carried out in ethanol gave a more complicated absorption in this region (equivalent to two protons) which could be seen to be a 1:3:3:1 quartet, J (HH′) $\approx$ 7 Hz, with further coupling to ^{195}Pt, J(PtH) $\approx$ 7 Hz (see Figure 1). A 1:2:1 triplet (equivalent to three protons) was found at $\delta \sim -1.50$ ppm with J(HH′) $\approx$ 7 Hz. No coupling to ^{195}Pt was observed and double resonance confirmed the presence of an ethyl group. Reactions involving C$_2$H$_2$ gave a broad singlet (equivalent to three protons), δ *ca.* -2.50 ppm, with poorly resolved platinum satellites, J(PtH) $\approx$ 7 Hz (see Figure 1). Reactions involving the monosubstituted acetylenes, RC≡CH, all led to absorptions equivalent to two protons in this region. The nature of the absorption was dependent on the alkyl group; *e.g.*, methylacetylene led to a 1:3:3:1 quartet, cyclohexylacetylene to a doublet, and phenylacetylene to a singlet. All absorptions were further broadened due to coupling with ^{195}Pt. The ^{1}H nmr data are consistent with the addition of the alcohol to the acetylene as in R′C≡CH + ROH → R′CH$_2$COR, and we assign the absorptions at δ *ca.* -5.00 to -4.75 ppm to the α-alkoxy protons, OCH$_2$R, and at δ *ca.* ~ -2.50 ppm to the α-carbene protons, CCH$_2$R′. Thus, our ^{1}H nmr data closely resemble those originally reported[10,11] for the carbene complexes (CO)$_5$MC(OR)R′ where M = Cr or W, R = CH$_3$ or C$_2$H$_5$, and R′ = C$_6$H$_5$ or CH$_3$. The ^{1}H nmr data for a series of I are presented in Table II.

Identification of the carbene group in the infrared and Raman spectra is difficult, although a strong in-

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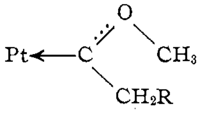
[10] E. O. Fischer and A. Maasböl, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964).

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

frared absorption at *ca.* 1300 cm^{-1} is considered to be ν_{str}(C–O).[10] All of our compounds show infrared and Raman absorptions characteristic of $P(CH_3)_2C_6H_5$ and $As(CH_3)_3$[12,13] and the presence of the octahedral PF_6^- ion is easily detected due to ν_3 (f_{1u}) at 850 cm^{-1} and ν_4 (f_{1u}) at 565 cm^{-1}, both of which appear as intense bands in the infrared spectra;[14] we also observe ν_1 (a_{1g}) at 741 cm^{-1} as a medium peak[15] in the Raman spectra. An absorption in the region 524–510 cm^{-1}, strong and polarizable in the Raman and weak in the infrared spectrum, is assigned to ν_{str}(Pt–C) for the platinum methyl group, although some coupling with other vibrational modes is possible, and it is unlikely to be a pure mode. Assignment of a band associated with ν_{str}(Pt–C) for the platinum–carbene carbon bond in the region 600–200 cm^{-1} is not possible at present. However, it is hoped that by a comparison with the vibrational spectra of *trans*-$PtX(L)Q_2^+$ where L = alkoxycarbene and X = halogen, further elucidication of this point will be possible. The proposed assignments for ν_{str}(C–O) and ν_{str}(Pt–C) are listed in Table I along with other characterization data.

The Nature of the Platinum–Carbene Bond.—X-Ray structural studies of alkoxy-[16,17] and aminocarbene[18,19] complexes have shown the stereochemistry about the carbene carbon atom to be planar. The carbon atom may be considered to be sp^2 hybridized, with a vacant p_z orbital capable of accepting electron density from either the metal or oxygen–nitrogen π orbitals. In complexes I the formal positive charge on the platinum is delocalized over the Pt$\cdots$C$\cdots$O bonds and this is probably reflected in the large long-range coupling: J(Pt–C–O–CH_2R) ≈ 7 Hz. Such coupling is not observed in the alkoxy- or aminocarbenetungsten pentacarbonyl compounds,[16,18] presumably because of the gyromagnetic ratio of $^{195}Pt > {}^{183}W$.[20] Complexes I do not show any homoallylic coupling and this suggests that the carbene ligand is in the cis isomer[21,22]



[(CH_3OCCH_3)W(CO)$_5$ which contains the trans isomer of the methoxymethylcarbene ligand shows J(CH_3–O–C–CH_3) ≈ 0.4 Hz and similar long-range couplings are found for ($C_2H_5OCCH_3$)W(CO)$_5$[11] and (RNHC-CH_3)Cr(CO)$_5$.[23,24]] It could, however, mean a decrease of the long-range coupling due to less C–O–R π bonding in I than in (CH_3OCCH_3)W(CO)$_5$, although the higher ν_{str}(C–O) frequency and lower value of δ(–OCH_3) in the ^{1}H nmr spectra of I indicate the contrary.

Recent spectroscopic studies of alkoxycarbenepentacarbonylchromium(0) and -tungsten(0) compounds suggest that the carbene ligand is comparable to phosphines in σ-donor strength and is a much better σ donor than a carbonyl ligand; at the same time they behave as strong π acceptors. Thus the alkoxyaminocarbene complexes of platinum(II)[19] and palladium(II)[24] and I might be expected to show "strong" and "stable" metal–carbene bonds. A preliminary study of the reactions of I shows that the α, α-addition properties associated with the carbene radical are not present. Reaction with HX (1 molar ratio) led to the isolation of *trans*-$[PtX(L)Q_2]^+PF_6^-$, where X = Cl or Br and L = CH_2CH_2C–OCH_2, accompanied by elimination of methane, while less protic acids C_6H_5OH and C_6H_5SH gave no reaction. No reaction was observed with CH_3COCl which suggests that I show the characteristic reluctance of cationic platinum(II) complexes to undergo oxidative addition reactions.[5]

Elucidation of the stereochemistry of complexes I, where Q = $P(CH_3)_2C_6H_5$, comes from the ^{1}H nmr spectra of the phosphine methyl protons. When the alkoxycarbene is CH_3OCCH_3, $C_2H_5OCCH_3$, $CH_3OCC_2H_5$, $CH_2CH_2COCH_2$, CH_3OC-*n*-C_3H_7, or CH_3OC-*n*-C_4H_9, a 1:2:1 triplet with platinum satellites is observed, characteristic of mutually trans phosphine methyl protons in square-planar platinum(II) complexes.[25] For CH_3OC-*n*-C_5H_{11}, CH_3OCCH_2-*c*-C_6H_{11}, $CH_3OCCH_2C_6H_5$, and $C_2H_5OCCH_2C_6H_5$ two sets of overlapping triplets are observed due to inequivalent methyl protons, $P(CH_3)(CH_3)'C_6H_5$, caused by the absence of the σ plane of symmetry[25] containing the Pt-C_2P_2 unit. Since the symmetry of I is low and a certain degree of d_π–p_π bonding is expected in the platinum–carbene bond, a preferred conformer is probable and free rotation about the platinum–carbene bond may be restricted by other than steric factors.[26] Variable-temperature ^{1}H nmr studies (+60 to −60°) on I for CH_3OCCH_3, $CH_2CH_2COCH_2$, and CH_3OC-*n*-C_5H_{11} showed no change in the phosphine methyl patterns from the respective room-temperature spectra, and consequently we consider that the 1:2:1 triplet pattern of the phosphine methyl protons arises from accidental magnetic degeneracy. This is supported by the fact that the carbene complexes of CH_3OCCH_2-*c*-C_6H_{11} and $CH_3OCCH_2C_6H_5$ show greatly different phosphine methyl patterns (see Figure 2) although their steric influence is expected to be almost identical. Thus it seems that the phosphine methyl proton resonances are relatively insensitive to changes in the alkyl group of the carbene CH_3OCR, whereas the phenyl group in $CH_3OCCH_2C_6H_5$ produces a more dramatic effect (presumably because of the magnetic influence of the delocalized π system).

A trans-influence series[2] has been formulated by

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[26] The ethoxy(phenylaminc)carbene complex of platinum(II)[19] has the carbene group perpendicular to the coordination plane of the platinum complex. It is not obvious, however, whether this is a result of platinum–carbene π bonding or steric factors and crystal-packing forces. The significance of π bonding in I is the subject of further discussion in part II of this series (submitted for publication) in which a comparison is made with the platinum–acetylene bond in III. The existence of free rotation about the platinum–carbene bond is currently under investigation.

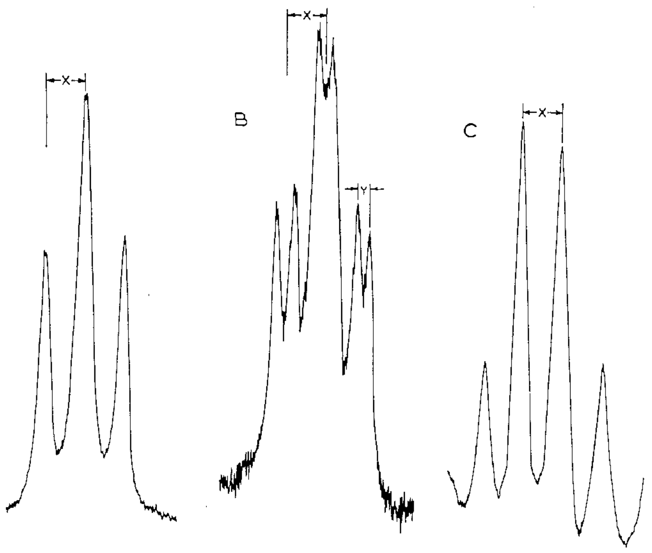
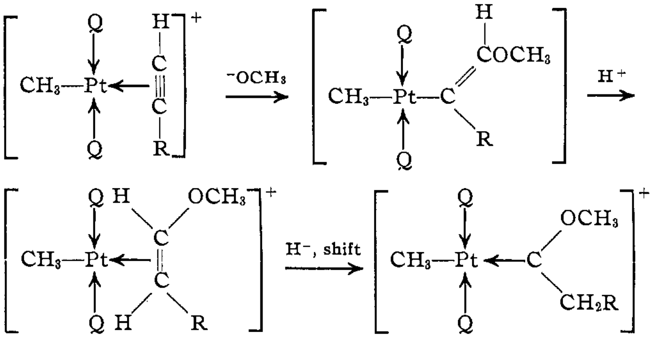


Figure 2.—The ^1H nmr resonances for the phosphine methyl protons of *trans*-$[PtCH_3(L)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$ recorded at 30° on HA-100 (A and B) and A-60 (C) spectrometers. Platinum side bands are not shown: (A) L = CH_3OCCH_3, $C_2H_5OCCH_3$, $CH_3OCC_2H_5$, CH_3OC-*n*-C_3H_7, CH_3OC-*n*-C_4H_9, and $CH_2OCCH_2CH_2$; $X \simeq 3.5$ Hz; (B) L = CH_3OC-*n*-C_5H_{11} and CH_3OCCH_2-*c*-C_6H_{11}; $X \simeq 3.5$ Hz, $Y \leq 1.5$ Hz; (C) L = $CH_3OCCH_2C_6H_5$ and $C_2H_5OCCH_2C_6H_5$; $X \simeq 3.5$ Hz.

adopting the definition of trans influence given by Pidcock, Richards, and Venanzi[27] (*viz.*, the tendency of a ligand to weaken the bond trans to itself) and by making the usual assumption that stretching frequency correlates with bond strength. For a series L–M–Cl an increase in σ-donor ability of L produces a decrease in ν_{str}(M–Cl).[2] Studies of a series *trans*-$PtHX(PR_3)_2^+$ show that J(Pt–H) increases as the σ-donor ability of X decreases. A similar trend is observed for J(Pt–C–H) of the platinum methyl group in a series *trans*-$PtCH_3X(PR_3)_2$[28] and *trans*-$PtCH_3(L)\{P(CH_3)_2C_6H_5\}^+$.[5] While factors associated with indirect couplings[29] such as J(Pt–C–H) are much less clear than those for direct couplings,[30] a semiempirical equation has been used for J(X–C–H) in which coupling is assumed to be directly proportional to the "s" character of the hybrid of X used in the X–C bond.[31] Our studies of I show ν_{str}(Pt–C) in the range 514–525 cm^{-1}, and J(Pt–C–H) = 48–51 Hz for the platinum methyl group which suggests that the alkoxycarbene group is exerting a very high trans influence. Such low values of ν_{str}(Pt–C) and J(Pt–C–H) are comparable to those found in platinum(IV) compounds with methyl trans to methyl.[25,32] This may be understood in terms of a σ-donor effect (the sp^2 carbene carbon atom acts as a strong donor[11]) since a rehybridization of platinum σ orbitals is believed to take place in response to changes in orbitals on the ligand used in σ bonding;[33] however, the effect of the vacant p_z orbital and the resultant d_π–p_π interaction is less clear. For carbon trans to carbon one would expect a large mutual trans influence and it is noteworthy that for *trans*-$PtX(\overline{CH_2CH_2COCH_2})\{P(CH_3)_2(C_6H_5\}_2^+$, J(Pt–C–O–CH_2) = 7 and 14 Hz when X = CH_3 and Cl, respectively. Recently a high trans influence has been suggested for the methoxyaminocarbene ligand in *cis*-$PtCl_2(RNC)(RNHCOCH_3)$ (R = *p*-tolyl, cyclohexyl) on the evidence of a lower ν_{str}(Pt–Cl) frequency than that found in the parent isocyanide complex *cis*-$Pt(RNC)_2Cl_2$.[34]

Mechanism of the Formation of I.—The complex nature of reaction 1 has already been mentioned, and, in addition to I, cationic acetylenic (III) and acetylide complexes have also been isolated.[9] Although several alkoxycarbene complexes are reported here the general reaction involving RC≡CH and R′OH does not always yield I with the formation of RCH_2COR'. An increase in chain length of the acetylene leads to the isolation of oils from which crystallization of I is difficult. Furthermore the formation of I is favored ($CH_3OH > C_2H_5OH$), and reactions involving C_2H_2 and *n*-propyl, isopropyl, and *tert*-butyl alcohols as solvents did not yield the corresponding alkoxycarbene complexes.

Although steric factors associated with the bulky *tert*-butyl and isopropyl groups might hinder the formation of I, the dramatic difference between 1-propanol and ethanol suggests this is not the dominant factor. We believe the formation of I takes place *via* nucleophilic attack of the cationic acetylenic complex *trans*-$PtCH_3(RC{\equiv}CH)Q_2^+$ followed by a hydride shift rearrangement. A schematic route is



Nucleophilic attack of C=C groups bound to platinum and palladium is well known[35] and recently the formation of σ Pt–C bonded complexes from both coordinated and uncoordinated olefins and acetylenes has been reported.[36,37] Our suggested mechanism proceeds *via* the formation of a cationic vinyl ether complex which rearranges by a hydride shift to yield I. Clearly only for monosubstituted acetylenes is this possible, and reactions involving disubstituted acetylenes have led to the isolation of III rather than I derived by an alkyl or aryl shift. Attempts to isolate I from the reaction *trans*-$PtClCH_3Q_2$ + $CH_2{=}CHOC_2H_5$ + $AgPF_6$ failed, and only the cation *trans*-$PtCH_3Q_3^+$ was characterized. This does not, however, disprove a mechanism proceeding *via* a cationic vinyl ether complex. The rate-controlling step in the formation of I is believed to be the nucleophilic attack of *trans*-$PtCH_3(RC{\equiv}CH)Q_2^+$ by the alcohol. Thus reaction involving 1-butyne-4-ol, $CH{\equiv}CCH_2CH_2OH$, led to the isolation of the cyclic carbene complex *trans*-$[PtCH_3(\overline{CH_2CH_2COCH_2})Q_2]^+$-

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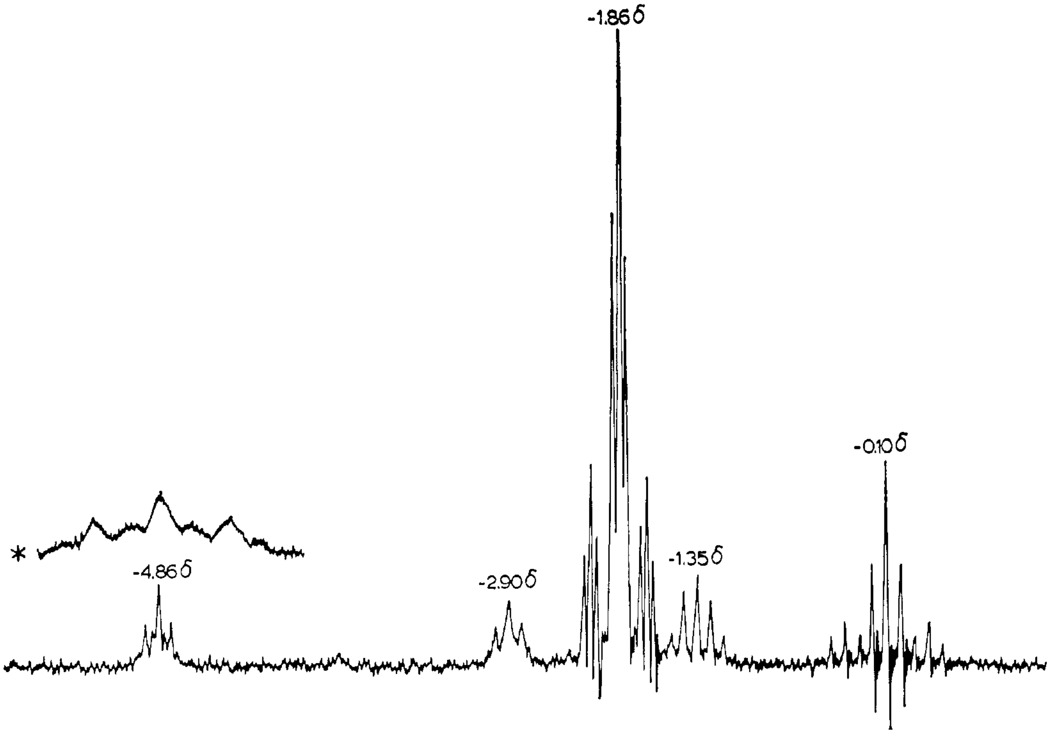

Figure 3.—The ^1H nmr spectrum of *trans*-$[PtCH_3(\overline{CH_2OCCH_2C}H_2)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$ recorded in $CHCl_3$ at 30° on an HA-100 spectrometer, showing the cyclic nature of the carbene ligand; *, sweep width × ∼5.

PF_6^- (see Figure 3 for ^1H nmr spectrum). In the presence of methanol as solvent some *trans*-$PtCH_3(CH_3OCCH_2CH_2CH_2OH)Q_2^+$ would be expected. (A reaction mechanism proceeding *via* formation of the latter followed by cyclization and elimination of methanol is considered unlikely since ethoxycarbene complexes (I) appear quite stable to methanol.) Reactions involving propargyl alcohol, $CH{\equiv}CCH_2OH$, led to rapid decomposition and the deposition of platinum metal, possibly due to the instability of a four-membered carbene ring. Reaction with trifluoropropyne, $CF_3C{\equiv}CH$, gave an unstable and as yet uncharacterized cationic product, although ^1H nmr and infrared spectra show the absence of the platinum methyl group and the presence of an olefinic group, $\nu_{str}(C{=}C)$ 1610 cm^{-1}.

A similarity may be seen between our suggested mechanism for the formation of I and that proposed for the oxidation of ethylene to acetaldehyde in the presence of $PdCl_2$[35] (the Wacker process). However, other mechanisms are also possible and it is hoped that the study of the reactivity of cationic acetylenic complexes of platinum(II) currently in progress will help to clarify this situation.

Experimental Section

The following chemicals were obtained commercially and were sufficiently pure to be used without further purification: K_2PtCl_4 from Johnson, Matthey and Mallory; $AgPF_6$ from Alfa Inorganics Inc.; C_2H_2 and $CH_3C{\equiv}CH$ from Matheson Ltd.; $C_2H_5C{\equiv}CH$, n-$C_3H_7C{\equiv}CH$, and n-$C_4H_9C{\equiv}CH$ from Farchan Research Laboratories; $C_6H_5C{\equiv}CH$ from Matheson Coleman and Bell; $CH{\equiv}CCH_2OH$, $CH{\equiv}CCH_2CH_2OH$, and c-$C_6H_{11}C{\equiv}CH$ from Aldrich Chemical Co. $CF_3C{\equiv}CH$ was prepared by the method of Finnegan and Norris.[38]

Infrared spectra were recorded on Beckman-IR10 and IR5 spectrophotometers and obtained from Nujol mulls between cesium iodide plates.

Raman spectra were obtained from crystalline samples in capillary tubes using a Spex Model 1400 spectrometer with the 6328-Å line of the helium–neon laser as source. Polarizability measurements were done in chloroform solutions. The complexes I were prone to decompose in the laser beam, especially if trace impurities produced a discoloration of the sample.

Proton nmr spectra were recorded on Varian T-60, A-60, and HA-100 spectrometers; variable-temperature studies were carried out in chloroform and dichloromethane solutions on the HA-100 spectrometer.

trans-$PtClCH_3Q_2$, where Q = $P(CH_3)_2C_6H_5$ or $As(CH_3)_3$, was prepared by the method of Ruddick and Shaw.[25,32]

All reactions were carried out under oxygen-free, dried nitrogen using standard Quickfit apparatus. Spectrograde solvents were used after the appropriate drying procedures had been employed.

The general method of preparation of I has already been outlined and therefore we describe only one preparation in detail.

***trans*-$\{PtCH_3(\overline{CH_2CH_2COC}H_2)[P(CH_3)_2C_6H_5]_2\}PF_6^-$.**—*trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ (0.3582 g) was placed in a round-bottomed 50-ml flask fitted with a magnetic stirring bar and was dissolved in methanol (25 ml) at 35° to give a clear solution. To this solution $CH{\equiv}CCH_2CH_2OH$ (55 μl) was added followed by $AgPF_6$ (0.1730 g) in methanol (5 ml). A thick white precipitate of AgCl formed instantaneously. The solution was stirred vigorously for 5 min, before removing the AgCl by gravity filtration using a fine-grade filter paper. The pale yellow filtrate was collected and subsequent evaporation under reduced pressure initiated the precipitation of a white finely divided crystalline compound. The solution was evaporated to about one-third its original volume and diethyl ether (20 ml) was added. The solution was cooled in ice and left in the refrigerator to crystallize (6 hr). The mother liquor was then decanted, and the crystals were washed with diethyl ether and dried under high vacuum for 15 min; mp 151–153°. Recrystallization from a methanol–ether solution gave *trans*-$[PtCH_3(\overline{CH_2CH_2COC}H_2)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$ (0.31 g, ∼65% yield) as thin crystalline plates, mp 155°.

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