Acknowledgment. We are grateful to Mr. J. J. McNeill and his staff at the Division of Chemical Physics, CSIRO, Clayton, Victoria, Australia, who prepared sapphire windows for the first cell in which the feasibility of this work was demonstrated. Mr. E. B. Taylor and his staff in this School of Chemistry constructed the rest of the first cell and the pair of cells described above which were used to obtain the spectra published here.

Registry No. Co^{2+}, 22541-53-3; Ni^{2+}, 14701-22-5; Pr^{3+}, 22541-14-6; Nd^{3+}, 14913-52-1.

References and Notes

(1) M. Kilpatrick and J. G. Jones in "The Chemistry of Non-aqueous Solvents", Vol. II, J. J. Lagowski, Ed., Academic Press, New York, N.Y., 1967, pp 64–68.
(2) A. W. Jache and G. H. Cady, *J. Phys. Chem.*, **56**, 1106 (1952).
(3) H. Selig and B. Frlec, *J. Inorg. Nucl. Chem.*, **29**, 1887 (1967).
(4) B. Frlec and H. H. Hyman, *Inorg. Chem.*, **6**, 1956 (1967).
(5) H. Selig and E. L. Gassner, *J. Inorg. Nucl. Chem.*, **30**, 658 (1968).
(6) T. A. O'Donnell in "Comprehensive Inorganic Chemistry", J. C. Bailar, H. J. Emeleus, R. S. Nyholm, and A. F. Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973, pp 1046–1049.
(7) L. Stein, J. Neil, and G. Alms, *Inorg. Chem.*, **8**, 2472 (1969).
(8) A. F. Clifford, H. C. Beachell, and W. M. Jack, *J. Inorg. Nucl. Chem.*, **5**, 57 (1957).
(9) T. L. Court and M. F. A. Dove, *J. Fluorine Chem.*, **6**, 491 (1975).
(10) H. H. Hyman and J. J. Katz in "Non-aqueous Solvent Systems", T. C. Waddington, Ed., Academic Press, New York, N.Y., 1965, pp 50–51.
(11) J. H. Canterford and T. A. O'Donnell in "Techniques of Inorganic Chemistry", Vol. VII, H. B. Jonassen and A. Weissberger, Ed., Interscience, New York, N.Y., 1968, p 295.
(12) W. P. Bryan and R. H. Byrne, *J. Chem. Educ.*, **47**, 361 (1970).
(13) G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry", Academic Press, New York, N.Y., 1963.
(14) K. Knox, R. G. Shulman, and S. Sugano, *Phys. Rev.*, **130**, 512 (1963).
(15) J. P. Young and G. P. Smith, *J. Chem. Phys.*, **40**, 913 (1964).
(16) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, N.Y., 1962.
(17) D. G. Karraker, *Inorg. Chem.*, **7**, 473 (1968).
(18) R. D. Peacock, *Struct. Bonding (Berlin)*, **22**, 83 (1975).
(19) W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49**, 4412, 4424 (1968).
(20) H. H. Caspers, H. E. Rast, and R. A. Buchanan, *J. Chem. Phys.*, **43**, 2124 (1965).

Contribution from the Department of Chemistry,
Princeton University, Princeton, New Jersey 08540

Reactions of Alkynyl- and Alkenylplatinum(II) Compounds. 1. Formation of Alkoxycarbene Ligands within the Coordination Sphere of Platinum

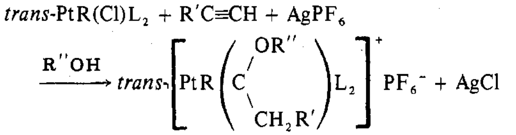
R. A. BELL, M. H. CHISHOLM,* D. A. COUCH, and L. A. RANKEL

Received July 22, 1976 AIC60799X

Alkynylplatinum compounds *trans*-$Pt(C{\equiv}CR)_2L_2$ and *trans*-$PtCl(C{\equiv}CR)L_2$, where R = H, Me, or Ph and L = PMe_2Ph or $AsMe_3$, have been prepared and reacted with acids HX in alcohols R′OH. When X = PF_6^- stable cationic alkoxycarbene complexes, *trans*-$[Pt(C{\equiv}CR)(C(CH_2R)OR')L_2]^+PF_6^-$ or *trans*-$[PtCl(C(CH_2R)OR')L_2]^+PF_6^-$, have been isolated for R′ = Me, Et, Pr^n, and Pr^i. When X = Cl^- or CF_3COO^-, the alkoxycarbene complex formed initially reacts to generate R′–X and the neutral acylplatinum compound. When X = CH_3COO^-, no apparent reaction occurs, although each of the weak acids nitromethane, ammonium chloride, and acetic acid react with *trans*-$Pt(C{\equiv}CH)_2L_2$ in MeOD to give *trans*-$Pt(C{\equiv}CD)_2L_2$. *trans*-$Pt(C{\equiv}CCF_3)_2(PMe_2Ph)_2$ does not react with HPF_6 in methanol; with HCl only *trans*-$Pt(CCl{=}CHCF_3)_2(PMe_2Ph)_2$ is formed. The α-chlorovinyl compounds *trans*-$PtCl(CCl{=}CHR)L_2$, where R = H and Me, react with alcohols R′OH to give *trans*-$PtCl(C(CH_2R)OR')L_2^+Cl^-$. The α-carbene carbon protons are acidic. For *trans*-$[PtY(C(CH_3)OMe)L_2]^+PF_6^-$ the acidity is dependent on the trans ligand Y, Y = Cl ∼ CF_3 > C≡CH > *p*-tolyl > CH_3. The α-carbene carbon protons readily exchange in MeOD, except when Y = CH_3. Addition of proton sponge to a methylene chloride solution of *trans*-$[PtY(C(CH_3)OMe)L_2]^+PF_6^-$ gives the σ-vinyl ether compounds *trans*-$PtY(C({=}CH_2)OMe)L_2$ and the ammonium hexafluorophosphate salt when Y = Cl or CF_3. When Y = *p*-tolyl, an equilibrium mixture is formed in methylene chloride: $[PtC(CH_3)OMe]^+ + \text{amine} \rightleftarrows [PtC({=}CH_2)OMe] + [(\text{amine})H]^+$. A general scheme which accounts for the formation of alkoxycarbene ligands within the coordination sphere of platinum is proposed. The reactions of platinum-stabilized vinyl carbonium ions, $PtC^+{=}CHR$, formed from (i) cationic π-acetylenic complexes, (ii) protonation of platinum acetylides, and (iii) solvolyses of α-chlorovinylplatinum(II) compounds, are discussed in the light of a number of H/D-labeled experiments.

Introduction

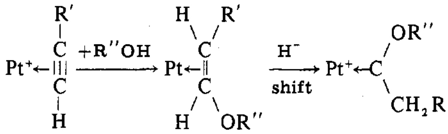
Cationic organoplatinum alkoxycarbene complexes have been prepared[1,2] from



$$\textit{trans}\text{-}PtR(Cl)L_2 + R'C{\equiv}CH + AgPF_6 \xrightarrow{R''OH} \textit{trans}\text{-}\left[PtR\left(C\begin{matrix}OR''\\ \\CH_2R'\end{matrix}\right)L_2\right]^+ PF_6^- + AgCl \quad (1)$$

where R = Me, Ph, C≡CCF_3, or CF_3; R′ = H, alkyl, or Ph; R″ = Me or Et; and L = PMe_2Ph or $AsMe_3$.

Formation of the alkoxycarbene ligand in (1) was initially considered to occur by a reaction sequence (2). Conversion



(2)

of a coordinated olefin to a coordinated carbene by a hydride shift, a Wagner–Meerwein rearrangement, could be the initial step in transition metal catalyzed olefin metathesis reactions.[3] However, for reactions 1 the sequence (2) was rejected[4] when stable π-vinyl ether complexes such as *trans*-$[PtMe(CH_2{=}CHOMe)(PMe_2Ph)_2]^+PF_6^-$ were isolated. This, together with other observations, led Chisholm and Clark[4,5] to propose a carbonium ion model for a number of reactions of unsaturated hydrocarbons π-bonded to organoplatinum cations. The proposed intermediate in the formation of the alkoxycarbene ligand in (1) was a platinum-stabilized vinyl carbonium ion, $PtC^+{=}CHR$.

If organoplatinum cations can induce carbonium ion reactivity in a π-bonded unsaturated hydrocarbon ligand and also stabilize the carbonium ion so formed, we anticipated that this carbonium ion character would be reflected in the reactions of unsaturated hydrocarbon ligands σ-bonded to platinum. In this paper we describe the preparation of cationic alkoxycarbeneplatinum(II) complexes from reactions of alkynyl- and alkenylplatinum(II) compounds. This work provides a new and quite general route to alkoxycarbene ligands and provides further support for the Chisholm and

Clark carbonium ion model. Preliminary reports of this work have been published.[6,7]

Results and Discussion

Synthesis of Alkynyl- and α-Chloroalkenylplatinum(II) Compounds. Platinum(II) acetylides, *trans*-$Pt(C{\equiv}CR)_2L_2$, where R = H, Me, Ph, or CF_3 and L = PMe_2Ph or AsMe, were readily synthesized by metathetic reactions involving *cis*-L_2PtCl_2 and alkynyllithium reagents in THF/hexane solvent mixtures. The presence of a large excess of $LiC{\equiv}CR$ was avoided in these reactions since this led to displacement of L and formation of alkynyl salts such as $Li_2Pt(C{\equiv}CR)_4$.[8]

trans-$PtCl(C{\equiv}CR)L_2$ complexes, where R = Me or Ph and L = PMe_2Ph or $AsMe_3$, were prepared by the addition of anhydrous HCl (1 equiv) to a benzene or dichloromethane solution of *trans*-$Pt(C{\equiv}CR)_2L_2$. Addition of anhydrous HCl (2 equiv) to *trans*-$Pt(C{\equiv}CR)_2L_2$ or addition of anhydrous HCl (1 equiv) to *trans*-$PtCl(C{\equiv}CR)L_2$, where R = Me and L = PMe_2Ph or $AsMe_3$, in benzene or dichloromethane gave *trans*-$PtCl(CCl{=}CHR)L_2$.

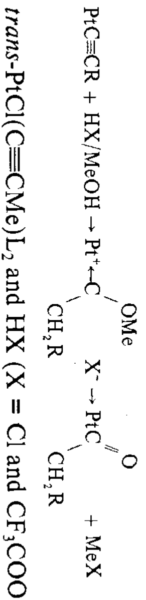
Addition of anhydrous HCl to *trans*-$Pt(C{\equiv}CH)_2(PMe_2Ph)_2$ in benzene, toluene, chloroform, and dichloromethane has been studied in detail[9] and is the subject of the following paper. The compounds *trans*-$PtCl(C{\equiv}CH)L_2$, *trans*-$Pt(CCl{=}CH_2)_2L_2$, and *trans*-$PtCl(CCl{=}CH_2)L_2$, where L = PMe_2Ph, have been isolated.

Addition of anhydrous HCl to *trans*-$Pt(C{\equiv}CCF_3)_2(PMe_2Ph)_2$ in benzene or dichloromethane gave *trans*-$Pt(CCl{=}CHCF_3)_2(PMe_2Ph)_2$; no elimination of trifluoropropyne was observed. Stone and his co-workers reported[10] that *trans*-$Pt(C{\equiv}CCF_3)_2(PEt_3)_2$ reacted with anhydrous HCl to give *trans*-$Pt(CCl{=}C(H)CF_3)_2(PEt_3)_2$.

Details of the preparations of these new compounds are given in the Experimental Section. Analytical data and other characterization data are given in Table I and pertinent ^1H NMR data are recorded in Table II.

Protonation of Alkynylplatinum Compounds in Alcohols. The nature of the product formed in the reaction between *trans*-$Pt(C{\equiv}CR)_2L_2$ or *trans*-$PtCl(C{\equiv}CR)L_2$ and anhydrous HX in an alcohol solvent R′OH is dependent on R, R′, and X. When R = H, Me, or Ph, R′ = Me, Et, Pr^n, or Pr^i, and X = PF_6, cationic alkoxycarbene complexes *trans*-$[Pt(C{\equiv}CR)(C(CH_2R)OR')L_2]^+PF_6^-$ or *trans*-$[PtCl(C(CH_2R)OR')L_2]^+PF_6^-$ were formed and isolated as air-stable, white, crystalline salts. Pertinent characterization data for a representative sample of these new compounds are given in Tables I and II.

The reaction between *trans*-$PtCl(C{\equiv}CR)L_2$, where R = H, Me, or Ph and L = PMe_2Ph or $AsMe_3$, and HX, where X = Cl or CF_3COO, in methanol led ultimately to the formation of acylplatinum compounds *trans*-$PtCl(C(CH_2R){=}O)L_2$, by way of sequence (3). The reactions between



$$PtC{\equiv}CR + HX/MeOH \rightarrow Pt^{+}{\leftarrow}C(OMe)(CH_2R)\ X^- \rightarrow PtC({=}O)(CH_2R) + MeX \quad (3)$$

trans-$PtCl(C{\equiv}CMe)L_2$ and HX (X = Cl and CF_3COO) in MeOH were followed by ^1H NMR spectroscopy. Initial formation of cationic alkoxycarbene complexes *trans*-$[PtCl(C(CH_2CH_3)OMe)L_2]^+X^-$ was apparently instantaneous and was followed by a slow reaction to give MeX and *trans*-$PtCl(C(CH_2R){=}O)L_2$. In a similar study *trans*-$PtCl(C{\equiv}CMe)L_2$ was reacted with HOAc (1 equiv) in MeOH. No reaction was observed. Thus formation of the alkoxycarbene ligand is related to the protic strength of the acids HX, $X^- = PF_6^- > Cl^- \sim CF_3COO^-$, and formation of the acylplatinum compound by MeX elimination is related to the nucleophilic properties of the anion, $Cl^- \sim CF_3COO^- \gg PF_6^-$.

Table I. Analytical and Other Characterization Data for Alkynyl- and Alkenylplatinum(II) Compounds

Compd[a]	Mp,[b] °C	% C		% H		% other		Solubilities[c]				IR absorptions, cm^{-1}	
		Calcd	Found	Calcd	Found	Calcd	Found	$(CH_3)_2CO$	CH_2Cl_2	C_6H_6	$(C_2H_5)_2O$	$\nu_{str}(C{\equiv}C)$	Other
$Pt(C{\equiv}CH)_2P_2$	171–173	46.07	46.10	4.61	4.63			s	s	s	ss	1968	
$Pt(C{\equiv}CH)ClP_2$	140	40.64	39.78	4.33	4.47	6.68 (Cl)	6.72 (Cl)	s	s	s	ss	1987	
$Pt(C{\equiv}CMe)_2P_2$	194	48.2	47.9	5.15	5.13			s	s	ss	ss	2120 w	
$Pt(C{\equiv}CMe)ClP_2$	148	41.7	42.45	4.60	4.64	6.51 (Cl)	6.01 (Cl)	vs	vs	s	ss	2110 w	
$Pt(C{\equiv}CPh)_2P_2$	196	57.06	57.17	4.75	4.79			s	s	ss	ss	2110 w	
$Pt(C{\equiv}CMe)_2A_2$	146–148 dec	28.09	29.98	4.68	4.80			vs	vs	vs	vs	2122	
$Pt(C{\equiv}CMe)ClA_2$	107–109	21.22	22.16	4.12	4.11			vs	vs	s		2138	
$Pt(C{\equiv}CCF_3)_2P_2$	140	40.18	40.26	3.37	3.25			s	s	ss	i	2135 vs	
$Pt(CCl{=}CHCF_3)_2P_2$	132–134	36.18	36.23	3.32	3.34	9.70 (F)	9.64 (F)	s	s	s	ss		1595 ($\nu(C{=}C)$)
$Pt(CCl{=}CH_2)_2P_2$	130	40.45	40.20	4.38	4.32	11.95 (Cl)	11.87 (Cl)	s	s	s	ss		1570 ($\nu(C{=}C)$)
$PtCl(CCl{=}CH_2)P_2$	96	38.03	38.30	4.23	4.19	12.50 (Cl)	11.18 (Cl)	s	s	s	ss		1570 ($\nu(C{=}C)$)
$PtCl(CCl{=}CHCH_3)P_2$	77	39.17	39.37	4.47	4.64			vs	vs		s		
$Pt(C{\equiv}CMe)(C(Et)OMe)A_2{}^+PF_6{}^-$	122 dec	22.59	22.53	4.20	4.28			s	s	i	ss	2070	
$Pt(C{\equiv}CH)(C(Me)OMe)P_2{}^+PF_6{}^-$	166–168 dec	36.05	36.31	4.15	4.25			s	s	i	i	1970	
$PtCl(C(Et)OEt)P_2{}^+PF_6{}^-$	172	34.19	34.15	4.34	4.26	4.81 (Cl)	4.62 (Cl)	ss	s	i	i		
$PtCl(C(Me)OPr^i)P_2{}^+PF_6{}^-$	153	34.19	34.20	4.34	4.37	4.81 (Cl)	4.65 (Cl)	ss	s	i	i		
$PtCF_3(C(Me)OMe)A_2{}^+PF_6{}^-$	180 dec	16.98	17.04	3.42	3.50			vs	vs	i	i		
$PtCl(C({=}CH_2)OMe)P_2$	95	40.46	40.37	4.79	4.61	6.30 (Cl)	6.13 (Cl)	vs	vs	s	ss		1598, 1545, 1525 ($\nu(C{=}C)$)
$PtCF_3(C({=}CH_2)OMe)A_2$	107–109	21.40	21.39	4.14	3.88			vs	vs	s	ss		1580, 1510 ($\nu(C{=}CH_2)$)

[a] A = $AsMe_3$; P = PMe_2Ph. All compounds are white or pale yellow. [b] Uncorrected. [c] Abbreviations for solubilities: s, soluble; ss, slightly soluble; vs, very soluble; i, insoluble.

Table II. ^{1}H NMR Data for Some Alkynyl- and Alkenylplatinum Compounds and Their Derivatives[a]

		Ligand (A or P) methyls			Acetylide R			Vinylic R, R′			Carbene				
Compd[b]	Solvent	δ	$^2J + {}^4J_{P-H}$	$^3J_{Pt-H}$	δ	J_{P-H}	J_{Pt-H}	δ	J_{P-H}	J_{Pt-H}	δ(OR)	J_{Pt-H}	δ(R)	J_{Pt-H}	J_{HH}
$Pt(C\equiv CCF_3)_2P_2$	CD_2Cl_2	1.93	8.0	32.8											
$Pt(CCl{=}CHCF_3)_2P_2$	CD_2Cl_2	1.75	8.0	34.6											
$Pt(C\equiv CCH_3)_2I_2P_2$	CD_2Cl_2	2.52	8.3	14.8	2.22	1.8	15.0								
$Pt(C\equiv CH_2P_2$	CD_2Cl_2	2.05	7.8	33.0	2.13	2.3	45								
$Pt(C\equiv CH)ClP_2$	CD_2Cl_2	1.90	8.1	31.4	2.12	2.3	71.6								
$Pt(C\equiv CCH_3)_2P_2$	$CDCl_3$	2.02	7.5	33.0	1.83	1.9	16.4								
$Pt(C\equiv CCH_3)ClP_2$	CD_2Cl_2	1.88	7.5	30.0	1.83	2.3	22.0								
$Pt(C\equiv CPh)_2P_2$	$CDCl_3$	2.06	7.5	33.0	7.1										
$Pt(CCl{=}CH_2)_2P_2$	CD_2Cl_2	1.84	7.6	34.0				5.92 (trans)	1.8	68					
								4.82 (cis)	1.6	25.5					
$Pt(CCl{=}CH_2)ClP_2$	CD_2Cl_2	1.86	7.6	33.6				5.93 (trans	1.5	114					
								4.92 (cis)	1.7	43.2					
$Pt(COMe{=}CH_2)ClP_2$	CD_2Cl_2	1.74	7.2	33.0				4.55 (trans		110					
								3.61 (cis)	1.3	44.5					
$Pt(ClC{=}C(CH_3)H)ClP_2$[c]	CD_2Cl_2	1.81	7.8	33.4				6.02 (H)	2 0	90.0					
								1.34 (CH_3)	1.7	18.0					
$Pt(ClC{=}C(H)CH_3)ClP_2$[d]	CD_2Cl_2	1.87	7.8	34.0				5.11 (H)	1.6	45.0					
								1.48 (CH_3)	2.7						
$Pt(C(Et)OEt)ClP_2{}^+PF_6{}^-$	CD_2Cl_2	2.02	7.8	30.0							4.98 (CH_2)		2.37 (CH_2)		7.0
		1.98									1.48 (CH_3)		0.80 (CH_3)		
$Pt(C(Me)OPr^i)ClP_2{}^+PF_6{}^-$	CD_2Cl_2	2.00	6.7	32.0							5.75 (CH)		2.47 (CH_3)	18.0	
											1.35 (CH_3)				
$Pt(C\equiv CH)(C(Me)OMe)P_2{}^+PF_6{}^-$	$CDCl_3$	2.07	8.1	33.6	2.48	3.0	45				4.56	6.6	2.01	7.0	
$Pt(C\equiv CCH_3)_2A_2$	$CDCl_3$	1.45		24.0	1.80		15.2								
$Pt(C\equiv CCH_3)ClA_2$	C_6D_6	1.14		23.6	2.00		22.8								
$Pt(C\equiv CCH_3)(C(Et)OMe)$- $A_2{}^+SbF_6{}^-$	C_6H_6	1.60		27.5	2.00		12.0				4.80	7.0	1.25 (CH_3)		
													2.70 (CH_2)		
$Pt(CF_3)(C(Me)OMe)A_2{}^+PF_6{}^-$	CD_2Cl_2	1.57		26.4							5.28	6.4	2.67	5.4	
$Pt(CF_3)(COMe{=}CH_2)A_2$[e]	CD_2Cl_2	1.34		24.0				4.53 (trans)		42.5					
								3.58 (cis)		22.0					

[a] Chemical shifts (δ) in ppm relative to TMS; coupling constants (J) in Hz; other expected resonances such as phenyl protons were observed. [b] All compounds are trans; P = PMe_2Ph; A = $AsMe_3$. [c] *trans*-$Pt-C{=}C-H$. [d] *trans*-$Pt-C{=}C-CH_3$. [e] δ(OMe) = 3.35.

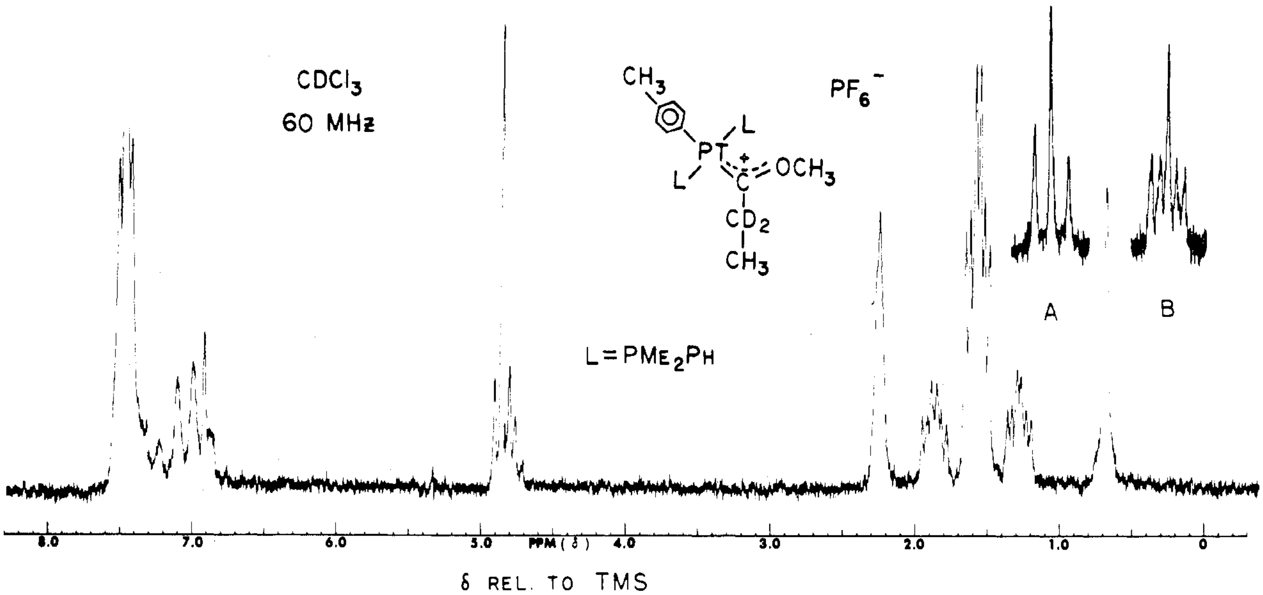
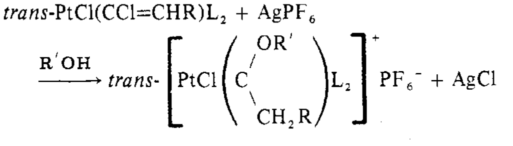


Figure 1. ^{1}H NMR spectrum of *trans*-$[Pt(p\text{-tol})(C(CD_2CH_3)OMe)(PMe_2Ph)_2]^+PF_6^-$ recorded in $CDCl_3$ (35 °C) at 60 MHz and prepared from the reaction between *trans*-$[Pt(p\text{-tol})(C(CH_2CH_3)OMe)(PMe_2Ph)_2]^+PF_6^-$ and MeOD. The CD_2CH_3 resonance appears as a singlet, $\delta \simeq 0.7$ ppm; inset A shows the CH_2CH_3 resonance as a 1:2:1 triplet, $J_{HH} \approx 7$ Hz; inset B shows the resonance for the $CH_xD_{2-x}CH_3$ protons, $x = 0, 1, 2$.

Rather interestingly *trans*-$Pt(C{\equiv}CCF_3)_2(PMe_2Ph)_2$ did not react with HPF_6 in methanol to give a carbene complex: the alkynylplatinum compound was recovered from this reaction in high yield. Similarly *trans*-$Pt(C{\equiv}CCF_3)_2(PMe_2Ph)_2$ did not react with HCl in methanol to give acylplatinum compounds. On prolonged reaction with HCl in methanol the vinylic compound *trans*-$Pt(CCl{=}CHCF_3)_2(PMe_2Ph)_2$ was isolated.

Alcoholysis of α-Chlorovinyl Compounds. *trans*-$PtCl(CCl{=}CHR)(PMe_2Ph)_2$ complexes, where R = H and Me, react in alcohols R′OH with $AgPF_6$ (1 equiv) to give cationic alkoxycarbene complexes according to (4) where L = PMe_2Ph



$$\textit{trans}\text{-}PtCl(CCl{=}CHR)L_2 + AgPF_6 \xrightarrow{R'OH} \textit{trans}\text{-}\left[PtCl\left(C\begin{matrix}OR' \\ \\ CH_2R\end{matrix}\right)L_2\right]^+ PF_6^- + AgCl \qquad (4)$$

and R′ = Me, Et, Pr^n, or Pr^i.

However, *trans*-$Pt(CCl{=}C(H)CF_3)_2(PMe_2Ph)_2$ did not react with $AgPF_6$ in methanol at 25 °C over a period of 24 h to produce any AgCl; the α-chlorovinylplatinum compound was recovered.

The presence of $AgPF_6$ is not essential for the formation of the alkoxycarbene ligand in (4); it only serves to allow the isolation of stable cationic alkoxycarbene complexes. In the absence of $AgPF_6$ the compounds *trans*-$[PtCl(C(CH_2R)OR')L_2]^+Cl^-$ are formed initially and then react further to give *trans*-$PtCl(C(CH_2R){=}O)L_2$ + R′Cl. We have found[9] that vinylplatinum compounds *trans*-$Pt(CCl{=}CHR)_2(PMe_2Ph)_2$ and *trans*-$PtCl(CCl{=}CHR)(PMe_2Ph)_2$, where R = H or Me, are labile toward the elimination of HCl. This elimination reaction forms the basis of the subsequent paper.[9]

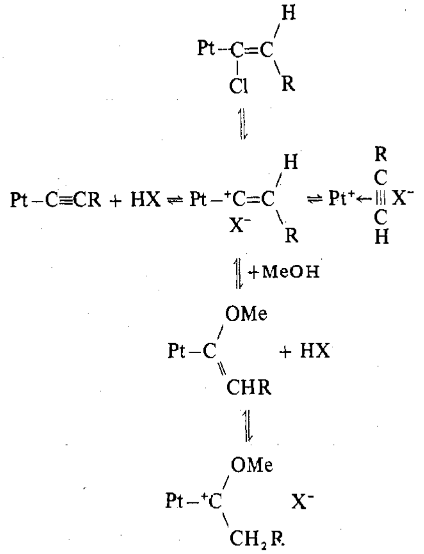
One question which arises from a consideration of reaction 4 is which chlorine atom goes to form AgCl. Reactions of *trans*-$PtBr(CCl{=}CHR)(PMe_2Ph)_2$, where R = H or Me, with $AgPF_6$ in methanol gave *trans*-$PtCl(C(CH_2R)OMe)(PMe_2Ph)_2PF_6$ (see Experimental Section) which suggests that Pt–X bond heterolysis (solvolysis) with either concomitant or subsequent vinyl–Cl migration to Pt is the kinetically favored path for generation of HX in reaction 4. This, of course, assumes the generally accepted thermodynamic bond strength order Pt–Br > Pt–Cl[11] and C–Cl > C–Br.[12]

The generality of the reaction $PtC{\equiv}CR + H^+/R'OH \rightarrow Pt^+{\leftarrow}C(CH_2R)OR'$ has not been exhaustively investigated. Since the reaction proceeds smoothly for R = H, Me, and Ph, we believe it should be applicable to most alkyl and aryl acetylides, except those bearing strongly electron-withdrawing substitutions, e.g., CF_3 or other functional groups which may preferentially react with H^+. A limitation of the alcohol R′OH is that it not be prone to acid-catalyzed elimination reactions: the reaction between *trans*-$PtCl(C{\equiv}CMe)L_2$ and HX, where X = Cl or PF_6, in *t*-BuOH gave *trans*-$PtCl(C(CH_2Me){=}O)L_2$.

Isotopic Labeling Studies and Mechanistic Implications. We suggest that formation of the alkoxycarbene ligand from either cationic acetylenic intermediates or σ-bonded acetylides involves the sequence of reactions shown in Scheme I. In support of this scheme we present the following observations and comments.

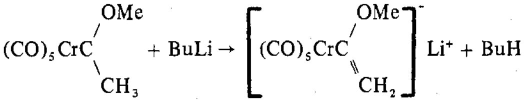
(1) The cationic alkoxycarbene complexes *trans*-$[PtX(C(CH_2R)OMe)L_2]^+PF_6^-$, where X = Cl, CF_3, $C{\equiv}CH$, or *p*-tolyl, R = H or Me, and L = PMe_2Ph or $AsMe_3$, react in MeOD to give *trans*-$[PtX(C(CD_2R)OMe)L_2]^+PF_6^-$. The rate of H/D exchange follows the order Cl ∼ CF_3 > $C{\equiv}CH$ > *p*-tolyl for which exchange is slow. H/D exchange was readily followed by ^{1}H NMR spectroscopy and was thereby seen to occur in a stepwise manner. Figure 1 shows ^{1}H NMR spectra recorded during the reaction of *trans*-$[Pt(p\text{-tol})(C(CH_2Me)OMe)(PMe_2Ph)_2]^+PF_6^-$ with MeOD in CD_2Cl_2 solution. In addition to the disappearance of the α-carbene methylene resonance, the methyl proton resonance of the carbene ethyl moiety changes with the deuterium substitution: $C(CH_2CH_3)OMe$ appears as a 1:2:1 triplet, $^2J_{HH}$ = 7 Hz, $C(CHDCH_3)OMe$ as a 1:1 doublet, and $C(CD_2CH_3)OMe$ as a singlet. During the course of the H/D exchange reaction

Scheme I



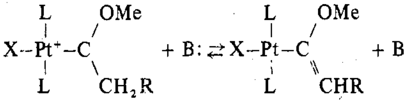
the $\mathrm{C(CH_nD_{2-n}\mathit{CH}_3)OMe}$ resonance is complex due to the presence of all three isotopic species (n = 0, 1, 2). Methylplatinum–alkoxycarbene complexes, X = Me, do *not* react with MeOD to give H/D exchange at the α-carbene carbon.

The acidity of the α-carbene methyl protons in $\mathrm{(CO)_5Cr(C(CH_3)OMe)}$ has been previously noted by Casey,[13a] i.e.



$$\mathrm{(CO)_5CrC(OMe)CH_3 + BuLi \rightarrow \left[(CO)_5CrC(OMe){=}CH_2\right]^{-} Li^{+} + BuH}$$

We suggest that the above H/D exchange reactions occur by the analogous reaction 5.[13b] Consistent with this proposal is



$$\mathrm{X{-}\overset{L}{\underset{L}{Pt^{+}}}{-}C(OMe)CH_2R + B: \rightleftarrows X{-}\overset{L}{\underset{L}{Pt}}{-}C(OMe){=}CHR + BH^{+}} \qquad (5)$$

our observation that *trans*-$\mathrm{[PtX(C(CH_3)OMe)L_2]^{+}PF_6^{-}}$ complexes react with proton sponge in methylene chloride to give *trans*-$\mathrm{PtX(C({=}CH_2)OMe)L_2}$ and the ammonium hexafluorophosphate salt, when X = Cl and $\mathrm{CF_3}$. *trans*-$\mathrm{[Pt(\mathit{p}\text{-}tol)(C(Me)OMe)(PMe_2Ph)_2]^{+}PF_6^{-}}$ reacts with proton sponge (1 equiv) in $\mathrm{CH_2Cl_2}$ to give an equilibrium mixture of the carbene (ca. 60%) and the σ-vinyl ether compound (ca. 40%).

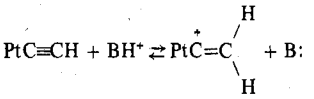
trans-$\mathrm{PtX(C({=}CH_2)OMe)L_2}$ complexes, where X = Cl or $\mathrm{CF_3}$, react in neutral $\mathrm{CH_3OD}$ to give *trans*-$\mathrm{PtX(C({=}CD_2)OMe)L_2}$. The latter do *not* react with anhydrous $\mathrm{NH_3}$ in methylene chloride to give vinylic H/D exchange.

These observations demonstrate that the acidities of the α-carbene carbon protons are dependent on the trans ligand X, X = Cl $\sim$ $\mathrm{CF_3}$ > C≡CH > *p*-tolyl > $\mathrm{CH_3}$. This series correlates with the electron-withdrawing properties of X and suggests that the position of equilibrium in (5) reflects the ability of platinum(II) to stabilize the electron-deficient carbene carbon. Consistent with this proposed correlation between proton acidity and carbene carbon stabilization is our observation that the dimethylaminocarbene complex *trans*-$\mathrm{[PtCl(C(Me)NMe_2)(AsMe_3)_2]^{+}PF_6^{-}}$ did not react in MeOD to give H/D exchange at the α-carbene methyl group.

It should also be noted that the position of equilibrium in (5) is dependent on the conjugate base B:. When cationic alkoxycarbene complexes *trans*-$\mathrm{[PtX(C(Me)OMe)L]^{+}PF_6^{-}}$ are dissolved in methanol, B: is MeOH and the position of equilibrium lies well to the left. When platinum σ-vinyl ether complexes are dissolved in neutral MeOH, B: is $\mathrm{OMe^{-}}$, and the position of equilibrium is well to the right.

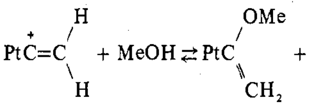
(2) Chisholm and Clark[4] originally reported that the reaction between *trans*-$\mathrm{PtMe(Cl)(AsMe_3)_2}$, HC≡CH, and $\mathrm{AgPF_6}$ in MeOD gave *trans*-$\mathrm{[PtMe(C(CH_2D)OMe)(AsMe_3)_2]^{+}PF_6^{-}}$. We have now repeated this reaction and carried out the analogous reaction involving $\mathrm{PMe_2Ph}$ in place of $\mathrm{AsMe_3}$. We find that *trans*-$\mathrm{[PtMe(C(CH_2D)OMe)L_2]^{+}PF_6^{-}}$ complexes are formed for both L = $\mathrm{PMe_2Ph}$ and $\mathrm{AsMe_3}$. Integration of the carbene methoxyl and carbene methyl proton resonances suggested, however, that some further deuteration of the α-carbene methyl group had occurred ($\mathrm{OMe{:}CH_2D}$ predicted 3:2, found 5:3). Analogous reactions involving propyne led to a mixture of C(CHDMe)OMe and $\mathrm{C(CD_2Me)OMe}$ labeled products. This was evident from the methyl proton resonance of the ethyl group which is sensitive to H/D substitution at the α-carbene carbon, as shown in Figure 1.

Since H/D exchange at the α-carbene carbon does *not* occur in methanol for X = Me, reaction 5 cannot be responsible for these observations. H/D exchange must occur prior to the formation of the alkoxycarbene ligand. Our proposal (Scheme I) is that the platinum–vinyl cations, $\mathrm{PtC^{+}{=}CHR}$, can undergo competing reactions. Proton abstraction, by the solvent or in general the conjugate base of the acid, may occur as shown in (6), or reaction with methanol may generate the



$$\mathrm{PtC{\equiv}CH + BH^{+} \rightleftarrows Pt\overset{+}{C}{=}CH_2 + B:} \qquad (6)$$

σ-vinyl ether complex, as in (7).



$$\mathrm{Pt\overset{+}{C}{=}CH_2 + MeOH \rightleftarrows PtC(OMe){=}CH_2 + H^{+}} \qquad (7)$$

Support for (6) is seen in the following. *trans*-$\mathrm{Pt(C{\equiv}CH)_2(PMe_2Ph)_2}$ does not exchange its acetylenic protons in neutral MeOD. However, addition of each of the weak acids $\mathrm{CH_3NO_2}$, $\mathrm{NH_4Cl}$, and $\mathrm{CH_3COOH}$ to *trans*-$\mathrm{Pt(C{\equiv}CH)_2(PMe_2Ph)_2}$ in MeOD catalyzes the formation of *trans*-$\mathrm{Pt(C{\equiv}CD)_2(PMe_2Ph)_2}$. [We noted previously that addition of $\mathrm{CH_3COOH}$ (1 equiv) to a methanolic solution of *trans*-$\mathrm{PtCl(C{\equiv}CMe)(AsMe_3)_2}$ did not lead to alkoxycarbene formation.] Thus formation of the alkoxycarbene ligand in methanol is sensitive to the nature of the conjugate base.

The observation that methylplatinum cations react with acetylene and propyne to give deuteration at the α-carbene carbon (which cannot be accounted for by (5)) indicates that the acidity of the vinylic proton in $\mathrm{PtC^{+}{=}CHR}$ is greater than that of the α-carbene carbon protons. This is not unexpected since the vinyl cation lacks heteroatom stabilization other than by platinum. However, that the basicities of the β carbons in the $\mathrm{PtC({=}CH_2)OMe}$ and PtC≡CH moieties are not vastly different is seen in the following.

When *trans*-$\mathrm{PtCl(C(CD_3)OMe)(PMe_2Ph)_2PF_6}$ and *trans*-$\mathrm{Pt(C{\equiv}CH)_2(PMe_2Ph)_2}$ were dissolved together in MeOD, significant quantities of *trans*-$\mathrm{Pt(C{\equiv}CD)_2(PMe_2Ph)_2}$ were formed. (No reaction other than H/D exchange of the platinum bis(acetylide) was observed.) In a blank reaction we found that *trans*-$\mathrm{Pt(C{\equiv}CD)_2(PMe_2Ph)_2}$ and *trans*-$\mathrm{PtCl(C{\equiv}CH)(PMe_2Ph)_2}$ did not react in MeOD to give any PtC≡CH/D exchange; the latter could have been observed as a result of either ligand exchange or H/D solvent exchange reactions. (We have previously noted that *trans*-$\mathrm{Pt(C{\equiv}CH)_2(PMe_2Ph)_2}$ does not undergo PtC≡CH/D exchange in neutral methanol.)

It is possible that the σ-vinyl ether complex $\mathrm{PtC({=}CH_2)OMe}$ is accessible through rapid reversible attack by

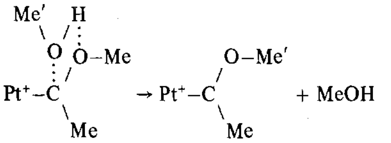
$^{-}$OMe on $PtC^{+}{=}CH_2$. This interpretation seems highly unlikely in view of the stability of such complexes toward the loss of methanol under the reaction conditions. A more plausible explanation of the observed exchange is that deprotonation of $PtC^{+}{=}CH_2$ by the conjugate base of a weak acid is rapid with respect to irreversible attack by methoxide ion.

(3) *trans*-$[PtX(C(CH_3)OMe)L_2]^{+}PF_6^{-}$ complexes, where X = Cl, CF_3, or C≡CH, react with CD_3OD to generate the $PtC(CD_3)OCD_3$ moiety. Exchange of the α-carbene methyl protons occurred much faster than methoxyl exchange. The relative rate of methoxyl group exchange was X = Cl ~ CF_3 > C≡CH ≫ *p*-tolyl and Me for which exchange was *not* observed.

We also found that the σ-vinyl ether complexes *trans*-$PtX(C({=}CH_2)OMe)L_2$, where X = Cl or CF_3, react with CD_3OD under neutral conditions to give *trans*-$PtX(C({=}CD_2)OCD_3)L_2$. H/D exchange occurred much faster for the vinylic protons than for the methoxyl group.

H/D exchange of the α-carbene carbon protons and the vinylic protons is satisfactorily accounted for by (5) and has been previously discussed. A mechanism leading to methoxyl exchange is indicated in Scheme I. Reaction 7, involving the microscopic reverse of the addition of MeOH to $PtC^{+}{=}CH_2$, could provide a route for methoxyl group exchange. However, since *trans*-$Pt(C{\equiv}CH)_2(PMe_2Ph)_2$ and *trans*-$PtCl(C{\equiv}CH)(PMe_2Ph)_2$ are stable with respect to addition of methanol to give σ-vinyl ether complexes, even in the presence of weak acids which effect PtC≡CH/D exchange, and since σ-vinyl ether complexes are stable with respect to formation of platinum acetylides by loss of methanol in both neutral and basic solutions, the back-reactions of (7) cannot occur to any significant extent. Indeed in the reaction leading to the formation of $PtC^{+}(CH_3)OMe$ from PtC≡CH and HX in MeOH, addition of MeOH to $PtC^{+}{=}CH_2$, reaction 7, must be the rate-determining step.

We suggest that methoxyl group exchange reactions proceed via alcoholysis of an alkoxycarbene ligand, as schematically represented by (8). This has parallel in the known aminolysis



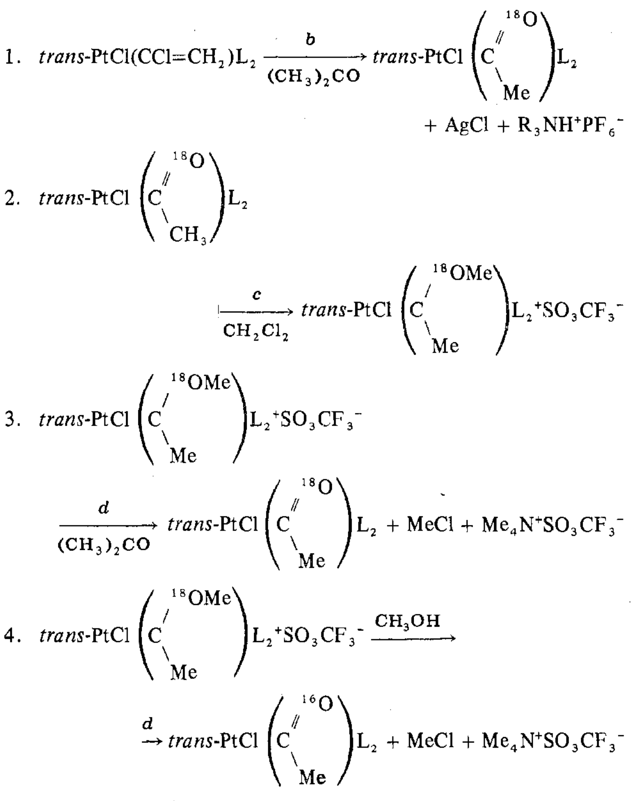
$$Pt^{+}{-}C(OMe)(Me) + Me'OH \rightarrow Pt^{+}{-}C(OMe')(Me) + MeOH \quad (8)$$

reactions of alkoxycarbene ligands which give aminocarbene ligands and alcohols.[14-16]

We have carried out the reactions shown in Scheme II and have thereby established that carbene–oxygen bond rupture occurs during methoxyl group exchange. CH_3–O bond rupture is commonly observed in the reactions of cationic alkoxycarbene complexes of platinum(II) with nucleophiles.[17] For example, *trans*-$[PtX(C(Me)OMe)L_2]^{+}PF_6^{-}$ complexes, where X = Cl or CF_3, react with Cl^{-} and Et_3N to give acylplatinum compounds, *trans*-$PtX(C(CH_3){=}O)L_2$, and MeCl and Et_3NMe^{+}, respectively. For reactions involving primary and secondary amines with alkoxycarbene complexes, aminocarbene and acyl complexes are formed competitively: the reaction product is dependent on both the nature of the trans ligand X and the concentration of amine.[17]

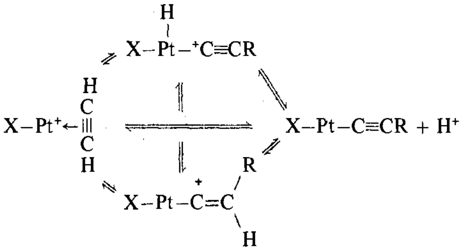
(4) The possibility that hydridoplatinum(IV) intermediates may be involved in these reactions cannot be ruled out. Indeed any of the proton-transfer reactions shown in Scheme III could be operative in leading to $PtC^{+}{=}CH_2$. For X = Me, formation of the $Pt^{+}C(CH_2D)OMe$ moiety from HC≡CH and MeOD clearly indicates that acetylenic protons are not lost from the coordination sphere of platinum and is consistent with a hydride shift, eq 9. The role of platinum in promoting such a π to σ rearrangement is not clear.

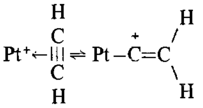
Scheme II[a]



[a] L = PMe_2Ph. [b] $+{}^{18}OH_2$ + $AgPF_6$ + R_3N. [c] $+CH_3SO_3CF_3$. [d] $+Me_4N^{+}Cl^{-}$; $\nu_{str}(C{=}{}^{18}O)$ 1601 cm^{-1}; $\nu_{str}(C{=}{}^{16}O)$ 1633 cm^{-1}.

Scheme III



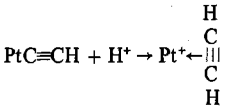


$$Pt^{+}{\leftarrow}\|\!|(HC{\equiv}CH) \rightleftharpoons Pt{-}\overset{+}{C}{=}CH_2 \quad (9)$$

Reversible protonation of platinum(II) compounds is well established. *trans*-$Pt(H)(Cl)(PEt_3)_2$ reversibly reacts with HCl at low temperatures to give $Pt(H)_2(Cl)_2(PEt_3)_2$ [18] and addition of HCl or HPF_6 to *trans*-$PtH(Cl)(PMe_2Ph)_2$ in MeOD catalyzes the formation of *trans*-$PtD(Cl)(PMe_2Ph)_2$. However, *trans*-$PtH(Cl)(PMe_2Ph)_2$ does not react in MeOD in the presence of nitromethane or ammonium chloride to give *trans*-$PtD(Cl)(PMe_2Ph)_2$. The latter findings contrast with the PtC≡CH/D exchange reactions described above. This leads us to believe that for *trans*-$Pt(C{\equiv}CH)_2(PMe_2Ph)_2$ protonation may occur preferentially at the C–C triple bond to give $PtC^{+}{=}CH_2$.

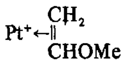
Previously it was found[4] that cationic alkoxycarbene complexes of platinum(IV) could be obtained from the reactions of platinum(IV) cations and acetylenes. Thus it seems that hydridoplatinum intermediates are not essential in the formation of the alkoxycarbene ligand since in the latter this would involve hydridoplatinum(VI) intermediates.

The possibility that a σ to π transformation



$$\mathrm{PtC{\equiv}CH + H^+ \rightarrow Pt^+{\leftarrow}\begin{matrix}H\\C\\|||\\C\\H\end{matrix}}$$

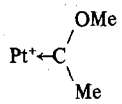
is involved in these reactions could be ascertained by the carbon-13 labeling of the acetylide ligand as either Pt—*C≡CH or Pt—C≡*CH. Synthetic routes to such specifically labeled compounds have not yet been achieved. However, since



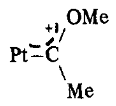
$$\mathrm{Pt^+{\leftarrow}\begin{matrix}CH_2\\ \|\\ CHOMe\end{matrix}}$$

intermediates can be ruled out,[4] this uncertainty does not detract from our suggestion that the $\mathrm{PtC^+{=}CH_2}$ moiety is an essential intermediate in the formation of alkoxycarbene ligands in the above reactions.

Recently compounds containing $\mathrm{TaCH_2}$,[19] $\mathrm{MoC{=}C(CN)_2}$,[20] and WCMe[21] moieties have been isolated and structurally characterized. The existence of compounds containing an MC=CH(R) moiety (R = H or alkyl) seems quite plausible; indeed a compound $\mathrm{CpMn(CO)_2(C{=}CHPh)}$, formed from the reaction between $\mathrm{CpMn(CO)_2(THF)}$ and PhC≡CH, has recently been structurally characterized.[22] There is therefore precedent for our proposal.[23] We have called $\mathrm{PtC^+{=}CHR}$ (R = H or alkyl) a platinum-stabilized vinyl carbonium ion, although it could alternately be named a vinylidene cation $\mathrm{[Pt{\leftarrow}C{=}CHR]^+}$ or a metalloallene cation $\mathrm{Pt^+{=}C{=}CHR}$. All of the reactions shown in Scheme I are simple acid–base reactions and so we believe a carbonium ion nomenclature is appropriate to the extent that it is appropriate to apply the nomenclature of organic chemistry to organic reactions which occur within the coordination sphere of a metal. The



moiety may also be described as a platinum-stabilized carbonium ion, as an oxonium ion, or as an ylide. The bonding description



is well illustrative of the reactivity of this group.

Conclusions

The formation of alkoxycarbene complexes from platinum(II) acetylides and platinum(II) vinyl compounds provides an efficient synthesis of these compounds and has two distinct advantages over the preparative route, eq 1. (1) The presence of free acetylenes in (1) leads to side reactions such as acetylene polymerizations. (2) Starting with an acetylide or vinyl ligand σ-bonded to platinum circumvents the limitation of (1) that there be a favorable equilibrium: $\mathrm{X{-}Pt^+(solvent) + acetylene \rightleftarrows X{-}Pt^+(acetylene) + solvent}$. In view of the large number of known transition metal acetylide complexes this route ($\mathrm{L_nMC{\equiv}CR + H^+/R'OH}$) could form the basis for an expansion of the chemistry surrounding the alkoxycarbene ligand.

Experimental Section

Chemicals and Instrumentation. $\mathrm{K_2PtCl_4}$ was obtained from Mathey Bishop Inc.; $\mathrm{^{18}OH_2}$ from Prochem; $\mathrm{CD_3OD}$ from Koch; $\mathrm{CH_3OD}$, $\mathrm{MeSO_3CF_3}$, and PhC≡CH from Aldrich; $\mathrm{CD_2Cl_2}$, $\mathrm{CDCl_3}$, and $\mathrm{(CD_3)_2CO}$ from Merck Sharp and Dohme; and acetylene and propyne from Matheson. Analyses were performed by Atlantic Microlab, Inc., and Chemalytics, Inc.

cis-$\mathrm{PtCl_2L_2}$, *trans*-$\mathrm{PtR(Cl)L_2}$, and *trans*-$\mathrm{PtR(I)L_2}$ where R = $\mathrm{CH_3}$, *p*-tolyl, or $\mathrm{CF_3}$ and L = $\mathrm{PMe_2Ph}$ or $\mathrm{AsMe_3}$ were prepared according to literature procedures.[11,24,25]

Infrared spectra were obtained from Nujol mulls between CsI or KBr plates using a Beckman IR-12 spectrophotometer. ^{1}H NMR spectra were recorded on Varian A-60 or HA 100 spectrometers.

***trans*-Pt(C≡CMe)$_2$(PMe$_2$Ph)$_2$.** *n*-Butyllithium (1.6 ml of a 2.5 M solution in hexane) was added via syringe to dry tetrahydrofuran (50 ml) under nitrogen at −78 °C. The reaction vessel was evacuated and, by use of a calibrated vacuum manifold, propyne (4.4 mmol, 15% molar excess) was condensed into the pale yellow solution. The solution was stirred magnetically and *cis*-$\mathrm{PtCl_2(PMe_2Ph)_2}$ (1.0 g, 1.85 mmol) was added. Stirring was continued and the reaction mixture was allowed to warm slowly to room temperature. After 1 h all of the solids had dissolved yielding a yellow solution. The solvent was stripped off and the resultant off-white residue was extracted with benzene (30 ml). LiCl and any other benzene-insoluble compounds were removed by centrifugation. The benzene-soluble extract was passed through a short Florisil column using benzene as eluent. The pale yellow benzene solution was collected and reduced in volume to ca. 10 ml using a rotary evaporator. Addition of petroleum ether produced white crystals which were dried under vacuum: *trans*-$\mathrm{Pt(C{\equiv}CMe)_2(PMe_2Ph)_2}$, mp 197 °C, 0.87 g (87% yield based on Pt).

Analogous procedures were used for the preparation of *trans*-$\mathrm{Pt(C{\equiv}CMe)_2(AsMe_3)_2}$ and of *trans*-$\mathrm{Pt(C{\equiv}CR)_2L_2}$ where R = $\mathrm{CF_3}$ or Ph and L = $\mathrm{PMe_2Ph}$ or $\mathrm{AsMe_3}$. (Phenylacetylene was added to the *n*-butyllithium solution via syringe.) In all cases the yields were high, ranging from 65 to 90% based on platinum.

***trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$.** A similar procedure to that described above was followed but with certain significant modifications. A 60–100% excess of LiC≡CH was used to maximize the yield and avoid the appearance of *trans*-$\mathrm{PtCl(C{\equiv}CH)(PMe_2Ph)_2}$ which is difficult to separate from *trans*-$\mathrm{Pt(C{\equiv}CH)_2(PMe_2Ph)_2}$. It is essential to work at −78 °C during this preparation in order to limit the formation of dilithioacetylide LiC≡CLi which precipitates from THF. Significant decomposition is encountered during the extraction stage of the reaction. Consequently the preparation time is minimized. A typical preparation is given below.

n-Butyllithium (1.75 ml of a 2.5 M solution in hexane) was added to dry THF (50 ml) at −78 °C. Acetylene (5 mmol) was condensed into the evacuated reaction flask using a calibrated vacuum manifold. To this stirred solution at −78 °C was added *cis*-$\mathrm{PtCl_2(PMe_2Ph)_2}$ (0.6 g, 1.1 mmol). The reaction mixture was stirred for 1 h at −78 °C and warmed to room temperature, and the solvent was stripped. The solids were extracted with benzene as above. Crystallization from benzene/petroleum ether solvent mixtures yielded *trans*-$\mathrm{Pt(C{\equiv}CH)_2(PMe_2Ph)_2}$, mp 173 °C, 370 mg (ca. 65% yield based on Pt).

***trans*-PtCl(C≡CMe)(PMe$_2$Ph)$_2$.** *trans*-$\mathrm{Pt(C{\equiv}CMe)_2(PMe_2Ph)_2}$ (0.3 g) was dissolved in chloroform (10 ml). The solution was frozen in liquid nitrogen and the reaction flask evacuated. Dry HCl (0.55 mmol) was condensed into the reaction vessel using a calibrated vacuum manifold. The reaction mixture was warmed to room temperature and stirred magnetically for 0.5 h. The solution was reduced in volume to ca. 4 ml and petroleum ether (30–60 °C) was added dropwise. White crystals formed which were collected and dried in vacuo: *trans*-$\mathrm{PtCl(C{\equiv}CMe)(PMe_2Ph)_2}$, mp 148 °C, 0.27 g (90% yield based on Pt).

A similar procedure was adopted for the preparation of *trans*-$\mathrm{PtCl(C{\equiv}CMe)(AsMe_3)_2}$ and *trans*-$\mathrm{PtCl(C{\equiv}CPh)L_2}$, where L = $\mathrm{PMe_2Ph}$ and $\mathrm{AsMe_3}$.

***trans*-PtCl(CCl=CHMe)(PMe$_2$Ph)$_2$.** *trans*-$\mathrm{PtCl(C{\equiv}CMe)(PMe_2Ph)_2}$ (0.3 g) was dissolved in methylene chloride (5 ml) and reacted with dry HCl (1 equiv) in the manner described above. The solution was reduced to ca. 1 ml, and a mixture of petroleum ether/diethyl ether (4:1) was added slowly. The solution was cooled to 0 °C and after 24 h colorless crystals formed. These were collected and dried in vacuo: *trans*-$\mathrm{PtCl(CCl{=}C(H)Me)(PMe_2Ph)_2}$, 0.28 mg (ca. 90% yield based on Pt).

trans-$\mathrm{PtCl(CCl{=}C(H)Me)(AsMe_3)_2}$ and *trans*-$\mathrm{PtCl(CCl{=}C(H)Ph)L_2}$ where L = $\mathrm{PMe_2Ph}$ and $\mathrm{AsMe_3}$ were prepared similarly.

The α-chloropropenylplatinum compounds exist as a mixture of *cis* and *trans* isomers with respect to the C–C double bond. See NMR data in Table II.

***trans*-Pt(CCl=CH$_2$)$_2$(PMe$_2$Ph)$_2$.** *trans*-$\mathrm{Pt(C{\equiv}CH)_2(PMe_2Ph)_2}$ (0.516 g) was dissolved in toluene (10 ml) and reacted with dry HCl

(2 equiv) in the manner described above. *trans*-$\mathrm{Pt(CCl{=}CH_2)_2(PMe_2Ph)_2}$ was obtained by crystallization from toluene/petroleum ether as white crystals, 550 mg (95% yield based on Pt).

trans-$\mathrm{Pt(CCl{=}C(H)CF_3)_2(PMe_2Ph)_2}$ was prepared similarly.

***trans*-$\mathbf{PtCl(CCl{=}CH_2)(PMe_2Ph)_2}$.** *trans*-$\mathrm{Pt(CCl{=}CH_2)_2(PMe_2Ph)_2}$ (0.27 g) was dissolved in toluene (5 ml) and reacted with dry HCl (1 equiv) in the manner described previously. Crystallization from petroleum ether/diethyl ether yields white crystals: *trans*-$\mathrm{PtCl(CCl{=}CH_2)(PMe_2Ph)_2}$, 0.23 g (90% yield based on platinum).

***trans*-$\mathbf{[PtCl(C(CH_2R')OR)(PMe_2Ph)_2]^+PF_6^-}$.** A general procedure for the synthesis of the carbene complexes where R = Me, Et, Pr^i, or Pr^n and R′ = H, Me, or Ph is outlined. In all cases the yield of the alkoxycarbene complexes is virtually quantitative.

trans-$\mathrm{PtCl(CCl{=}CH_2)(PMe_2Ph)_2}$ (ca. 200 mg) was dissolved in dry dichloromethane (10 ml). To this magnetically stirred solution under nitrogen was added $\mathrm{AgPF_6}$ (1 equiv) dissolved in the appropriate alcohol ROH (2 ml) via syringe. A precipitate of AgCl formed immediately. The mixture was centrifuged to remove AgCl and the solution was reduced in volume to ca. 5 ml. The addition of diethyl ether precipitated the carbene complex as white crystals.

The complexes *trans*-$\mathrm{[PtCl(C(CH_2R')OR)(PMe_2Ph)_2]^+PF_6^-}$ may alternatively be prepared from the acetylides *trans*-$\mathrm{PtCl(C{\equiv}CR')(PMe_2Ph)_2}$ in the manner described below for the preparation of *trans*-$\mathrm{[Pt(C{\equiv}CR')(C(CH_2R')OR)(PMe_2Ph)_2]^+PF_6^-}$.

***trans*-$\mathbf{[Pt(C{\equiv}CR')(C(CH_2R')OR)(PMe_2Ph)_2]^+PF_6^-}$.** A general procedure for the synthesis of the acetylide–carbene complexes is outlined for R′ = H, Me, or Ph and R = Me, Et, Pr^i, or Pr^n. In all cases the yield of the carbene complexes was ca. 80% based on platinum.

An alcoholic solution of hexafluorophosphoric acid, $\mathrm{HPF_6}$, was prepared by reacting $\mathrm{AgPF_6}$ dissolved in the appropriate alcohol, ROH, with dry HCl (1 equiv). The AgCl formed was removed by centrifugation.

To a solution of *trans*-$\mathrm{Pt(C{\equiv}CR')_2(PMe_2Ph)_2}$ (ca. 200 mg) in methylene chloride (ca. 10 ml) was added 1 equiv of $\mathrm{HPF_6}$ in the alcohol ROH (ca. 2 ml). The reaction mixture was stirred for ca. 10 min. Then the volume of solution was reduced to ca. 6 ml and petroleum ether was added. The carbene complex *trans*-$\mathrm{Pt(C{\equiv}CR')(C(CH_2R')OR)(PMe_2Ph)_2{}^+PF_6^-}$ crystallized from solution.

***trans*-$\mathbf{Pt(C{\equiv}CCF_3)_2(PMe_2Ph)_2 + HPF_6/MeOH}$.** $\mathrm{AgPF_6}$ (25.2 mg, 0.1 mmol) was dissolved in methanol (2 ml). HCl (0.1 mmol) was condensed into this solution using a calibrated vacuum line. The AgCl formed was removed by filtration through a glass wool plug and the filtrate was added directly to a magnetically stirred solution of *trans*-$\mathrm{Pt(C{\equiv}CCF_3)_2(PMe_2Ph)_2}$ (70 mg, 0.106 mmol) in methanol (10 ml). The reaction mixture was stirred for 1 h. The solvent was stripped off and a ^{1}H NMR spectrum of the residue was recorded in $\mathrm{CD_2Cl_2}$. No apparent reaction had occurred. The ^{1}H NMR spectrum and the IR spectrum showed the presence of only *trans*-$\mathrm{Pt(C{\equiv}CCF_3)_2(PMe_2Ph)_2}$.

***trans*-$\mathbf{PtBr(CCl{=}C(H)Me)(PMe_2Ph)_2}$.** *trans*-$\mathrm{PtCl(CCl{=}C(H)Me)(PMe_2Ph)_2}$ (200 mg) was dissolved in dry acetone (15 ml). Tetramethylammonium bromide (54 mg, 1 equiv) was added and the solution was stirred for 1 h. The solvent was stripped off and the residue extracted with benzene (5 ml). The extract was centrifuged and reduced in volume to ca. 2 ml. Addition of petroleum ether (ca. 5 ml) and cooling of the mixture to ca. 10 °C slowly precipitated white crystals: *trans*-$\mathrm{PtBr(CCl{=}C(H)Me)(PMe_2Ph)_2}$, 189 mg (88% yield based on Pt). Anal. Calcd: Cl, 5.67; Br, 12.77. Found: Cl, 7.37; Br, 12.49.

This compound is assumed to be *trans*-$\mathrm{PtBr(CCl{=}C(H)Me)(PMe_2Ph)_2}$ rather than *trans*-$\mathrm{PtCl(CBr{=}C(H)Me)(PMe_2Ph)_2}$ for the reasons outlined in the text.[11,12] The analytical data are not entirely satisfactory: presumably some *trans*-$\mathrm{PtCl(CCl{=}C(H)Me)(PMe_2Ph)_2}$ is still present in this sample.

***trans*-$\mathbf{PtBr(CCl{=}C(H)Me)(PMe_2Ph)_2 + AgPF_6/MeOH}$.** *trans*-$\mathrm{PtBr(CCl{=}C(H)Me)(PMe_2Ph)_2}$ (30 mg, prepared above) was dissolved in acetone (2 ml) and methanol (1 ml). To this solution $\mathrm{AgPF_6}$ (12 mg, 1 equiv) was added. The reaction mixture was centrifuged to remove the insoluble silver halide. The solution was collected and reduced to ca. 1 ml. The addition of a small amount of petroleum ether (ca. 2 ml) precipitated the carbene product which was identified as *trans*$\mathrm{[PtCl(C(Et)OMe)(PMePh)_2]^+PF_6^-}$ by ^{1}H NMR. Anal. Calcd: Cl, 4.90; Br, 0.00. Found: Cl, 5.18; Br, <0.1.

***trans*-$\mathbf{PtCl(C(CH_3){=}O)(PMe_2Ph)_2}$.** *trans*-$\mathrm{PtCl(CCl{=}CH_2)(PMe_2Ph)_2}$ (200 mg) was dissolved in acetone (15 ml). Water (0.5 ml) was added and the solution was stirred for 0.5 h. The solution was reduced in volume to ca. 2 ml. The addition of diethyl ether (ca. 5 ml) caused the formation of white crystals: *trans*-$\mathrm{PtCl(C(CH_3){=}O)(PMe_2Ph)_2}$, 160 mg (yield ca. 80% based on Pt), mp 149 °C, $\nu_{\mathrm{str}}(\mathrm{C{=}O})$ 1633 $\mathrm{cm^{-1}}$.

A similar reaction involving *trans*-$\mathrm{Pt(CCl{=}C(H)Me)(PMe_2Ph)_2}$ yielded *trans*-$\mathrm{PtCl(C(Et){=}O)(PMe_2Ph)_2}$.

***trans*-$\mathbf{PtCl(C{\equiv}CMe)(AsMe_3)_2 + CF_3COOH/MeOD}$.** *trans*-$\mathrm{PtCl(C{\equiv}CMe)(AsMe_3)_2}$ (50 mg, 0.1 mmol) was dissolved in $\mathrm{CH_3OD}$ (0.25 ml) in a thick-walled NMR tube. The ^{1}H NMR spectrum was recorded. $\mathrm{CF_3COOH}$ (7.4 µl, 0.1 mmol) was added to this solution and the ^{1}H NMR spectrum recorded. At $t = 5$ min, the resonances due to *trans*-$\mathrm{PtCl(C{\equiv}CMe)(AsMe_3)_2}$ had almost disappeared. New resonances assignable to *trans*-$\mathrm{PtCl(C(CD_2Me)OMe)(AsMe_3)_2{}^+CF_3COO^-}$ were present: δ(OMe) 4.8, $^4J_{\mathrm{PtH}} \simeq 9$ Hz. With time the resonances due to *trans*-$\mathrm{PtCl(C(CD_2Me)OMe)(AsMe_3)_2O_2CCF_3}$ diminished as new resonances assignable to *trans*-$\mathrm{PtCl(C(CD_2Me){=}O)(AsMe_3)_2}$ appeared. After 3 days formation of the acylplatinum compound was complete. Crystallization from benzene/petroleum ether gave white crystals which showed a strong infrared band at 1625 $\mathrm{cm^{-1}}$ characteristic of $\nu_{\mathrm{str}}(\mathrm{C{=}O})$ in acylplatinum(II) compounds.

Similar reactions were carried out involving *trans*-$\mathrm{PtCl(C{\equiv}CMe)L_2}$, where L = $\mathrm{PMe_2Ph}$ or $\mathrm{AsMe_3}$, and anhydrous HCl in methanol. The initial reaction to give the carbene complex was fast and was followed by a slow reaction to give MeCl and the acylplatinum(II) compound.

Under similar reaction conditions *trans*-$\mathrm{Pt(C{\equiv}CMe)_2(AsMe_3)_2}$ and *trans*-$\mathrm{PtCl(C{\equiv}CMe)(AsMe_3)_2}$ were reacted with $\mathrm{CH_3COOH}$ in methanol. After 1 week the ^{1}H NMR spectrum showed only the presence of the starting materials; no reaction had occurred.

***trans*-$\mathbf{[Pt(}$*p*-$\mathbf{tol)(C(CH_2R)OMe)(PMe_2Ph)_2]^+PF_6^-}$ (R = H, $\mathbf{CH_3}$).** *trans*-$\mathrm{Pt(C_6H_4CH_3)I(PMe_2Ph)_2}$ (200 mg) was dissolved in dry methylene chloride (5 ml) and methanol (2 ml). A stream of propyne was passed through the solution for 2 min. $\mathrm{AgPF_6}$ (1 equiv) in methanol (2 ml) was added to this solution with stirring. A yellow precipitate (AgI) formed immediately upon the addition of the $\mathrm{AgPF_6}$ solution. The solution was centrifuged and the supernatant liquid reduced in volume to ca. 2 ml. Addition of petroleum ether resulted in the formation of white crystals, *trans*-$\mathrm{[Pt(C_6H_4CH_3)(C(CH_2CH_3)OMe)(PMe_2Ph)_2]^+PF_6^-}$ (205 mg, 90% yield based on platinum).

trans-[Pt(*p*-tol)$\mathrm{(C(Me)OMe)(PMe_2Ph)_2]^+PF_6^-}$ was made in the above manner but using acetylene in place of propyne.

The compounds *trans*-$\mathrm{[PtCF_3(C(CH_2R)OMe)(AsMe_3)_2]^+PF_6^-}$, where R = H or Me, were prepared in a similar manner from the reactions between *trans*-$\mathrm{Pt(CF_3)I(AsMe_3)_2}$, $\mathrm{RC{\equiv}CH}$, and $\mathrm{AgPF_6}$ in methanol. Reactions carried out in ethanol yielded the corresponding ethoxycarbene complexes.

***trans*-$\mathbf{PtMe(Cl)(PMe_2Ph)_2 + HC{\equiv}CH + AgPF_6 + MeOD}$.** *trans*-$\mathrm{PtMe(Cl)(PMe_2Ph)_2}$ (0.30 g, 0.57 mmol) was dissolved in $\mathrm{CH_3OD}$ (10 ml) and methylene chloride (1.5 ml). A stream of acetylene was passed through the solution with stirring. $\mathrm{AgPF_6}$ (0.144 g, 0.57 mmol) in $\mathrm{CH_3OD}$ was added dropwise. A fine precipitate of AgCl formed immediately. The solution was stirred for 0.5 h and then centrifuged, and the supernatant solution was collected. Solvent was stripped yielding an orange solid. This was dissolved in $\mathrm{CD_2Cl_2}$ (1 ml) and a ^{1}H NMR spectrum was recorded. This showed the expected spectrum of *trans*-$\mathrm{[PtMe(C(CH_xD_{3-x})OMe)(PMe_2Ph)_2]^+PF_6^-}$. The integral ratio of the methoxyl proton resonance (δ 4.7) to the α-carbene methyl proton resonance (δ 2.2) was 2:1. The crude product was purified by short-column chromatography using Florisil and chloroform as eluents. Subsequent crystallization from $\mathrm{CH_3OH/Et_2O}$ gave pale yellow crystals of *trans*-$\mathrm{[PtMe(C(CH_xD_{3-x})OMe)(PMe_2Ph)_2]^+PF_6^-}$ (97.6 mg, 27% yield based on Pt), mp 150 °C. The ^{1}H NMR spectrum was again recorded in $\mathrm{CD_2Cl_2}$ solution. The integral ratio $\mathrm{OCH_3{:}CH_xD_{3-x}}$ was 2:1.

In similar experiments using propyne and MeOD *trans*-$\mathrm{[PtMe(C(CH_xD_{2-x}CH_3)OMe)(PMe_2Ph)_2]^+PF_6^-}$ was prepared. The presence of the isotopically labeled species, $x = 1$ and 0, was evident from the ^{1}H NMR spectrum. The $\mathrm{C(CH_xD_{2-x}C}H_3\mathrm{)OMe}$ resonance is sensitive to the value of x as shown in Figure 1.

α-Carbene Carbon H/D Exchange Reactions. *trans*-$\mathrm{[PtMe(C(CH_2R)OMe)L_2]^+PF_6^-}$ complexes, where R = H or Me and L = $\mathrm{PMe_2Ph}$ or AsMe, were dissolved in MeOD. After 14 h the solvent was stripped off and the ^{1}H NMR spectrum of the carbene complexes were recorded. No H/D exchange was apparent either from :COMe/:CMe integration or from the appearance of the $\mathrm{:CCH_2C}H_3$ resonance.

The compounds *trans*-$[\mathrm{PtX(C(CH_2R)OMe)L_2}]^+\mathrm{PF_6}^-$, where X = *p*-tolyl, C≡CH, $\mathrm{CF_3}$ or Cl and L = $\mathrm{PMe_2Ph}$ or $\mathrm{AsMe_3}$, all readily exchanged their α-carbene carbon protons for deuterons in analogous experiments. We obtained a qualitative measure of the rate of H/D exchange in the following manner.

Approximately 40 mg of the appropriate carbene complex was placed in a thin-walled NMR tube and dissolved in $\mathrm{CD_2Cl_2}$ (0.4 ml). To this solution was added $\mathrm{CH_3OD}$ (99.5 atom %, 100 μl). The H/D exchange rate was monitored by following the appearance of the methanol OH resonance and by the disapperance of the carbene methyl resonance. In the case of ethylcarbene complexes the nature of the $\mathrm{:CCH_2C}H_3$ resonance provided a measure of deuterium incorporation at the α position. The t_∞ spectra were attained after ca. 1 h when X = Cl or $\mathrm{CF_3}$ and ca. 2 days when X = *p*-tolyl.

Carbene Methoxyl Group Exchange. Following the above procedure the protiomethyl(methoxy)carbene complexes *trans*-$[\mathrm{PtX(C(Me)OMe)L_2}]^+\mathrm{PF_6}^-$ were reacted with $\mathrm{CD_3OD}$. The diminution of the carbene methoxyl resonance and the appearance of the methanol, $\mathrm{C}H_3\mathrm{OH}$, resonance were easily monitored by ^{1}H NMR spectroscopy. The t_∞ spectra were achieved at ca. 12 h for X = Cl and $\mathrm{CF_3}$ and at ca. 2 weeks for X = C≡CH. No methoxyl group exchange was observed for X = *p*-tolyl or Me. In all of the above reactions α-carbene methyl proton for deuteron exchange was faster than methoxyl group exchange. For X = Me *no* exchange was observed.

Carbene Ethoxyl–Methoxyl Group Exchange. *trans*-$[\mathrm{PtCF_3(C(Me)OEt)(AsMe_3)_2}]^+\mathrm{PF_6}^-$ (50 mg) was dissolved in methanol. After 1 h the methanol was stripped off and the ^{1}H NMR spectrum of the residue recorded. This showed the complete and quantitive formation of *trans*-$[\mathrm{PtCF_3(C(Me)OMe)(AsMe_3)_2}]^+\mathrm{PF_6}^-$.

***trans*-$\mathrm{PtX(C({=}CH_2)OMe)L_2}$.** The σ-vinyl ether compounds *trans*-$\mathrm{PtX(C({=}CH_2)OMe)L_2}$, where X = Cl or $\mathrm{CF_3}$ and L = $\mathrm{PMe_2Ph}$ or $\mathrm{AsMe_3}$, were all prepared in the manner outlined below.

trans-$[\mathrm{PtCF_3(C(Me)OMe)(AsMe_3)_2}]^+\mathrm{PF_6}^-$ (349.4 mg, 0.468 mmol) was dissolved in methylene chloride (6 ml). Proton sponge, 1,8-bis(dimethylamino)naphthalene (36.2 mg), in methylene chloride (1 ml) was added. A precipitate formed immediately. The mixture was stirred for 10 min and then pumped to dryness. Benzene (5 ml) was added and the amine hydrohexafluorophosphate was removed by centrifugation. The benzene solution was collected and reduced in volume to ca. 1 ml. Addition of petroleum ether caused the formation of white crystals which were collected and dried in vacuo: *trans*-$\mathrm{PtCF_3(C({=}CH_2)OMe)(AsMe_3)_2}$, 153.3 mg (78% yield based on Pt), mp 107–109 °C.

***trans*-Pt(*p*-tol)(C(=CHMe)OMe)(PMe$_2$Ph)$_2$.** *trans*-$[\mathrm{Pt(}p\mathrm{\text{-}tol)(C(Et)OMe)(PMe_2Ph)_2}]^+\mathrm{PF_6}^-$ (50 mg) and proton sponge (13 mg, 1 equiv) were dissolved in $\mathrm{CD_2Cl_2}$ (0.5 ml) in an NMR tube. A fine white precipitate formed. The ^{1}H NMR spectrum showed the presence of the methoxyvinyl compound (δ(OMe) 3.93, δ (CH*Me*) = 1.23, doublet, $J_{\mathrm{H-H}}$ = 5 Hz) and the methoxycarbene complex (δ(OMe) 4.8, $^4J_{\mathrm{PtH}}$ = 6 Hz, $\delta(\mathrm{C(CH_2C}H_3\mathrm{)OMe})$ 0.78, triplet, $J_{\mathrm{H-H}}$ = 7 Hz). Integration of the methoxyl resonances indicated that the ratio of the σ-vinyl ether complex to the carbene complex was ca. 2:3.

σ-Vinyl Ether H/D Exchange Reactions. The compounds *trans*-$\mathrm{PtX(C({=}CH_2)OMe)L_2}$, where X = Cl or $\mathrm{CF_3}$ and L = $\mathrm{PMe_2Ph}$ or $\mathrm{AsMe_3}$, were reacted with $\mathrm{CH_3OD}$ and $\mathrm{CD_3OD}$ in NMR tube reactions in the manner described previously for methoxy(methyl)carbene complexes. The H/D exchange of the vinylic protons was much faster than that of the methoxyl group exchange.

In a similar experiment *trans*-$\mathrm{PtCF_3(C({=}CD_2)OCD_3)(AsMe_3)_2}$ was reacted with anhydrous $\mathrm{NH_3}$ in $\mathrm{CD_2Cl_2}$. No reaction was observed.

***trans*-Pt(C≡CD)$_2$(PMe$_2$Ph)$_2$.** *trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$ (0.4 g) was dissolved in MeOD (3 ml) and methylene chloride (2 ml). NaOH (5 mg) was added and the solution was stirred for 3 days at room temperature under an atmosphere of dry nitrogen. Solvent was removed under vacuum and white crystals formed ($\mathrm{CH_2Cl_2}$ is removed preferentially; the bis(acetylide) is only very sparingly soluble in methanol). The crystals were collected, washed with methanol, and dried in vacuo; mp 173 °C. Infrared analysis showed that deuteration was almost complete: Pt(C≡CD)$_2$(PMe$_2$Ph)$_2$, ν_{str}(C—D) 2542, ν_{str}(C≡CD) 1852 cm^{-1}; Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$, ν_{str}(≡C—H) 3278, ν_{str}(C≡CH) 1968 cm^{-1}.[26]

***trans*-Pt(CCl=CD$_2$)$_2$(PMe$_2$Ph)$_2$.** *trans*-Pt(C≡CD)$_2$(PMe$_2$Ph)$_2$ was reacted with DCl (2 equiv) in a directly analogous procedure to that previously described for the preparation of *trans*-Pt(CCl=CH$_2$)$_2$(PMe$_2$Ph)$_2$. Some proton contamination of the CCl=CD$_2$ moiety was always encountered. This could have arisen from hydroxyl/D$^+$ exchange reactions involving the glass or the presence of trace quantities of water.

Acetylide H/D Exchange Reactions. *trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$ (70 mg) was dissolved in MeOD (2 ml) and $\mathrm{CH_2Cl_2}$ (1 ml). After 6 days the solvent was stripped off and an infrared spectrum was recorded on the white solids. Only *trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$ was observed: no H/D exchange occurred.

trans-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$ (70 mg) was dissolved in $\mathrm{CH_3NO_2}$ (1 ml) and MeOD (1 ml). After 1 day the solvent was stripped off and an infrared spectrum of the white solid was recorded. In addition to bands at 3278 and 1968 cm^{-1} associated with Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$, bands at 2542 and 1852 cm^{-1} were present. The relative intensities of these bands suggested a PtC≡CH to PtC≡CD ratio of ca. 4:1.

Similar H/D exchange reactions occurred when *trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$ was reacted with $\mathrm{NH_4Cl}$ or $\mathrm{CH_3COOH}$ in MeOD.

Hydridoplatinum(II) H/D Exchange Reactions. *trans*-Pt(H)Cl(PMe$_2$Ph)$_2$ (50 mg) was dissolved in $\mathrm{CH_2Cl_2}$ (1 ml), $\mathrm{CH_3OD}$ (1 ml), and $\mathrm{CH_3NO_2}$ (1 ml). This was stirred for 3 days. The solvent was stripped off and the solids recrystallized from benzene/petroleum ether. The infrared spectrum showed the presence of only *trans*-Pt(H)Cl(PMe$_2$Ph)$_2$: ν_{str}(Pt–H) 2183 cm^{-1}.

In similar reactions *trans*-Pt(H)Cl(PMe$_2$Ph)$_2$ dissolved in MeOD and reacted with HCl or $\mathrm{HPF_6}$ gave *trans*-Pt(D)Cl(PMe$_2$Ph)$_2$: ν_{str}(Pt–D) 1570 cm^{-1}.

***trans*-Pt(C≡CD)$_2$L$_2$ + *trans*-Pt(C≡CH)ClL$_2$.** *trans*-Pt(C≡CD)$_2$(PMe$_2$Ph)$_2$ (40 mg) and *trans*-PtCl(C≡CH)(PMe$_2$Ph)$_2$ (40 mg) were dissolved together in $\mathrm{CH_2Cl_2}$ (2.5 ml). The solution was stirred under a nitrogen atmosphere for 14 h at which time a sample of the solution was examined by infrared spectroscopy. No *trans*-PtCl(C≡CD)(PMe$_2$Ph)$_2$ or *trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$ was detected. MeOD (1 ml) was added and the solution was stirred for 12 h. The infrared spectrum of the same was again recorded; no *trans*-PtCl(C≡CD)(PMe$_2$Ph)$_2$ was detected: *trans*-PtCl(C≡CH)(PMe$_2$Ph)$_2$, ν_{str}(≡C—H) 3278, ν_{str}(C≡CH) 1987 cm^{-1}; *trans*-PtCl(C≡CD)(PMe$_2$Ph)$_2$, ν_{str}(C≡CD) 1877 cm^{-1}, ν_{str}(≡C—D) 2560 cm^{-1}.

***trans*-PtCl(C(Me)OMe)(PMe$_2$Ph)$_2$SbF$_6$ + *trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$.** About 20 mg of each of *trans*-$[\mathrm{PtCl(C(Me)OMe)(PMe_2Ph)_2}]^+\mathrm{SbF_6}^-$ and *trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$ were dissolved together in a 1:1 mixture of $\mathrm{CH_3OD/CH_2Cl_2}$ (4 ml). The solution was stirred magnetically for 4 h under a dry nitrogen atmosphere. Solvent was stripped off and the residues were extracted with benzene (2 ml). The benzene-soluble products were dried in vacuo. Infrared spectroscopy showed this to be *trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$ with ca. 50% deuterium incorporation of the acetylenic group: ν_{str}(C—H) 3278, ν_{str}(C—D) 2542 cm^{-1}, ν_{str}(C≡CH) 1968, ν_{str}(C≡CD) 1852 cm^{-1}. *Note*: no *trans*-PtCl(C≡CD)(PMe$_2$Ph)$_2$ or *trans*-PtCl(C≡CH)(PMe$_2$Ph)$_2$ was detected.

***trans*-PtCl(C(Me)=^{18}O)(PMe$_2$Ph)$_2$.** *trans*-PtCl(CCl=CH$_2$)(PMe$_2$Ph)$_2$ (300 mg) was dissolved in dry acetone (4 ml). To this magnetically stirred solution under an atmosphere of nitrogen was added $^{18}\mathrm{OH_2}$ (100 μl) via microsyringe followed by $\mathrm{AgPF_3}$ (134 mg, 1 equiv) in acetone (1 ml). An immediate precipitate of AgCl formed. The solution was stirred for 5 min and then proton sponge (113 mg, 1 equiv) in acetone (1 ml) was added. The solution was stirred for a further 5 min and then pumped to dryness. The solids were extracted with benzene. The benzene-soluble extract was pumped to dryness yielding *trans*-PtCl(C(Me)=O)(PMe$_2$Ph)$_2$ (265 mg, 90% yield based on Pt), mp 149 °C. The infrared spectrum showed two strong peaks at 1601 and 1633 cm^{-1} which we assign to ν_{str}(C=^{18}O) and ν_{str}(C=^{16}O) respectively.

***trans*-PtCl(C(Me)=^{18}O)(PMe$_2$Ph)$_2$ + MeSO$_3$CF$_3$.** The ^{18}O acylplatinum complex (100 mg) was dissolved in dry methylene chloride (2 ml), with stirring, under an atmosphere of nitrogen. $\mathrm{MeSO_3CF_3}$ (15 μl, 1 equiv) was added via microsyringe. The solution was stirred for 1 h during which time the solution turned from colorless to pale yellow. The solvent was stripped off and the residue redissolved in a minimum amount of methylene chloride (ca. 0.5 ml). Addition of benzene (ca. 2 ml) resulted in the formation of an oil, from which waxy, fibrous, white crystals grew upon cooling to ca. 5 °C. The crystals were collected and dried: yield 80 mg (ca. 60% yield based on Pt) of *trans*-$[PtCl(C(Me)^{18}OMe)(PMe_2Ph)_2]^+SO_3CF_3^-$. This compound was not subjected to elemental analysis. The ^1H NMR spectrum clearly indicated the authenticity of the sample. ^1H NMR data in acetone-d_6 at 60 MHz, 40 °C: δ(OMe) 4.8, $^4J_{PtH} = 9.5$ Hz; $\delta(PMeMe')$ 2.00, 2.02, $^4J + {}^2J_{PH} = 8.6$ Hz, $^3J_{PtH} = 31$ Hz; $\delta(CCH_3)$ 2.35 (δ in ppm relative to TMS).

***trans*-$PtCl(C(Me)^{18}OMe)(PMe_2Ph)_2SO_3CF_3$ + NMe_4Cl.** *trans*-$PtCl(C(Me)^{18}OMe)(PMe_2Ph)_2SO_3CF_3$ (40 mg) was dissolved in acetone-d_6 (0.5 ml) and tetramethylammonium chloride (12 mg, a twofold excess) was added. The reaction was monitored by ^1H NMR spectroscopy. After 24 h the solution was pumped to dryness and the solid extracted with benzene. The benzene extract was reduced in volume to ca. 1 ml and petroleum ether (bp 30–60 °C) was added yielding white crystals, mp 149 °C. The infrared spectrum of the crystals was identical with that of the ^{18}O-enriched acylplatinum compound prepared previously: $\nu_{str}(C{=}^{18}O)$ 1601; $\nu_{str}(C{=}^{16}O)$ 1633 cm^{-1}.

***trans*-$PtCl(C(Me)^{18}OMe)(PMe_2Ph)_2SO_3CF_3$ + (1) $Me^{16}OH$ + (2) NMe_4Cl.** About 40 mg of the ^{18}O-enriched carbene complex *trans*-$PtCl(C(Me)^{18}OMe)(PMe_2Ph)_2SO_3CF_3$ was dissolved in dry methanol ($CH_3{}^{16}OH$) and allowed to stand at room temperature for 24 h. Tetramethylammonium chloride (12 mg, 2 equiv) was added and the reaction mixture was stirred for 12 h. The solvent was pumped off and the residue extracted with benzene and crystallized from benzene/petroleum ether (bp 30–60 °C) yielding white crystals, mp 149 °C. The infrared spectrum showed only a single strong band at 1633 cm^{-1}, characteristic of $\nu_{str}(C{=}^{16}O)$ in *trans*-$PtCl(C(Me){=}O)(PMe_2Ph)_2$.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. MPS 73-05016) for their support of this work. We also thank Matthey Bishop for a loan of platinum.

Registry No. $Pt(C\equiv CCF_3)_2P_2$, 38682-79-0; $Pt(CCl{=}CHCF_3)_2P_2$, 52638-04-7; $Pt(C\equiv CCH_3)_2I_2P_2$, 61484-33-1; $Pt(C\equiv CH)_2P_2$, 60314-10-5; $Pt(C\equiv CH)ClP_2$, 60293-86-9; $Pt(C\equiv CCH_3)_2P_2$, 52638-03-6; $Pt(C\equiv CCH_3)ClP_2$, 52638-05-8; $Pt(C\equiv CPh)_2P_2$, 28775-98-6; $Pt(CCl{=}CH_2)_2P_2$, 60293-84-7; $Pt(CCl{=}CH_2)ClP_2$, 60293-85-8; $Pt(COMe{=}CH_2)ClP_2$, 61483-27-0; $Pt(ClC{=}C(CH_3)H)ClP_2$, 61521-21-9; $Pt(ClC{=}C(H)CH_3)ClP_2$, 61521-22-0; $Pt(C(Et)OEt)ClP_2{}^+PF_6^-$, 52749-38-9; $Pt(C(Me)OPr^i)ClP_2{}^+PF_6^-$, 61483-29-2; $Pt(C\equiv CH)(C(Me)OMe)P_2{}^+PF_6^-$, 61483-31-6; $Pt(C\equiv CCH_3)_2A_2$, 61483-32-7; $Pt(C\equiv CCH_3)ClA_2$, 61483-33-8; $Pt(C\equiv CCH_3)(C(Et)OMe)A_2{}^+SbF_6^-$, 61505-82-6; $Pt(CF_3)(C(Me)OMe)A_2{}^+PF_6^-$, 61483-35-0; $Pt(CF_3)(COMe{=}CH_2)A_2$, 61483-36-1; *cis*-$PtCl_2(PMe_2Ph)_2$, 15393-14-3; *trans*-$PtBr(CCl{=}C(H)Me)(PMe_2Ph)_2$, 61521-23-1; *trans*-$[PtCl(C(Et)OMe)(PMe_2Ph)_2]^+PF_6^-$, 52749-36-7; *trans*-$PtCl(C(CH_3){=}O)(PMe_2Ph)_2$, 30180-03-1; *trans*-$PtCl(C(CD_2Me)OMe)(AsMe_3)_2{}^+CF_3COO^-$, 61483-38-3; *trans*-$PtCl(C(CD_2Me){=}O)(AsMe_3)_2$, 61483-39-4; *trans*-$Pt(C_6H_4CH_3)I(PMe_2Ph)_2$, 61483-40-7; *trans*-$[Pt(C_6H_4CH_3)(C(CH_2CH_3)OMe)(PMe_2Ph)_2]^+PF_6^-$, 61483-42-9; *trans*-$PtMe(Cl)(PMe_2Ph)_2$, 24833-58-7; *trans*-$[PtMe(C(CH_3)OMe)(PMe_2Ph)_2]^+PF_6^-$, 27776-75-6; *trans*-$[PtCF_3(C(Me)OEt)(AsMe_3)_2]^+PF_6^-$, 61483-44-1; *trans*-$Pt(p\text{-tol})(C({=}CHMe)OMe)(PMe_2Ph)_2$, 61483-45-2; *trans*-$Pt(C\equiv CD)_2(PMe_2Ph)_2$, 61426-25-3; *trans*-$Pt(H)Cl(PMe_2Ph)_2$, 12112-64-0; *trans*-$Pt(D)Cl(PMe_2Ph)_2$, 61483-46-3; *trans*-$[PtCl(C(Me)OMe)(PMe_2Ph)_2]^+SbF_6^-$, 61483-47-4; *trans*-$PtCl(C(Me){=}{}^{18}O)(PMe_2Ph)_2$, 61483-48-5; *trans*-$[PtCl(C(Me)^{18}OMe)(PMe_2Ph)_2]^+SO_3CF_3^-$, 61483-50-9; *trans*-$[Pt(p\text{-tol})(C(CD_2CH_3)OMe)(PMe_2Ph)_2]^+PF_6^-$, 61483-52-1; MeOH, 67-56-1; EtOH, 64-17-5; Pr^iOH, 67-63-0; MeOD, 1455-13-6.

References and Notes

(1) M. H. Chisholm and H. C. Clark, *Chem. Commun.*, 763 (1970).
(2) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 1711 (1971).
(3) T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, **97**, 1592 (1975).
(4) M. H. Chisholm and H. C. Clark, *J. Am. Chem. Soc.*, **94**, 1532 (1972).
(5) M. H. Chisholm and H. C. Clark, *Acc. Chem. Res.*, **6**, 202 (1973).
(6) M. H. Chisholm and D. A. Couch, *J. Chem. Soc., Chem. Commun.*, 42 (1974).
(7) R. A. Bell and M. H. Chisholm, *J. Chem. Soc., Chem. Commun.*, 818 (1974).
(8) R. Nast, J. Voss, and R. Kramolowsky, *Chem. Ber.*, **108**, 1511 (1975).
(9) R. A. Bell and M. H. Chisholm, *J. Chem. Soc., Chem. Commun.*, 200 (1976); *Inorg. Chem.*, following paper in this issue.
(10) M. I. Bruce, D. A. Harbourne, F. Waugh, and F. G. A. Stone, *J. Chem. Soc. A*, 356 (1968).
(11) (a) F. R. Hartley in "The Chemistry of Platinum and Palladium", Applied Science Publishers, 1973; (b) U. Belluco in "Organometallic and Coordination Chemistry of Platinum", Academic Press, New York, N.Y., 1974.
(12) R. W. Alder, R. Baker, and J. M. Brown, "Mechanisms in Organic Chemistry", Wiley, New York, N.Y., 1971.
(13) (a) C. P. Casey and R. L. Anderson, *J. Am. Chem. Soc.*, **96**, 1230 (1974). (b) A closely related reaction has recently been reported: *trans*-$Ni(C_6Cl_5)(C(Me)OMe)(PMe_2Ph)_2{}^+ClO_4^-$ + Et_3N → *trans*-$Ni(C_6Cl_5)(C({=}CH_2)OMe)(PMe_2Ph)_2$ + $Et_3NH^+ClO_4^-$ [K. Oguro, M. Wada, and R. Okawara, *J. Chem. Soc., Chem. Commun.*, 899 (1975)].
(14) F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 487 (1972).
(15) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972).
(16) E. O. Fischer, *Pure Appl. Chem.*, **30**, 353 (1972).
(17) M. H. Chisholm, H. C. Clark, W. S. Johns, J. E. H. Ward, and K. Yasafuku, *Inorg. Chem.*, **14**, 900 (1975).
(18) D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 854 (1973).
(19) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6578 (1975).
(20) R. M. Kirshner, J. A. Ibers, M. S. Saran, and R. B. King, *J. Am. Chem. Soc.*, **95**, 5775 (1973).
(21) E. O. Fischer, G. Kreis, C. G. Kreiter, J. Muller, G. Huttner, and H. Lorenz, *Angew. Chem., Int. Ed. Engl.*, **12**, 564 (1973).
(22) A. N. Nesmeyanov, G. G. Aleksandrov, A. B. Antonova, K. N. Anisimov, N. E. Kolobova, and Y. T. Struchkov, *J. Organomet. Chem.*, **110**, C36 (1976).
(23) We have also learned that a compound $[FeCl(P\text{-}P)_2(C{=}C(H)Ph)]^+BF_4^-$ has been obtained from the reaction between $FeCl_2(P\text{-}P)_2$ and $PhC\equiv CH$ in MeOH in the presence of NH_4BF_4; (P-P) = $Et_2PCH_2CH_2PEt_2$. M. J. Mays, Cambridge University, personal communication].
(24) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969).
(25) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2964 (1969).
(26) The decrease in $\nu(C\equiv C)$ upon deuteration is much larger than that observed in phenylacetylene [see G. W. King and S. P. So, *J. Mol. Spectrosc.*, **36**, 468 (1970)]. However, pure acetylene shows similar shifts upon deuteration: C_2H_2, 3287 (IR) and 1973 (Raman) cm^{-1}; C_2HD, 2584 (IR) and 1851 cm^{-1} (IR, Raman) [see M. Avran and G. Mateeschu, "Infrared Spectroscopy", Wiley-Interscience, New York, N.Y., 1972].