of the carbene-like ligands but do not allow a determination of the configuration of the presumably planar ligands. Preliminary X-ray results[17] indicate that the complex has a trans arrangement of ligands about platinum.

---

[17] J. H. Enemark, personal communication.

Acknowledgment.—This research was supported by Grants GM-18357 and AM 12182 from the National Institutes of Health. We thank Dr. A. Burke for experimental assistance during the early stages of this work, Professor L. F. Dahl for a preprint of ref 16, and Professor J. H. Enemark for helpful discussions.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WESTERN ONTARIO, LONDON, ONTARIO, CANADA

Reactions of 3,3,3-Trifluoropropyne with Methylplatinum(II) Complexes

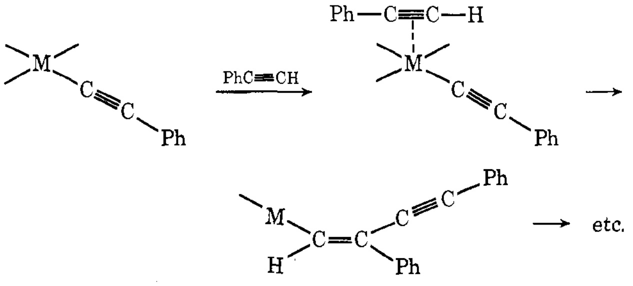
BY T. G. APPLETON, H. C. CLARK,* AND R. J. PUDDEPHATT

Received October 26, 1971

3,3,3-Trifluoropropyne, $CF_3C{\equiv}CH$, reacts with complexes of the types *cis*-$Pt(CH_3)_2L_2$ and *trans*-$PtCl(CH_3)L_2$, where L = $P(CH_3)_2(C_6H_5)$ (Q), $As(CH_3)_3$, or $As(CH_3)_2(C_6H_5)$, to give varying amounts of polymer and organoplatinum products. Polymerization occurs by an ionic mechanism. Major products from the reaction of $PtCl(CH_3)Q_2$ with $CF_3C{\equiv}CH$ in benzene are *trans*-$PtCl(-C{\equiv}CCF_3)Q_2$, *trans*-$PtCl\{C(CF_3){=}CHCl\}Q_2$, *trans*-$Pt(-C{\equiv}CCF_3)_2Q_2$, and $PtCl_2(CH_3)_2Q_2$. In alcohols, ROH, $PtCl(CH_3)Q_2$ reacts with $CF_3C{\equiv}CH$ to give complexes of the type *trans*-$PtCl\{C(CF_3){=}CH(OR)\}Q_2$.

Introduction

Continuing our studies[1-3] on the reactions of unsaturated compounds with methylplatinum(II) complexes, we have investigated the reactions of 3,3,3-trifluoropropyne, $CF_3C{\equiv}CH$, with complexes *trans*-$PtCl(CH_3)L_2$ and *cis*-$Pt(CH_3)_2L_2$, where L = $P(CH_3)_2(C_6H_5)$, $As(CH_3)_3$, or $As(CH_3)_2(C_6H_5)$; Q will be substituted for $P(CH_3)_2(C_6H_5)$. The reactions of this acetylene with a variety of metal complexes have been reported.[4-7] We have found that $CF_3C{\equiv}CH$ is polymerized by methylplatinum(II) complexes. Our results suggest that this polymerization does not occur by the mechanism which has been proposed[8-10] for the polymerization of phenylacetylene by complexes of platinum group metals

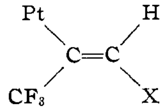


Rather, polymerization is anionic, initiated by the electron-rich organoplatinum complex, either directly or *via* a five-coordinate intermediate.

Results

Characterization of Reaction Products.—When the polymer was obtained, it formed as a white precipitate in the reaction mixture. A typical polymeric product decomposed slowly above 115°, gave infrared bands at 1610 and 1670 cm^{-1} arising from C=C groupings, and was insoluble or very sparingly soluble in common organic solvents. These properties suggest that the polymer is cross-linked, since linear polyacetylenes are usually highly colored, and soluble in organic solvents,[11] although X-ray powder photographs show an unexpectedly large degree of crystallinity.

The filtrate after removal of polymer usually contained a fairly complex mixture of organoplatinum complexes. In some cases the major products could be isolated using column chromatography. Otherwise, the products were identified, or their natures ascertained, from nmr spectra (especially ^{19}F nmr) of crude of partially separated reaction mixtures. Major products in most reactions contained 3,3,3-trifluoropropynylplatinum groups, $Pt{-}C{\equiv}CCF_3$, or substituted vinylplatinum groups of the type



The spectroscopic features of these groups, used to characterize the complexes, are described below.

The 3,3,3-trifluoropropynylplatinum complexes[12] show a strong infrared absorption in the region 2100–2150 cm^{-1} corresponding to C≡C stretching. Their ^{19}F nmr spectra show sharp peaks in the region 46–48 ppm upfield from $CFCl_3$ with coupling (19–35 Hz) to ^{195}Pt ($I = {}^1/_2$, 34% abundant). For phosphine complexes, coupling with ^{31}P nuclei is also observed.

The complexes containing vinylplatinum groups, $PtC(CF_3){=}CH(X)$ (X = OR, Cl), show a moderately

---

(1) H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, **9**, 2670 (1970).

(2) H. C. Clark and R. J. Puddephatt, *ibid.*, **10**, 18 (1971).

(3) H. C. Clark and R. J. Puddephatt, *ibid.*, **10**, 416 (1971).

(4) D. A. Harbourne and F. G. A. Stone, *J. Chem. Soc. A*, 1765 (1968).

(5) M. I. Bruce, D. A. Harbourne, F. Waugh, and F. G. A. Stone, *ibid.*, 895 (1968).

(6) R. S. Dickson and P. J. Fraser, *Aust. J. Chem.*, **23**, 2403 (1970).

(7) J. T. Mague, E. H. Gause, and M. O. Nutt, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971, No. INOR 133.

(8) L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennedy, *J. Org. Chem.*, **27**, 3930 (1962).

(9) A. Furlani, I. Collamati, and G. Sartori, *J. Organometal. Chem.*, **17**, 463 (1969).

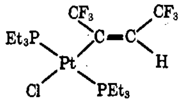
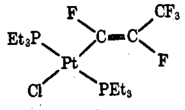
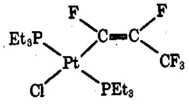
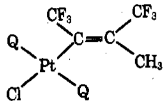
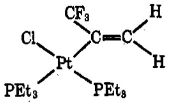
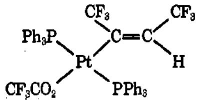
(10) H. Dietl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **92**, 2276 (1970).

(11) W. W. Hausser and R. Kuhn, *Z. Phys. Chem., Abt. B*, **29**, 363 (1935).

(12) M. I. Bruce, D. A. Harbourne, F. Waugh, and F. G. A. Stone, *J. Chem. Soc. A*, 356 (1968).

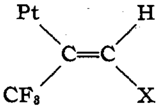
TABLE I

PLATINUM–FLUORINE COUPLING CONSTANTS IN SOME SUBSTITUTED VINYL–PLATINUM COMPLEXES (Hz)

	$J_{\text{Pt-F}}$ (gem)	$J_{\text{Pt-F}}$ (trans)	$J_{\text{Pt-F}}$ (cis)	Ref
 A	142.3	5.82		*a*
 B		5.82		*a*
 C			13.45	*a*
 D	128.3	6.2		1
 E	72.7			4
 F	130			*b*

[a] H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, **89**, 533 (1967). [b] D. M. Barber, R. D. W. Kemmitt, and G. W. Littlecott, *Chem. Commun.*, 613 (1969).

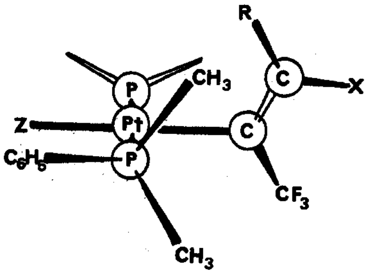
strong peak corresponding to C=C stretching near 1600 cm^{-1}. A sharp singlet occurs in the ^{19}F spectrum near 50 ppm upfield from CFCl$_3$, with "satellites" from coupling to ^{195}Pt (120–130 Hz). Comparison of this coupling constant with those in the literature (Table I) indicates that the trifluoromethyl group is geminal to Pt. No measurable coupling to ^{31}P was observed in the phosphine complexes obtained (in which the phosphine ligands were both cis to the vinyl group). The resonance from the vinylic proton occurs near 5 ppm downfield from TMS. Small couplings (<2 Hz) to the phosphorus nuclei and coupling to ^{195}Pt (55–57 Hz) are observed. Platinum–proton coupling constants in a number of vinylplatinum complexes have been reported by Mann, Shaw, and Tucker.[13] For the compounds they studied $J_{\text{Pt-H(gem)}} = 8$ Hz, $J_{\text{Pt-H(trans)}} = 120\text{–}150$ Hz, and $J_{\text{Pt-H(cis)}} = 63\text{–}81$ Hz. The platinum–proton coupling constants in our compounds correspond to $J_{\text{Pt-H(cis)}}$. The stereochemistry about the double bond is thus



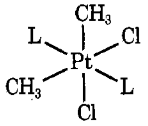
The absence of coupling between the CF$_3$ group and the vinylic proton is also consistent with this structure.[14] When X is an alkoxy group, typical peaks occur in the nmr spectra.

For phosphine complexes, assignment of geometrical isomers with respect to platinum was based on the well-known rule[15,16] that with trans complexes the phosphine methyl groups give 1:2:1 triplets from coupling with both ^{31}P nuclei, while cis complexes give doublets, since each methyl group couples to only one ^{31}P nucleus. For arsine complexes, probable assignments could be made by comparison with the corresponding phosphine complexes and by taking into account the trans influences of other groups coordinated to the platinum atom.

The phosphine methyl region of the spectrum of *trans*-PtI$\{$-C(CF$_3$)=CH(OCH$_3$)$\}$Q$_2$, like that of the complexes[1] *trans*-PtCl$\{$-C(CF$_3$)=C(CH$_3$)(CF$_3$)$\}$Q$_2$, shows two overlapping triplets, corresponding to nonequivalent phosphine methyl groups. The complexes *trans*-PtCl$\{$-C(CF$_3$)=CH(X)$\}$Q$_2$ (X = Cl, OR) show only one triplet (apart from "satellites" from coupling to ^{195}Pt). Nonequivalence of the phosphine methyl groups implies that the vinyl group occupies the position illustrated below, perpendicular to the plane of the complex,[1] with slow rotation about the Pt–C bond. This need not necessarily imply extensive π back-bonding to the vinyl group, since it is clear from models that the bulky phosphines will greatly hinder free rotation about the Pt–C bond. The group "X" is remote from the phosphines and will have little effect on the phosphine methyl groups, but the group "R" lies almost above the Pt atom and could be quite close to the phosphine methyl groups. When R = H and Z = Cl, the phosphine groups are not greatly constrained sterically, and the phosphine methyl group inequivalence is not apparent in the spectrum, but when Z is the larger iodide or R is a methyl group, the nonequivalence is enhanced.



The platinum(IV) complexes



obtained in some reactions have been described previously.[16]

In Table II, analytical data are listed for all the complexes isolated. Spectroscopic data are given in

---

[13] B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Commun.*, 1333 (1970).

[14] W. R. Cullen, D. J. Dawson, and G. E. Styan, *Can. J. Chem.*, **43**, 3392 (1965).

[15] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).

[16] J. D. Ruddick and B. L. Shaw, *ibid.*, 2801, 2964 (1969).

TABLE II

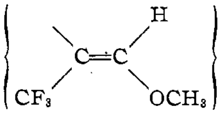
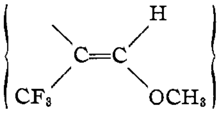
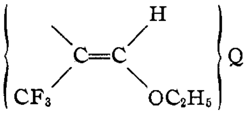
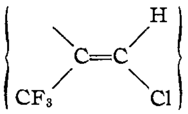
ANALYTICAL DATA

Compound[a]	Anal, % calcd, (% found) C	H	F	Mp,[b] °C	Mol wt[c] calcd (found)
$(CF_3CCH)_n$	38.3 (36.2)	1.1 (1.5)	60.6 (58.5)		
trans-$Pt(-C{\equiv}CCF_3)_2Q_2$	40.2 (40.2)	3.4 (3.4)	17.3 (16.6)[e]	146–150	
trans-$Pt(-C{\equiv}CCF_3)_2A'_2$	23.2 (23.6)	2.9 (2.7)	18.3 (18.3)	198–201[d]	621 (626)
trans-$Pt(-C{\equiv}CCF_3)_2A_2$	35.4 (35.5)	3.0 (3.0)	15.3 (15.2)	159	745 (697)
trans-$PtCl(-C{\equiv}CCF_3)Q_2$	38.0 (38.1)	3.7 (3.8)	9.5 (9.8)	99–103	560 (602)
cis-$Pt(CH_3)(-C{\equiv}CCF_3)Q_2$	41.5 (41.3)	4.4 (4.7)	9.8 (9.2)[e]	118–119	579 (590)
trans-$Pt(CH_3)(-C{\equiv}CCF_3)Q_2$	41.5 (41.5)	4.4 (4.3)	9.8 (9.6)	71–79	
trans-$PtCl\{C(CF_3){=}CH(OCH_3)\}Q_2$	38.0 (38.3)	4.1 (4.0)	9.0 (8.8)	106–108	
trans-$PtI\{C(CF_3){=}CH(OCH_3)\}Q_2$	33.2 (33.4)	3.6 (3.4)	7.9 (7.8)	136	
trans-$PtCl\{C(CF_3){=}CH(OC_2H_5)\}Q_2$	39.0 (38.9)	4.4 (4.4)	8.8 (9.0)	94–95	
trans-$PtCl\{C(CF_3){=}CHCl\}Q_2$[f]	35.9 (35.8)	3.6 (3.8)	9.0 (11.0)[e]	104–105	

[a] $Q = P(CH_3)_2(C_6H_5)$, $A = As(CH_3)_2(C_6H_5)$, $A' = As(CH_3)_3$. All white solids. [b] Corrected. [c] Where measured. [d] Decomposed. [e] Satisfactory F analysis not obtained. [f] Cl: calcd, 11.1; found, 11.5.

TABLE III

SPECTROSCOPIC DATA

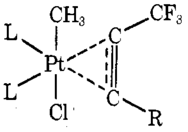
Compound[a]	δ_{L-CH_3}[b,c,e]	$^2J_{P-CH_3}$ or $^2J + {}^4J_{P-CH_3}$, Hz	$^3J_{Pt-L-CH_3}$,[b] Hz	δ_{CF_3}[d,e]	J_{Pt-CF_3}, Hz	J_{P-CF_3}, Hz	Other peaks in nmr	$\nu_{C=C}$[f] or $\nu_{C\equiv C}$, cm^{-1}
trans-$Pt(-C{\equiv}CCF_3)_2Q_2$	−1.99 t	7.9	32.4	47.3 t	25.0	3.4		2185 m 2140 s
trans-$Pt(-C{\equiv}CCF_3)_2A'_2$	−1.63 s		23.5	46.8 s	25.0			2130 s
trans-$Pt(-C{\equiv}CCF_3)_2A_2$	−1.91 s		23.2	47.2 s	24.6			2140 s
trans-$PtCl(-C{\equiv}CCF_3)Q_2$	−1.92 t	7.8	29.7	46.9 t	34.1	3.5		2160 s
cis-$Pt(CH_3)(-C{\equiv}CCF_3)Q_2$[g]	−1.24[h] d −1.64[i] d	8.6 9.0	27.0 20.1	45.0 d–d	27.5	5.6[j] 2.8[k]	Pt–CH_3 peaks Obscured	2140 s 2080 sh
trans-$Pt(CH_3)(-C{\equiv}CCF_3)Q_2$	−1.88	7.0	32.5	45.6 t	25.8	3.3	δ_{Pt-CH_3} 0.16 t $J_{Pt-CH_3} = 57.8$ Hz $^3J_{P-Pt-CH_3} = 7.2$ Hz	2120 m
trans-PtCl  Q_2	−1.77	7.3	29.3	49.8 s	128.2	<1	δ_{OCH_3} −3.22 s $\delta_{H(vinyl)}$ −4.97 t $^3J_{Pt-H} = 55.7$ Hz $^4J_{P-H} = 1.7$ Hz	1603 ms
trans-PtI  Q_2	−1.88 t −1.95 t	7.2	29.6	51.3 s	125.8	<1	δ_{OCH_3} −3.265 $\delta_{H(vinyl)}$ −5.05 t $^3J_{Pt-H} = 56.4$ Hz $^4J_{P-H} = 1.7$ Hz	1603 ms
trans-PtCl  Q_2	−1.85	8.0	28.5	49.7 s	128.4	<1	δ_{OCH_2} −3.55 q $\delta_{CH_3-CH_2}$ −1.12 t $J_{CH_3-CH_2} = 7.1$ Hz $\delta_{H(vinyl)}$ −5.22 t $^3J_{Pt-H} = 57.0$ $^4J_{P-H} = 2.0$	1602 ms
trans-PtCl  Q_2	−1.77	7.4	29.8	52.8 s	121.5	<1	$\delta_{H(vinyl)}$ −5.42 q–t $^3J_{Pt-H} = 60.0$ Hz	1566 m

[a] $Q = P(CH_3)_2(C_6H_5)$; $A = As(CH_3)_2(C_6H_5)$; $A' = As(CH_3)_3$. Unless otherwise stated, spectrum run in $CHCl_3$. [b] L = P, As. [c] Ppm upfield from TMS. [d] Ppm upfield from $CFCl_3$. [e] Key: s, singlet; d, doublet; t, triplet; q, quartet. [f] Nujol mulls. Key: s, strong; m, medium; sh, shoulder. [g] In benzene. [h] Trans to CH_3. [i] Trans to $C{\equiv}CCF_3$. [j] Trans P. [k] Cis P.

Table III. Results of some typical reactions (reactions 1–24) are listed in Table IV.

Discussion

Properties of Five-Coordinate Intermediates.—In the reactions of *trans*-$PtCl(CH_3)L_2$ with $CF_3C{\equiv}CCF_3$,[1,2] complexes of the type



($R = CF_3$) were isolated and found to be intermediates in insertion and disproportionation reactions.

The five-coordinate complexes are in many respects analogous to the much studied Pt(0) complexes PtL_2(acetylene),[17] the acetylene bonding by donating π electrons into a Pt σ orbital and accepting Pt d_π electrons into its π*-antibonding orbitals.[18] The π back-bonding is an important factor in the bonding, since five-coordinate complexes are detected only when the electron density on Pt is very high and when the acetylene has electron-withdrawing substituents.[2,17]

Several differences would be expected between the

---

(17) T. G. Appleton, M. H. Chisholm, and H. C. Clark, to be submitted for publication.

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

TABLE IV

RESULTS OF SOME TYPICAL REACTIONS

Reaction no.	Complex[a] (mmol)	Solvent (ml)	Amt of $CF_3C{\equiv}CH$, mmol	Reaction conditions[b]	Amt of CF_3CCH as polymer	Pt-containing products[a,c] identified or isolated
1	*trans*-$PtClMeQ_2$ (1.9)	C_6H_6 (10)	15	25°, 48 hr	2.1 mmol	*trans*-$PtClMeQ_2$
2	*trans*-$PtClMeQ_2$ (1.7)	C_6H_6 (8)	14	50–60°, 2.5 days	12.7 mmol	*trans*-$PtCl(-C{\equiv}CCF_3)Q_2$ (~30%), *trans*-$PtCl[-(CF_3)C{=}C(Cl)H]Q_2$ (~10%), *trans*-$PtClMeQ_2$ (~10%), *trans*-$Pt(-C{\equiv}CCF_3)_2Q_2$ (~5%), $PtCl_2Me_2Q_2$ (~5%) with complex mixtures containing small quantities of other products.
3	*trans*-$PtClMeQ_2$ (0.95)	CH_3OH	5	25°, 5 days	Trace	*trans*-$PtCl[-CF_3C{=}CH(OCH_3)]Q_2$ (65% after purification), CH_4 in gas phase
4	*trans*-$PtClMeQ_2$	C_2H_5OH	3	50°, 2 days	Significant amount	*trans*-$PtCl[-(CF_3)C{=}CH(OC_2H_5)]Q_2$ with small amount of *trans*-$PtCl(-C{\equiv}CCF_3)Q_2$, *trans*-$PtCl[-(CF_3)C{=}CH(Cl)]Q_2$, and other products
5	*trans*-$PtIMeQ_2$ (0.16)	CH_3OH (3)	7	25°, 7 days	Nil	*trans*-$PtI[-(CF_3)C{=}CH(OCH_3)]Q_2$, CH_4 in gas phase
6	*trans*-$PtClMeA'_2$ (0.21) (by nmr)	C_6H_6 (0.4)	1	25°, 1 day	Trace	*trans*-$PtCl[-(CF_3)C{=}CH(Cl)]A'_2$, *trans*-$PtCl(-C{\equiv}CCF_3)A'_2$, *trans*-$Pt(-C{\equiv}CCF_3)_2A'_2$, $PtCl_2Me_2A'_2$
7	*trans*-$PtClMeA'_2$ (0.35)	CH_3OH (5)	2	25°, 2 days	Nil	*trans*-$PtClMeA'_2$
8	*trans*-$PtClMeA'_2$ (0.35)	CH_3OH (5)	2	50°, 4 days	Some polymer	Mainly products containing $PtC{\equiv}CCF_3$
9	*cis*-$PtMe_2Q_2$ (2)	C_6H_6 (10)	13.5	25°, 2 days	12.8 very rapid	*cis*-$PtMe_2Q_2$; from ir, trace of $PtC{\equiv}CCF_3$
10	*cis*-$PtMe_2Q_2$ (0.3)	C_6H_6 (2)	7.5	25°, 48 hr	5.5	1:2 trans:cis $PtMe(-C{\equiv}CCF_3)Q_2$
11	*cis*-$PtMe_2Q_2$ (0.3)	CH_2Cl_2 (2)	7.5	25°, 48 hr	2.7	3:2 trans:cis $PtMe(-C{\equiv}CCF_3)Q_2$
12	*cis*-$PtMe_2Q_2$ (0.3)	$(C_2H_5)_2O$ (2)	7.5	25°, 48 hr	1.6	1:5 trans:cis $PtMe(-C{\equiv}CCF_3)Q_2$
13a	*cis*-$PtMe_2Q_2$ (0.3)	$(CH_3)_2CO$ (2)	7.5	25°, 48 hr	NIL	2:3 trans:cis $PtMe(-C{\equiv}CCF_3)Q_2$
13b	*cis*-$PtMe_2Q_2$ (0.074) (by nmr)	$(CD_3)_2CO$ (0.3)	1	25°, 1 week	Some polymer after 1 week	40% *cis*-$PtMe_2Q_2$, 50% *cis*-$PtMe(-C{\equiv}CCF_3)Q_2$, 10% *trans*-$PtMe(-C{\equiv}CCF_3)Q_2$, 20% CH_4 (in soln)
14	*cis*-$PtMe_2Q_2$ (0.3)	CH_3OH (2)	7.5	25°, 48 hr	Trace	*trans*-$Pt(-C{\equiv}CCF_3)_2Q_2$ and complex mixture of other products; from nmr, no methoxy groups present
15a	*cis*-$PtMe_2Q_2$ (0.2) + 2,6-di(*tert*-butyl)-*p*-cresol (0.001 g)	C_6H_6 (5)	5	25°	Polymer after 3.75 hr	Not examined
15b	*cis*-$PtMe_2Q_2$ (0.2)	C_6H_6 (5)	5	25°	Polymer after 3.5 hr	Not examined
16	Benzoyl peroxide (0.13 g)	C_6H_6 (3)	6.5	25°, 13 hr 60°, 3 days 100, 3 days	Nil	
17	*cis*-$PtMe_2A'_2$ (1.08)	C_6H_6 (5)	5.5	25°, 7 days	1	*trans*-$Pt(-C{\equiv}CCF_3)_2A'_2$ (~30%) and complex mixture of products
18	*cis*-$PtMe_2A_2$ (0.7)	C_6H_6 (3)	6	25°, 10 days	1.5	*trans*-$Pt(-C{\equiv}CCF_3)_2A_2$ (~40%) and mixture of products
19	*trans*-$Pt(-C{\equiv}CCF_3)_2Q_2$ (0.3)	C_6H_6 (2)	3	25°, 7 days	Nil	*trans*-$Pt(-C{\equiv}CCF_3)_2Q_2$
20	*trans*-$PtCl(-C{\equiv}CCF_3)Q_2$ (0.17)	C_6H_6 (4)	7	60°, 4 days	Trace	*trans*-$PtCl(-C{\equiv}CCF_3)Q_2$
21a	*cis*-$PtMe(-C{\equiv}CCF_3)Q_2$ (0.17)	C_6H_6 (5)	5	25°	Polymer after 2 days	Not examined
21b	*trans*-$PtMe(-C{\equiv}CF_3)Q_2$ (0.04)	C_6H_6 (2)	6.5	25°	Trace polymer after 2 days	Not examined
22	*trans*-$PtCl[-(CF_3)C{=}CH(OCH_3)]Q_2$ (0.5)	C_6H_6 (4)	6.5	60°, 6 days	Trace	*trans*-$PtCl[-(CF_3)C{=}CH(OCH_3)]Q_2$ (ir shows trace of $PtC{\equiv}CCF_3$)
23	*cis*-$PtCl_2Q_2$ (0.43)	C_6H_6 (3)	7	60°, 4 days	0.75	*cis*-$PtCl_2Q_2$
24	$P(C_6H_5)_3$ (0.34)	C_6H_6 (5)	5	25°	No insoluble polymer	Solution immediately turned dark brown; presumably linear conjugated polymer

[a] $Q = P(CH_3)_2(C_6H_5)$, $A = As(CH_3)_2(C_6H_5)$, $A' = As(CH_3)_3$, $Me = CH_3$. [b] All reactions in sealed Pyrex tubes. [c] Predominant product listed first.

five-coordinate complexes formed with $CF_3C{\equiv}CH$ and with $CF_3C{\equiv}CCF_3$. (i) $CF_3C{\equiv}CH$ is a dipolar molecule, the proton end being positive.[19] This charge asymmetry will be accentuated on coordination, since π back-donation will be greater at the CF_3 end of the molecule. The net effect of coordination of the acetylene would be transfer of charge from between the carbon atoms to the π^* orbitals at the CF_3 end. (ii) $CF_3C{\equiv}CH$ possesses an acidic proton, so that acetylide-type complexes may be formed. Since complexation will remove electrons from this end of the molecule, acidity will increase. (iii) The asymmetry of $CF_3C{\equiv}CH$, and the lower total electron-withdrawing capacity of its substituents compared with that of $CF_3C{\equiv}CCF_3$, will probably cause its five-coordinate

---

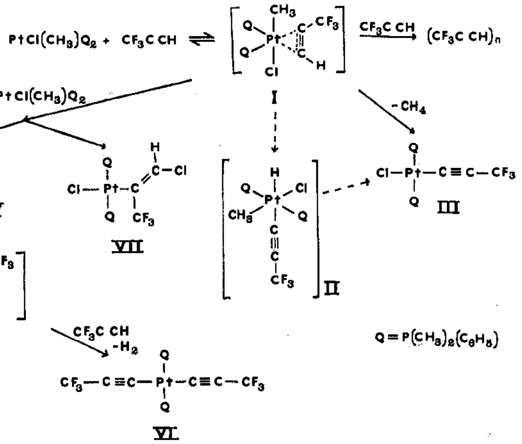
(19) R. N. Haszeldine, *J. Chem. Soc.*, 3490 (1952).

complexes to be less stable. No such complex has been isolated or detected spectroscopically. It must be present in very small proportions in solutions containing $CF_3C{\equiv}CH$ and $PtCl(CH_3)L_2$.

The complexes $Pt(CH_3)_2L_2$ also probably react *via* five-coordinate intermediates too reactive to be detected.[2]

Reaction of *trans*-$PtCl(CH_3)L_2$ with $CF_3C{\equiv}CH$ in Benzene.—At room temperature (reaction 1) *trans*-$PtCl(CH_3)Q_2$ with $CF_3C{\equiv}CH$ in benzene gave some polymer, but the starting material was not consumed. At 50–60°, however, (reaction 2) a variety of platinum-containing products were isolated. Probable reactions involved are summarized in Scheme I.

SCHEME I

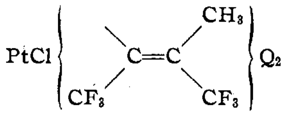


Elimination of methane from I, perhaps *via* a platinum(IV) hydride[20-25] (II), gives *trans*-$PtCl(-C{\equiv}CCF_3)Q_2$ (III). This appears to be the predominant reaction. No hydrido complexes were detected from pmr spectra of the reaction mixture.

Disproportionation products analogous to IV and V occur in reactions of $PtCl(CH_3)Q_2$ with $CF_3C{\equiv}CCF_3$.[2] We have not isolated V in the reaction products, although the corresponding triphenylphosphine complex is known.[4] In the presence of a large excess of $CF_3C{\equiv}CH$, V would probably react fairly rapidly to give *trans*-$Pt(-C{\equiv}CCF_3)_2Q_2$ (VI).[9,26,27] This is supported by the experimental observation that $PtCl_2(CH_3)_2Q_2$ (IV) and $Pt(-C{\equiv}CCF_3)_2Q_2$ (VI) are formed in equal amounts [since it is found (reaction 20) that $PtCl(-C{\equiv}CCF_3)Q_2$ (III) does not react with excess $CF_3C{\equiv}CH$ to give (VI)].

Complex VII is also presumably formed by reaction of $PtCl(CH_3)Q_2$ with I, by nucleophilic attack of Pt—Cl on the positive end of the coordinated acetylene. The other product in this reaction would be expected to be $Pt(CH_3)_2Q_2$, but neither this complex nor the products of its reaction with $CF_3C{\equiv}CH$ (see below) were isolated.

Although the major product from the reaction of $PtCl(CH_3)Q_2$ with $CF_3C{\equiv}CCF_3$ was the insertion product

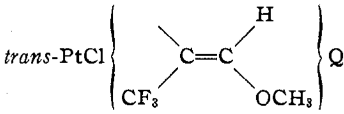


$\mathrm{PtCl}\{\mathrm{C(CF_3)}{=}\mathrm{C(CH_3)CF_3}\}\mathrm{Q_2}$

the corresponding reaction with $CF_3C{\equiv}CH$ must be relatively unimportant.

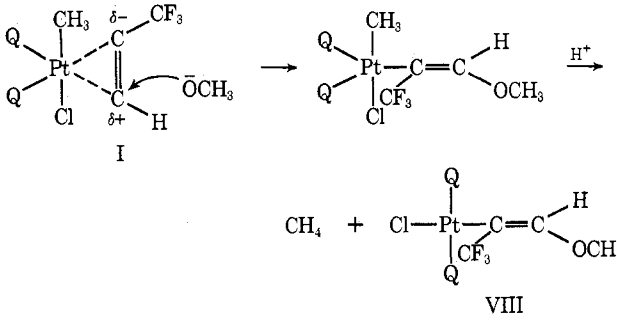
The reactions of *trans*-$PtCl(CH_3)L_2$ (L = arsine) with $CF_3C{\equiv}CH$ in benzene (reaction 6) were studied less thoroughly but appear to be similar.

Reaction of *trans*-$PtCl(CH_3)L_2$ with $CF_3C{\equiv}CH$ in Alcohols.—$PtCl(CH_3)Q_2$ reacts with $CF_3C{\equiv}CH$ in methanol at room temperature to give the vinyl ether complex (reaction 3)

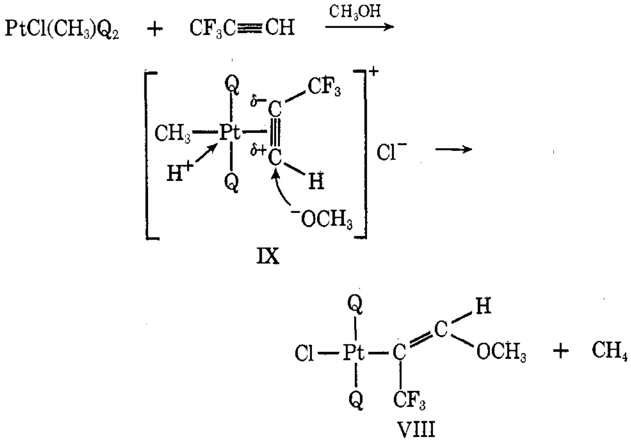


trans-$\mathrm{PtCl}\{\mathrm{C(CF_3)}{=}\mathrm{C(H)OCH_3}\}\mathrm{Q_2}$

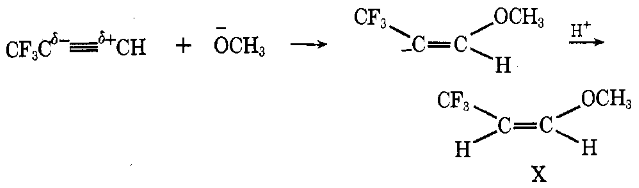
The reaction could be envisaged as proceeding by methoxide attack on $CF_3C{\equiv}CH$ activated by formation of a five-coordinate intermediate (I)



The reaction may be stepwise, as shown, or concerted. Alternatively, the reaction may be considered as proceeding *via* a cationic four-coordinate complex[28]



The reaction can be compared with the base-catalyzed reaction of trifluoropropyne itself[19]



---

(20) J. H. Nelson, H. B. Jonassen, and D. M. Roundhill, *Inorg. Chem.*, **8**, 2591 (1969).

(21) P. B. Tripathy and D. M. Roundhill, *J. Amer. Chem. Soc.*, **92**, 3825 (1970).

(22) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

(23) R. J. Cross and F. Glockling, *ibid.*, 5422 (1965).

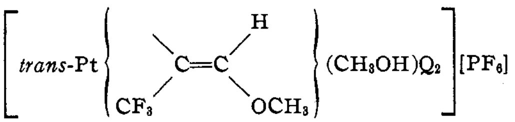
(24) J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, **89**, 844 (1967).

(25) C. K. Brown and G. Wilkinson, *Chem. Commun.*, 70 (1971).

(26) D. M. Blake and C. J. Nyman, *J. Amer. Chem. Soc.*, **92**, 5359 (1970).

(27) W. R. Cullen and F. L. Hou, *Can. J. Chem.*, **49**, 3404 (1971).

In the cationic complex, as with the five-coordinate complex, coordination of $CF_3C{\equiv}CH$ activates the acetylene toward nucleophilic attack at the proton end. Evidence so far tends to favor the cationic mechanism. *cis*-$Pt(CH_3)_2Q_2$, which cannot readily give a cationic acetylene complex, yields only a trace of methoxy complex with $CF_3C{\equiv}CH$ in methanol (reaction 14). Reaction of trifluoropropyne with *trans*-$[Pt(CH_3)(CH_3OH)Q_2][PF_6]$ in methanol gives[28]

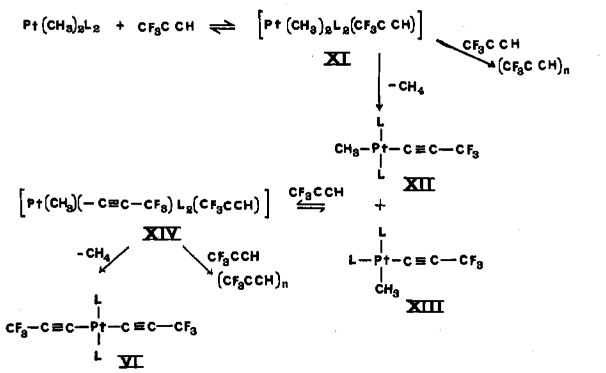


$$\left[trans\text{-}Pt\left\{\begin{matrix} & & H \\ & C{=}C & \\ CF_3 & & OCH_3\end{matrix}\right\}(CH_3OH)Q_2\right][PF_6]$$

If the reasoning above is correct, alcoholic solutions of $PtX(CH_3)L_2$ (X = halide) with $CF_3C{\equiv}CH$ will probably contain finite concentrations of both $PtX(CH_3)(CF_3CCH)L_2$ (I) and $[Pt(CH_3)(CF_3CCH)L_2]Cl$ (IX), reactions of I giving products analogous to those obtained in benzene and reactions of IX giving vinyl ether complexes (VIII). The actual products predominating in any one reaction will depend on the comparative stabilities and reactivities of these two complexes. When L = $P(CH_3)_2(C_6H_5)$, reactions in ethanol and methanol proceed mainly *via* the cationic intermediate IX, although traces of products typical of the reaction in benzene were detected in the ethanol reaction. When L = $As(CH_3)_3$, reactions *via* the cationic complex IX are less important, and the products are characteristic of reactions *via* I (reactions 7, 8).

Reactions of *cis*-$Pt(CH_3)_2L_2$ with $CF_3C{\equiv}CH$.—*cis*-$Pt(CH_3)_2Q_2$ (Q = $P(CH_3)_2(C_6H_5)$) with $CF_3C{\equiv}CH$ in most solvents (reactions 10–13) gives, presumably *via* the five-coordinate intermediate XI, a mixture of the isomers of the methyl(propynyl)platinum complex (XII + XIII). In methanol a complex mixture was obtained, from which *trans*-$Pt(-C{\equiv}CCF_3)_2L_2$ was isolated (reaction 14). No attack on the acetylene by methanol occurred.

SCHEME II



When L = $As(CH_3)_3$ or $As(CH_3)_2(C_6H_5)$ the main product from the reaction with $CF_3C{\equiv}CH$ in benzene (reactions 17, 18) was *trans*-$Pt(-C{\equiv}CCF_3)_2L_2$, although, especially with the trimethylarsine complex, a very complex mixture of products was also obtained.

Mechanism of Polymer Formation.—It is quite clear that polymerization of $CF_3C{\equiv}CH$ in these reactions does not occur by insertion of the acetylene into the $PtC{\equiv}CCF_3$ grouping, although this type of mechanism is generally favored for polymerization of terminal acetylenes.[8–10] The alkynyl–metal bond (M = Ni,[29–31] Pd,[32] or Pt[12,27,32–36]) is generally stable and unreactive, at least when stabilizing ligands are present. When $PtCl(CH_3)Q_2$ is shaken at room temperature with $CF_3C{\equiv}CH$ in benzene, significant quantities of polymer are formed within 24 hr, although very little of the methylplatinum complex is consumed (reaction 1). When *cis*-$Pt(CH_3)_2Q_2$ is shaken with a moderate excess of $CF_3C{\equiv}CH$ in benzene, all the acetylene is polymerized and none of the starting complex is consumed (reaction 9). These reactions suggest that it is the starting material which is responsible for the polymerization, rather than a reaction product, the alternative being that traces of some alkynyl or vinyl complex present in solution are the real catalysts. However, all of the major reaction products are less effective than the starting complexes in catalyzing polymerization. *trans*-$Pt(-C{\equiv}CCF_3)_2Q_2$ gives no reaction at all with $CF_3C{\equiv}CH$ in benzene (reaction 19); *trans*-$PtCl(-C{\equiv}CCF_3)Q_2$ gives only a trace of polymer after several days at 60° (reaction 20); and *cis*-$Pt(CH_3)(-C{\equiv}CCF_3)Q_2$ is much less effective in causing polymerization than *cis*-$Pt(CH_3)_2Q_2$ (reaction 21a). Insufficient pure *trans*-$Pt(CH_3)(-C{\equiv}CCF_3)Q_2$ was available for a valid comparison to be made, but traces of this complex in benzene do not promote polymerization (reaction 21b). The vinyl–platinum bond is also not prone to insertion by $CF_3C{\equiv}CH$, since no reaction occurs between *trans*-$PtCl\{-C(CF_3){=}CH(CH_3)\}Q_2$ and $CF_3C{\equiv}CH$ in benzene (reaction 22).

It is also clear that free radicals (which could conceivably be generated in the decomposition of some of the proposed reaction intermediates) do not initiate the polymerization of $CF_3C{\equiv}CH$, since addition of a radical scavenger has little effect on the polymerization by $Pt(CH_3)_2Q_2$ (reaction 15) and since addition of a radical generator to $CF_3C{\equiv}CH$ in benzene does not cause polymerization (reaction 16).

Since phosphines are known to polymerize $CF_3C{\equiv}CCF_3$,[37] we considered the possibility that polymerization of $CF_3C{\equiv}CH$ might be caused by traces of free phosphine (possibly present in the complex *cis*-$Pt(CH_3)_2Q_2$, owing to the high trans effect of the methyl groups). However, in benzene, highly colored soluble linear conjugated polymer[11] is formed with phosphines, quite different from the white cross-linked polymer typically obtained in the methylplatinum reactions (reaction 24).

Several ionic polymerization mechanisms, initiated by the platinum complex, are possible. A direct transfer of charge from the electron-rich Pt atom to the acetylene may occur

---

[28] M. H. Chisholm and H. C. Clark, *J. Amer. Chem. Soc.*, **94**, 1532 (1972).

[29] P. Hong, K. Sonogashira, and N. Hagihara, *Tetrahedron Lett.*, 1633 (1970).

[30] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

[31] G. R. Davies, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1750 (1967).

[32] G. Calvin and G. E. Coates, *J. Chem. Soc.*, 2008 (1960).

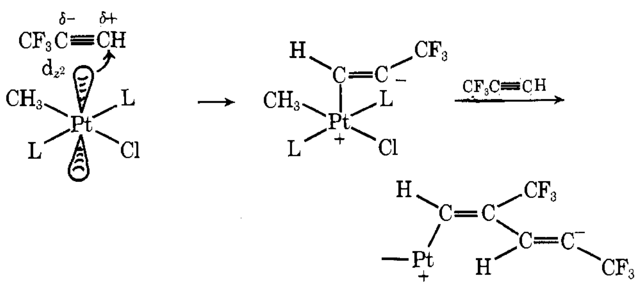
[33] I. Collamati and A. Furlani, *J. Organometal. Chem.*, **17**, 457 (1969).

[34] R. Ettore, *ibid.*, **19**, 247 (1969).

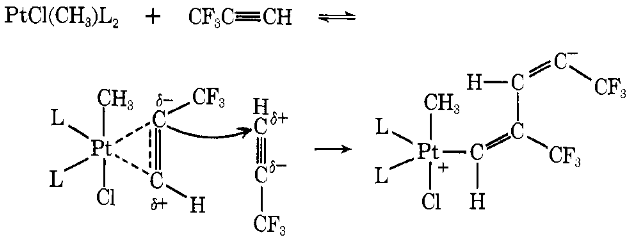
[35] J. Chatt, C. Eaborn, and P. N. Kapoor, *ibid.*, **23**, 109 (1970).

[36] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).

[37] W. R. Cullen and D. S. Dawson, *Can. J. Chem.*, **45**, 2887 (1967).



Alternatively, the polymerization could be initiated by the attack of a $CF_3C{\equiv}CH$ molecule on the five-coordinate complex



The ionic dimer, stabilized by interaction with the platinum complex, could then be attacked by another molecule of the acetylene, and so on. These mechanisms may be compared with that proposed for polymerization of $CF_3C{\equiv}CCF_3$ by phosphines[37] and for the reactions of $CF_3C{\equiv}CCF$ with some ruthenium complexes.[38]

In the absence of any information as to the stereochemistry of the rather intractable polymer, it is difficult to deduce further details of the reaction or definitely to determine the nature of the initiation step. Both types of mechanism would be promoted by a high electron density on Pt, this being the main reason methylplatinum complexes are more efficient as polymerization catalysts than most other Pt(II) compounds, *e.g.*, *cis*-$PtCl_2Q_2$ (reaction 23). If the suggestion that arsines transfer less charge to Pt than phosphines[39] is correct, the lower tendency of arsine complexes to catalyze polymerization (reactions 6, 17, 18) could be explained by the first mechanism. Arsines tend to stabilize five-coordinate intermediates more than phosphines,[2] so that, if polymerization occurs *via* such a complex, arsine complexes might have been expected to be more efficient than phosphine complexes. However, it is possible that the five-coordinate complexes with arsine ligands have a greater tendency to react giving acetylide complexes than to undergo acetylene attack, initiating polymerization.

It would be expected that the anionic polymerization would be hindered by acids.[40] The susceptibility of methylplatinum(II) complexes to attack by acids limits the experiments which could test this, but it should be noted that polymerization does not readily occur in acetone (reaction 13), acidic *via* the *enol* form, or in methanol, which can ionize (reaction 14). Any inhibition of polymerization by the acidity of trifluoropropyne itself[41] would also be more important in these polar solvents.

Experimental Section

Instrumentation and the preparation of methylplatinum complexes have been previously described.[1] Trifluoropropyne was prepared by the method of Finnegan and Norris.[42]

Since space does not permit details to be given of all the reactions carried out, details are given below for some of those which led to isolation of the complexes in Tables II and III, where analytical and spectroscopic data are listed.

Reaction of *trans*-$PtCl(CH_3)Q_2$ with $CF_3C{\equiv}CH$ in Benzene (Reaction 2).—*trans*-$PtCl(CH_3)_2Q_2$ (0.885 g, 1.7 mmol) was placed in a 50-ml capacity thick-walled Pyrex Carius tube. Benzene (8 ml) was distilled into the tube on the vacuum line and 14 mmol of $CF_3C{\equiv}CH$ condensed in. The tube was sealed and shaken at 50–60°. Within 2 hr polymer began to form as a thick white precipitate. After 2.5 days the tube was opened and a small quanity of $CF_3C{\equiv}CH$ was recovered (identified by its infrared spectrum). The polymer was filtered off and washed well with benzene (1.19 g, 12.7 mmol of CF_3CCH). The filtrate was evaporated to give a clear, pale brown oil. This was chromatographed on a Florisil column (Fisher, 100–200 mesh) 13 in. × 1 in. The mixture was introduced onto the column in pentane–dichloromethane (the minimum volume of CH_2Cl_2 to allow dissolution), and the column was eluted using pentane, then pentane containing increasing proportions of dichloromethane, then dichloromethane alone, then CH_2Cl_2 containing increasing proportions of acetone, and finally acetone alone.

The first product eluted from the column was *trans*-$Pt(-C{\equiv}CCF_3)_2Q_2$ (3:1 pentane:dichloromethane by volume). These fractions were combined and recrystallized from ether–hexane to give the product as colorless crystals (total weight 0.04 g).

Next was *trans*-$PtCl(-C{\equiv}CCF_3)Q_2$ (1:4 pentane–dichloromethane), at first pure, then contaminated with *trans*-$PtCl\{-C(CF_3){=}CH(Cl)\}Q_2$. These fractions containing a mixture were combined and recrystallized from ether–pentane to give pure *trans*-$PtCl(-C{\equiv}CCF_3)Q_2$ (0.2 g) as colorless needles. The recrystallization residue was combined with a similar sample from a duplicate experiment, and the components were separated by further chromatography, using the same solvents. First fractions contained pure $PtCl(-C{\equiv}CCF_3)Q_2$. Later fractions contained predominantly $PtCl\{-C(CF_3){=}CH(Cl)\}Q_2$ together with appreciable amounts of $PtCl(-C{\equiv}CCF_3)Q_2$. After successive recrystallizations from ether–pentane, the vinyl complex was obtained pure (0.12 g from the combined experiments) (colorless crystals).

With 9:1 dichloromethane–acetone *trans*-$PtCl(CH_3)Q_2$ (0.1 g) was eluted from the column, then $PtCl_2(CH_3)_2Q_2$ (identified by nmr but not purified). Elution with acetone gave small quantities of yellow-brown oils with a multitude of peaks in the ^{19}F nmr.

Reaction of *trans*-$PtCl(CH_3)Q_2$ with $CF_3C{\equiv}CH$ in Methanol (Reaction 3).—$PtCl(CH_3)Q_2$ (0.473 g) was placed in a 25-ml Carius tube into which 4 ml of methanol was distilled on the vacuum line. $CF_3C{\equiv}CH$ (7 mmol) was condensed in and the tube was sealed. After being shaken at room temperature, the tube was opened and the solution was filtered from the trace of polymer it contained and was then evaporated to dryness (from its infrared spectrum the gas phase contained some methane and a small amount of $CF_3C{\equiv}CH$). The solid was recrystallized from ether–pentane to give *trans*-$PtCl\{-C(CF_3){=}CH(OCH_3)\}Q_2$ as colorless crystals (first crop 0.314 g, 55%).

trans-$PtI(CH_3)Q_2$ reacted similarly to give *trans*-$PtI\{-C(CF_3){=}CH(OCH_3)\}Q_2$ (recrystallized from methanol, 40%) (reaction 5), and *trans*-$PtCl(CH_3)Q_2$ with $CF_3C{\equiv}CH$ in ethanol gave *trans*-$PtCl\{-C(CF_3){=}CH(OC_2H_5)\}Q_2$ (recrystallized twice from ether–pentane, 56%) (reaction 4).

***cis*-$Pt(CH_3)_2Q_2$ with $CF_3C{\equiv}CH$ in Ether.**—A solution of *cis*-$Pt(CH_3)_2Q_2$ (0.17 g, 0.34 mmol) in diethyl ether (1 ml) was shaken with $CF_3C{\equiv}CH$ (1.8 mmol) in a sealed (25 ml) tube at room temperature. Polymer began to precipitate after about 1 hr. The tube was opened. Only a trace of $CF_3C{\equiv}CH$ remained together with some methane. The solution was filtered, and the ether was evaporated. The resulting oil was recrystallized from ether–pentane to give white crystals of *cis*-$Pt(CH_3)(-C{\equiv}CCF_3)Q_2$ (0.056 g, 29%).

***cis*-$Pt(CH_3)_2Q_2$ with $CF_3C{\equiv}CH$ in Acetone.**—$CF_3C{\equiv}CH$ (6.8 mmol) was condensed into a Carius tube (50-ml capacity)

---

(38) R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. A.*, 2981 (1970).

(39) M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, **11**, 1269 (1972).

(40) W. Szarc, "Carbanions, Living Polymers and Electron-Transfer Processes," Interscience, New York, N. Y., 1968, pp 19, 22, 646–652.

(41) Suggested by a referee.

(42) W. G. Finnegan and W. P. Norris, *J. Org. Chem.*, **28**, 1139 (1963).

containing 1.03 g of *cis*-$\mathrm{Pt(CH_3)_2Q_2}$ (2.05 mmol) and 15 ml of acetone. The tube was sealed and shaken at room temperature for 1 week. No polymer precipitated. The tube was opened, and the solution was filtered and then evaporated to a brown oil, which, from its nmr spectrum (dissolved in chloroform), contained *cis*-$\mathrm{Pt(CH_3)_2Q_2}$ and *cis*- and *trans*-$\mathrm{Pt(CH_3)(-C{\equiv}CCF_3)Q_2}$. The oil was dissolved in ether, and pentane was added to precipitate out $\mathrm{Pt(CH_3)_2Q_2}$ and *cis*-$\mathrm{Pt(CH_3)(-C{\equiv}CCF_3)Q_2}$. The ether–pentane solution was decanted from the precipitated oil and then evaporated to dryness. The resultant yellow-brown oil, consisting mainly of *trans*-$\mathrm{Pt(CH_3)(-C{\equiv}CCF_3)Q_2}$, was dissolved in pentane and then chromatographed on Florisil, using pentane and then pentane containing increasing proportions of diethyl ether to elute the column. A colorless oil was obtained on evaporation of the appropriate fractions and solidified to a white solid on standing. A total of 0.05 g was obtained as pure *trans*-$\mathrm{Pt(CH_3)(-C{\equiv}CCF_3)Q_2}$.

***cis*-$\mathrm{Pt(CH_3)_2\{As(CH_3)_2(C_6H_5)\}_2}$ with $\mathrm{CF_3C{\equiv}CH}$ in Benzene (Reaction 18).**—*cis*-$\mathrm{Pt(CH_3)_2\{As(CH_3)_2(C_6H_5)\}_2}$ (0.386 g, 0.7 mmol) in 3 ml of benzene was shaken with 6 mmol of $\mathrm{CF_3C{\equiv}CH}$ in a sealed Carius tube. Within 12 hr, a small amount of polymer had precipitated, and the initially colorless solution had turned pale brown. After 10 days the tube was opened, 0.145 g polymer was filtered off, and the filtrate was evaporated. The residue consisted of an orange mixture of a solid with an oil. On addition of pentane, the oil dissolved, but most of the solid remained (0.11 g). Recrystallization of this solid from ether–pentane gave 0.05 g of *trans*-$\mathrm{Pt(-C{\equiv}CCF_3)_2\{As(CH_3)_2(C_6H_5)\}_2}$ as a white solid.

Acknowledgment.—We thank the National Research Council of Canada for continued financial support.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF HAWAII, HONOLULU, HAWAII 96822

Halide-Bridged Electrode Reactions of Platinum Complexes Containing Unsaturated Ligands

BY CHIU-NAN LAI AND ARTHUR T. HUBBARD*

Received December 1, 1971

Electrochemical interconversion of complexes of Pt(II) and Pt(IV) is accelerated by the presence of halide ions and halogen ligands. The influence of the halogens is consistent with the suggestion that halide acts as a bridging group between the reactant complex and the electrode surface or compact double layer. In particular, oxidation of Pt(II) may involve the transfer of electron density from filled orbitals of the complex, such as $a_{1g}(\sigma^*)$ $[5d_{z^2}]$, through unfilled orbitals such as nd_{z^2} of an intervening halide ion to certain unfilled orbitals of the compact layer or the electrode surface. Or, oxidation may proceed through orbitals such as nd_{z^2} of a halide ligand of the Pt(II) complex rather than through a free halide ion. Similarly, reduction of Pt(IV) complexes, for instance those of D_{4h} symmetry such as $\mathrm{Pt^{IV}L_4X_2}$, may proceed through interaction of a low-energy unfilled orbital of Pt(IV), such as $a_{1g}(\sigma^*)$, with filled orbitals of the compact layer or the electrode surface by way of the unfilled nd_{z^2} orbital of a bridging halide ligand. Pt(II) complexes containing unsaturated ligands such as $\mathrm{CN^-}$ or $\mathrm{SCN^-}$ are less rapidly oxidized than their saturated analogs. Evidence is presented that unsaturated ligands having suitable π^* orbitals stabilize the particular orbitals from which electron density is removed in the rate-limiting step. Pt(IV) complexes having a $\mathrm{CN^-}$ ligand situated trans to a lone halide ligand are reduced with difficulty, whereas complexes having a trans pair of halide ligands react readily; this trend is consistent with stabilization of the leaving trans axis and destabilization of the interaction between the bridging ligand and the electrode surface due to $d-\pi^*$ back-bonding between Pt(IV) and the unsaturated ligand.

Introduction

Electrochemical interconversion of platinum(II) and -(IV) complexes is stereospecific.[1-4] Oxidation of Pt(II) complexes in the presence of halide ions proceeds readily to give *trans*-dihaloplatinum(IV) or *trans*-haloaquoplatinum(IV) complexes,[2] *i.e.*

$$\mathrm{Pt^{II}L_4 + X^- + Y \rightleftharpoons \textit{trans}\text{-}Pt^{IV}L_4XY + 2e^-} \qquad (1)$$

$$(\mathrm{X^- = Cl^-, Br^-, I^-;\ Y = X^-, H_2O})$$

Detailed kinetic characterization of the reactions with consideration of the charge and structure of the electrical double layer[4] as well as of the reactant complex[2] has led to the axial ligand-bridge mechanism, according to which electron transfer proceeds through an adsorbed-halide bridge located between the electrode and the platinum complex in the transition state,[1-4] *i.e.*, eq 2.

When halide is present as a ligand but not as the free ion, the oxidation of Pt(II) is thought to proceed through an equatorially ligand-bridged transition state,[2] *i.e.*, eq 3.

Reduction of Pt(IV) complexes appears to follow eq 1–3, traversing the equations in the opposite direction. Reduction of a given Pt(IV) complex may not regenerate the Pt(II) starting material, in that removal of a trans axis other than the one added by oxidation may occur. In fact, parallel reduction to a mixture of Pt(II) products sometimes takes place when more than one potential ligand bridge is present in the Pt(IV) coordination sphere.[5]

Pt(II) complexes containing unsaturated ligands, for instance $\mathrm{CN^-}$, $\mathrm{SCN^-}$, and aromatic amines, appear to follow eq 1–3 but react more slowly than complexes of similar charge and structure containing only saturated ligands. The present studies demonstrate the influence of unsaturated ligands on Pt(II) reactivity and attempt to explain the results in terms of molecular orbital theory. It appears possible, in turn, to use these results to establish certain general mechanistic details of

---

(1) W. R. Mason and R. C. Johnson, *J. Electroanal. Chem.*, **14**, 345 (1967).

(2) J. R. Cushing and A. T. Hubbard, *ibid.*, **23**, 183 (1969).

(3) A. L. Y. Lau and A. T. Hubbard, *ibid.*, **24**, 237 (1970).

(4) A. L. Y. Lau and A. T. Hubbard, *ibid.*, **33**, 77 (1971).

(5) R. F. Lane and A. T. Hubbard, University of Hawaii, unpublished experiments.