exocyclic double bond, generally increase toward the extremities of the molecule (Table III and Figure 1). The largest thermal amplitudes are approximately in plane for phenyl B, but C(18) and C(19) display their largest vibrational components perpendicular to the plane of phenyl A.

The molecular packing can be seen in a three-dimensional view down the z axis in Figure 2. No unusually short intermolecular contacts are present. The only intermolecular approaches smaller than 3.75 Å are C(3) $(x, y, z) \cdots$ C(13) $(1/2 - x, \bar{y}, -1/2 + z)$ (3.649 ± 0.005 Å), C(6) $(x, y, z) \cdots$ C(16) $(x, -1/2 - y, 1/2 + z)$ (3.729 ± 0.005 Å), and C(12) $(x, y, z) \cdots$ C(19) $(x, y, 1 + z)$ (3.708 ± 0.005 Å) along the x, y, and z directions, respectively. Molecules related by centers of symmetry pack with their phenyl B rings parallel; the distance 3.86 Å between such planes is about 0.46 Å longer than the closest packing between phenyls.[36]

Acknowledgment. We are grateful to F. Johnson for suggesting the problem and supplying the crystals and to F. P. Boer for helpful discussions.

Supplementary Material Available. A listing of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche 105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-6593.

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Reactions of Dimethyl Acetylenedicarboxylate and Related Acetylenes with Methylplatinum(II) Complexes

T. G. Appleton, M. H. Chisholm, H. C. Clark,* and K. Yasufuku

Contribution from the Department of Chemistry, University of Western Ontario, London N6A 3K7, Ontario, Canada. *Received January 18, 1974*

Abstract: The reaction of *trans*-$PtXCH_3Q_2$ (X = Cl, Br, I; Q = $P(CH_3)_2C_6H_5$) with $RC{\equiv}CCO_2CH_3$ affords *trans*-$PtXQ_2[C(COOCH_3){=}C(Cl)R]$ in the presence of a radical initiator (R = CO_2CH_3) or by addition of HCl (R = CO_2CH_3, C_6H_5, CH_3, H). *trans*-$PtXQ_2[C(COOCH_3){=}C(COOCH_3)CH_3]$ is obtained from the reaction of *trans*-$[PtCH_3(acetone)Q_2]^+PF_6^-$ with the acetylene (R = CO_2CH_3) followed by treatment with LiX. Based on the formation of these products and other observations, a mechanism for the formation of the β-chlorovinylplatinum compound in $CHCl_3$ is proposed. This involves initial formation of the 1:1 complex with acetylene, followed by nucleophilic attack on the acetylene by HCl which is generated *via* a radical process.

Very recently, the possibility of a radical reaction of $CH_3O_2CC{\equiv}CCO_2CH_3$ (dma) with the methyl–platinum bond of *trans*-$PtCH_3XQ_2$ (Q = $P(CH_3)_2C_6H_5$), I (Ia has X = Cl), was reported.[1] Such an insertion reaction of an organometallic compound by a free radical process is very interesting and apparently consistent with other more recent reports[2] of radical behavior by organoplatinum complexes. We have now examined this and related reactions in detail.

The product previously identified[1] incorrectly as the insertion product, *trans*-$PtXQ_2[C(CO_2CH_3){=}C(CO_2CH_3)CH_3]$ (III) (IIIa has X = Cl), is now shown to be the β-chlorovinylplatinum compound, *trans*-$PtXQ_2[C(CO_2CH_3){=}C(Cl)CO_2CH_3]$ (IV) (IVa has X = Cl). The radical aspects of the reaction can be attributed to the radically induced formation of HCl which then participates in the formation of IV. We have also studied further the importance of the 1:1 adducts formed from some acetylenes and I.

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Results and Discussion

Preparation and Identification of III and IV. In chloroform solution, Ia and dma form the 1:1 adduct IIa which undergoes further reaction to give a product containing the α,β-dicarbomethoxyvinyl group, IVa, as well as *trans*-$PtCl_2(CH_3)_2Q_2$ (V), *cis*-$PtCl_2Q_2$ (VI), and small amounts of dma oligomers. The oligomers and free dma were removed by washing with H_2O, VI was removed by chromatography, and IVa was isolated from V by fractional crystallization. The overall reaction is therefore described by eq 1 and 2a.

$$\underset{\text{Ia}}{\textit{trans}\text{-}PtCH_3ClQ_2} + \text{dma} \rightleftharpoons \underset{\text{IIa}}{\textit{trans}\text{-}PtCH_3ClQ_2\cdot\text{dma}} \quad (1)$$

$$\text{IIa} \xrightarrow[\text{(b) } +\text{HCl (eq 2b)}]{\text{(a) } h\nu \text{ or initiator (eq 2a)}} \underset{\text{IVa}}{\textit{trans}\text{-}PtClQ_2[C(CO_2CH_3){=}C(Cl)CO_2CH_3]} + \text{V} + \text{VI} \quad (2)$$

The ^1H nmr spectrum (in $CDCl_3$) of IVa shows the $-CO_2CH_3$ signals at δ 3.66 and 3.48 as two singlets, the upfield signal having satellites due to coupling with ^{195}Pt (J_{PtH} = 3.0 Hz). The phosphine–methyl signals at δ 1.83 and 1.76 appear as two overlapped triplets ($^{2+4}J_{PH}$ = 7.8 and 8.0 Hz) with ^{195}Pt satellites (J_{PtH} = 27.6 and 30.8 Hz, respectively) showing that the phos-

phorus nuclei are trans to each other. The ir spectrum shows the $\nu_{C=O}$ and ν_{C-O-C} absorptions for the ester groups at 1700 (s) and 1220 cm^{-1} (s), $\nu_{C=C}$ at 1555 cm^{-1} (vw broad), as well as the characteristic absorptions of Q. The mass spectrum shows the molecular ion $[M]^+$ at *m/e* 684 (calcd *m/e* = 684) with the characteristic isotopic pattern expected for $-PtCl_2$, followed by ions corresponding to fragments $[M - Cl]^+$, $[M - PPhMe_2]^+$, $[M - C(CO_2CH_3)=C(Cl)CO_2CH_3]^+$, and $[M - ClC(CO_2CH_3)=C(Cl)CO_2CH_3]^+$. These data indicate that IVa is the β-chloro-α,β-dicarbomethoxyvinylchloroplatinum complex and not the analogous β-methyl compound, IIIa.

The latter compound, III, has, however, been prepared by the reaction of dma with the methylplatinum cation,[3] according to eq 3.

$$trans\text{-}[PtCH_3Q_2(acetone)]^+PF_6^- + dma \xrightarrow[\text{in } CH_2Cl_2 \text{ or } CHCl_3]{LiX} trans\text{-}PtXQ_2C[(CO_2CH_3)=C(CO_2CH_3)CH_3] \quad (3)$$

IIIa, X = Cl
b, X = I

The nmr spectrum of IIIa shows the vinyl CH_3 signal at δ 2.01; since it overlaps part of the P–CH_3 signal, any coupling to ^{31}P or ^{195}Pt is obscured. In other respects, the nmr and ir spectra are in full accord with those expected for structure IIIa. The mass spectrum shows $[M]^+$ at *m/e* 664 (calcd *m/e* for IIIa = 664) with the isotopic pattern expected for –PtCl followed by fragments corresponding to ions $[M - Cl]^+$, $[M - C(CO_2CH_3)=C(CO_2CH_3)CH_3]^+$, and $[M - ClC(CO_2CH_3)=C(CO_2CH_3)CH_3]^+$.

The vinylic double bond of III might be expected to have the cis stereochemistry, since the insertion products of $CF_3C{\equiv}CCF_3$ into the CH_3—Pt bond of neutral methylplatinum complexes[4] or their cations[3] have all shown the *cis*-$PtC{=}CCH_3$ structure. On the other hand, attempts to cleave the Pt–vinyl bond as a means of determining the stereochemistry at the PtC=CCl double bond of IVa failed; the compound is very stable in both acidic and alkaline conditions. However, the stereochemistry is apparently trans based on the nmr spectra of related β-chlorovinylplatinum compounds obtained as follows.

The addition of HCl gas to the $CHCl_3$ solution of IIa immediately gave IVa in very good yield (reaction 2b). On the other hand, the immediate addition of HCl into a freshly prepared solution of I and dma afforded only a mixture of *trans*-$PtCl_2Q_2$ and free dma with a very small amount of IVa; under these conditions the equilibrium concentration of IIa is apparently only slowly attained. However, IVa was obtained in fairly good yield from HCl addition to a solution of I and dma which had stood for 1 day.

$$trans\text{-}PtCl_2Q_2 + RC{\equiv}CCO_2CH_3 \xrightarrow{HCl} trans\text{-}PtClQ_2[C(CO_2CH_3)=C(Cl)R] \quad (4)$$

IVd, R = C_6H_5
e, R = CH_3
f, R = H

From the similar reaction (4) of $RC{\equiv}CCO_2CH_3$ with *trans*-$PtCl_2Q_2$, β-chlorovinylplatinum compounds IVd, e, and f were prepared, which could not be obtained by reaction 2, since 1:1 adducts with Ia could not be isolated for these acetylenes. The physical properties and analyses of the products and the spectroscopic data are shown in Tables I and II.

Another product of reaction 4 is *cis*-$PtCl_2Q_2$ (VI), which, under the same conditions, is unreactive toward these acetylenes. Yields of IV in reaction 4 decrease in the order of the electron-withdrawing ability of R (CO_2CH_3 > C_6H_5 > H > CH_3), suggesting that coordination of the acetylenes to platinum is required for the formation of IV in eq 4 as well as in eq 1, although 1:1 adduct formation has not been detected for the acetylenes of reaction 4. Indeed, $PhC{\equiv}CCH_3$ did not give any chlorovinyl product but only VI.

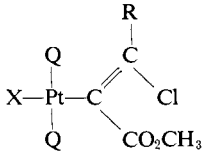
In methanolic solution also, Ia and dma forms IIa; however, further reaction involving nucleophilic attack of ^-OMe on coordinated dma occurs,[5] giving the β-methoxyvinylplatinum compound VIIa.

$$trans\text{-}PtClCH_3Q_2 + RC{\equiv}CCO_2CH_3 \xrightarrow[\text{in } CH_3OH]{} trans\text{-}PtClQ_2[C(CO_2CH_3)=C(OCH_3)R] \quad (5)$$

VIIa, R = CO_2CH_3
b, R = C_6H_5

$PhC{\equiv}CCO_2CH_3$, for which 1:1 adduct formation has not been detected, likewise gave VIIb, but $CH_3C{\equiv}CCO_2CH_3$ did not give the analogous product.

Nmr Spectra. In all of the products, one resonance attributable to CO_2CH_3 showed coupling with ^{195}Pt ($J_{PtH} \sim 3.0$ Hz), while in IIIa, b, IVa, b, c, and VIIa another resonance (which is not coupled) also assignable to CO_2CH_3 appears at lower field. The former resonance (coupled to ^{195}Pt) can be assigned to the α-CO_2CH_3 group; it is analogous to the peak for the α-CF_3 group vicinal to platinum[6] in the ^{19}F spectra of the related trifluoromethylvinyl platinum complexes. The formation of α-carbomethoxyvinyl compounds from the asymmetric acetylenes, *i.e.*, attachment of the vinylic carbon with the more electron withdrawing group to platinum, is consistent with the formation of *trans*-$PtClQ_2[C(CF_3)=C(X)H]$ (X = OCH_3 or Cl)[7] from Ia with $CF_3C{\equiv}CH$. J_{PtH} = 61.2 and J_{PH} = 4.0 Hz for the β-vinylic proton in IVf indicate that the hydrogen is cis with respect to the Pt moiety, on the basis of reported values for a number of vinylplatinum complexes.[7,8] The stereochemistry of IVa–e and IVg is presumably then the same as in IVf with a *trans*-PtC=CCl arrangement.



The vinylic CH_3 protons in IVe and in IIIa and b show very similar values for $J_{PtH} \sim 2.8$ Hz, again consistent with a cis arrangement of the $PtC{=}CCH_3$ group for III.

The phosphine methyl regions of the proton spectra of IVa–e, IIIa and b, and VIIa and b show two over-

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Table I

Compound		Mp, °C	Analysis, % calcd (% found) C	H	Halogen	Mol wt m/e^a
trans-PtCl{C(COOCH$_3$)=C(COOCH$_3$)CH)}Q$_2$	IIIa	153–155	41.61 (41.23)	4.71 (4.65)	Cl 5.33 (5.51)	664
trans-PtI{C(COOCH$_3$)=C(COOCH$_3$)CH$_3$}Q$_2$	IIIb	171–172	36.57 (36.34)	4.14 (4.14)	I 16.80 (16.58)	
trans-PtCl{C(COOCH$_3$)=C(Cl)COOCH$_3$}Q$_2$	IVa	124–125	38.60 (38.59)	4.12 (4.22)	Cl 10.36 (10.47)	684
trans-PtBr{C(COOCH$_3$)=C(Cl)COOCH$_3$}Q$_2$	IVb	141–143	36.25 (36.23)	3.87 (3.92)	Cl 4.86 (4.76) Br 10.96 (10.85)	728
trans-PtI{C(COOCH$_3$)=C(Cl)COOCH$_3$}Q$_2$	IVc	147–148	34.06 (34.22)	3.64 (3.55)	Cl 4.57 (4.78) I 16.36 (16.23)	
trans-PtCl{C(COOCH$_3$)=C(Cl)C$_6$H$_5$}Q$_2$	IVd	169–171	44.46 (44.52)	4.30 (4.36)		
trans-PtCl{C(COOCH$_3$)=C(Cl)CH$_3$}Q$_2$	IVe	133–135	39.39 (39.28)	4.41 (4.45)		640
trans-PtCl{C(COOCH$_3$)=C(Cl)H}Q$_2$	IVf	119–121	38.35 (38.74)	4.18 (4.27)		626
trans-PtCl{C(COOCH$_3$)=C(Cl)COOCH$_3$}(PPh$_2$Me)$_2$	IVg	160–161	47.54 (47.52)	3.99 (4.06)		
trans-PtCl{C(COOCH$_3$)=C(OCH$_3$)C$_6$H$_5$}Q$_2$	VIIIb	173–174	46.46 (46.26)	4.77 (4.58)	Cl 5.08 (5.26)	698
trans-PtCl(C$_6$H$_5$)Q$_2$(CH$_3$Q$_2$CC≡CCO$_2$CH$_3$)	VIII	72–80	46.33 (47.30)	4.58 (5.18)	Cl 4.88 (4.70)	

[a] Peak for "^{35}Cl^{37}Cl^{194}Pt + ^{37}Cl^{35}Cl^{196}Pt" or "^{35}Cl^{194}Pt^{37}Cl^{196}Pt."

lapping triplets (with ^{195}Pt satellites), corresponding to nonequivalent phosphine methyl groups. Similar nonequivalence of the phosphine methyl groups has also been observed in *trans*-PtXQ$_2$[C(CF$_3$)=C(CF$_3$)CH$_3$][4] and in *trans*-PtIQ$_2$[C(CF$_3$)=C(OCH$_3$)H].[9] Such nonequivalence may arise from a conformation of the vinylic groups perpendicular to the plane of the complex, with a rotation about the Pt–C bond which is slow on the nmr time scale. IVf and *trans*-PtClQ$_2$[C(CF$_3$)=C(OCH$_3$)H] both of which have the sterically small hydrogen as the cis substituent do not show this nonequivalence.

Mechanism of Reaction 2a. The product from reaction 2a has thus been characterized as IVa, while IIIa cannot be converted, under the same conditions as eq 2a, into IVa. Nevertheless, reaction 2a shows the characteristics of a radical reaction.

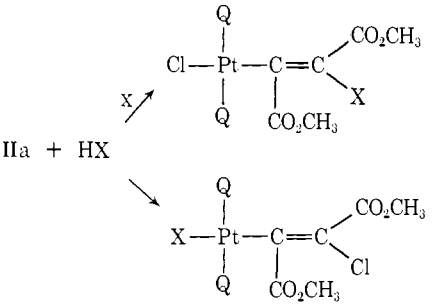
It is very dependent on the particular sample of Ia. For some samples, reaction proceeded as above, while for others only the 1:1 adduct, IIa, was formed; there was no formation of IVa and only disproportionation to V and VI occurred over several weeks. Furthermore, addition of an "unreactive" solution or an inhibitor (DPPH, galvinoxyl) to a "reactive" solution immediately inhibited both the formation of IVa and disproportionation. On the other hand, both reactions occurred on the addition of a small amount of a free-radical initiator (benzoyl peroxide (BPO) or azobisisobutyronitrile) to an "unreactive" solution or on uv irradiation.

For the formation of IVa, the initiator must be added only after the equilibrium concentration of IIa has been attained. If the initiator is added sooner, the methyl transfer reaction giving V and VI is predominant. This latter reaction also takes place in CH_2Cl_2 solution, but at a much reduced rate and does not occur in nonchlorinated solvents even though the 1:1 adduct is formed.

From the similar reaction of *trans*-PtCH$_3$IQ$_2$, Ic, with dma in $CHCl_3$, the β-chlorovinyliodoplatinum complex IVc (and not either the β-iodovinylchloro or the β-iodovinyliodo compound) was obtained; IVc was also prepared from the reaction of IVa with LiI in acetone. The formation of IVc from Ic and the obviously important role of chloroform as solvent in eq 2a, indicate that one of the two chlorines in IVa comes from the solvent, although the direct transfer of chlorine from $CHCl_3$ to the vinylic position might seem unlikely energetically.

On the other hand, it is well known that hydrogen chloride is one of the products of the decomposition of chloroform in either the presence[10] or absence[11] of air. It is thus probable that HCl is generated in eq 2a *via* a radical process and this is further confirmed by observations of the behavior of *trans*-PtClQ$_2$CO$_2$CH$_3$. This compound reacts with HCl immediately giving methanol and *cis*-PtCl$_2$Q$_2$ (probably *via* *trans*-[PtClQ$_2$CO]$^+$Cl$^-$ followed by CO liberation). The nmr spectrum of $CHCl_3$ solutions of *trans*-PtClQ$_2$CO$_2$CH$_3$ showed the rapid generation of CH_3OH either in the presence of air or on exposure to light in the absence of air, but not in the absence of air or light; also, the formation of CH_3OH was found to be much slower when dma was added. Initiation and inhibition effects then clearly arise from reaction with chloroform. We thus conclude that eq 2a is a reaction of the 1:1 adduct IIa with radically generated HCl accompanying the methyl transfer reaction.

The attack of HCl on the 1:1 adduct cannot be interpreted as a simple nucleophilic attack of Cl^- on the coordinated acetylene as has been suggested[3,7] for the corresponding attack by methoxide (see reaction 5), since the reaction product of IIa with HBr or HI was not the expected β-bromovinyl- or β-iodovinylchloroplatinum compound but rather the β-chlorovinylbromo- (IVb) or -iodoplatinum derivative (IVc).



A plausible explanation for the formation of IVc from both *trans*-PtICH$_3$·dma with HCl and *trans*-PtClCH$_3$Q$_2$·dma with HI is given in Scheme I.

Reaction of IIa with HX may cause the elimination of CH_4 followed by the rapid formation of IVc *via* a

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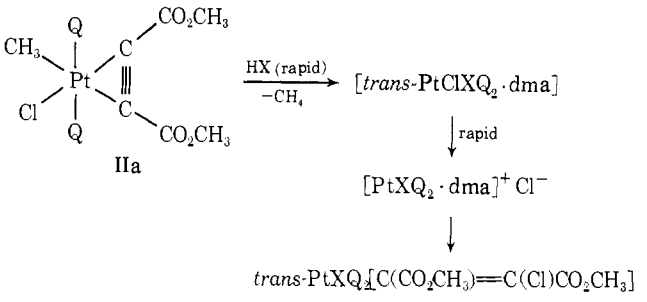
Table II. Spectroscopic Data

Compound		δ_{COOCH_3}	J_{Pt-H}, Hz	δ_{P-CH_3}	$^2J + {}^4J_{P-CH_3}$, Hz	$^3J_{Pt-H}$, Hz	Other signals in nmr	$\nu_{C=C}$, cm^{-1}	$\nu_{C=O}$, cm^{-1}
trans-$PtCl\{C(COOCH_3)=C(COOCH_3)CH_3\}Q_2$	IIIa	3.56		1.83	7.8	31.0	$=C-CH_3$ δ 2.01	1590 m	1700 s
		3.34	3.4	1.80	7.8	32.0	J_{PtH} = 2.7 Hz		
trans-$PtI\{C(COOCH_3)=C(COOCH_3)CH_3\}Q_2$	IIIb	3.62		1.96	7.6	30.8	$=C-CH_3$ δ 2.08	1568 m	1698 s
		3.45	3.4	1.90	7.7	31.8	J_{PtH} = 2.8 Hz		
trans-$PtCl\{C(COOCH_3)=C(Cl)COOCH_3\}Q_2$	IVa	3.66		1.83	7.8	27.6		1555 w	1700 s
		3.48	3.1	1.76	8.0	30.8			
trans-$PtBr\{C(COOCH_3)=C(Cl)COOCH_3\}Q_2$	IVb	3.69		1.87	7.8	28.0		1560 w	1700 s
		3.49	3.2	1.81	7.8	31.8			
trans-$PtI\{C(COOCH_3)=C(Cl)COOCH_3\}Q_2$	IVc	3.84		1.98	7.4	29.0		1568 m	1598 s
		3.60	3.0	1.91	7.6	30.8			
trans-$PtCl\{C(COOCH_3)=C(Cl)C_6H_5\}Q_2$	IVd	3.39	3.0	1.83	7.7	29.0		1592 w	1698 s
				1.73	7.7	31.5			
trans-$PtCl\{C(COOCH_3)=C(Cl)CH_3\}Q_2$	IVe	3.33	2.8	1.83	7.6	29.0	$=C-CH_3$ δ 1.91		
				1.81	7.8	31.0	J_{PtH} = 2.8 Hz	1630 w	1700 s
trans-$PtCl\{C(COOCH_3)=C(Cl)H\}Q_2$	IVf	3.31	2.7	1.82	7.7	30.0	=C—H δ 5.17		
							J_{PH} = 4.0 Hz, J_{PtH} = 61.2 Hz	1570 w	1702 s
trans-$PtCl\{C(COOCH_3)=C(Cl)COOCH_3\}(PPh_2Me)_2$	IVg	3.58		2.07	7.9	31.6			
		3.23	3.0						
trans-$PtCl\{C(COOCH_3)=C(OCH_3)COOCH_3\}Q_2$	VIIa	3.62		1.82	7.6	27.6	$=C-OCH_3$ δ 3.33		
		3.44	3.0	1.77	7.8	30.5	J_{PtH} = 1.4 Hz		
trans-$PtCl\{C(COOCH_3)=C(OCH_3)C_6H_5\}Q_2$	VIIb	3.40	3.0	1.83	7.4	29.2	$=C-OCH_3$ δ 3.42	1580 w	1682 s
				1.78	7.9	31.8	J_{PtH} = 1.8 Hz		
trans-$PtClCH_3Q_2(CH_3O_2CC{\equiv}CCO_2CH_3)$	IIa	3.66		1.65	7.0	31.0	Pt—CH_3 δ − 0.35		
		3.43	~1.5	1.61	7.0	32.0	J_{PH} = 15.0 Hz, J_{PtH} = 57.0 Hz		
trans-$PtCl(C_6H_5)Q_2(CH_3O_2CC{\equiv}CCO_2CH_3)$	VIII	3.74		1.54	7.2	32.5			
		3.52	~1.5	1.47	7.8	33.5			

Scheme I



cationic acetylene species. The formation of *trans*-$PtClXQ_2$ by dissociation of its acetylene complex would also be expected for this reaction sequence. Note that reaction 4 may also proceed *via* the formation in a preequilibrium step of an acetylene complex of *trans*-$PtCl_2Q_2$. Thus the nucleophilic attack of Cl^- to the coordinated acetylenes affords the β-chlorovinylplatinum compounds, while the reaction of HX with Pt(0)–acetylene complexes affords β-hydrogenvinylplatinum compounds[8,12,13] and the reaction of HCl with Pt–acetylide complexes affords α-chlorovinylplatinum compounds.[14]

Methyl Transfer Reaction. The dma acts as a retardant in eq 2a, while it is also necessary to initiate the methyl transfer reaction of Ia in $CHCl_3$ (see Table III).

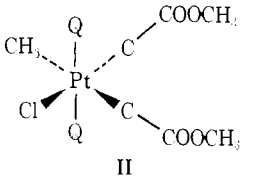
Table III. Reaction of *trans*-$PtClCH_3Q_2$ with Acetylenes in $CHCl_3$

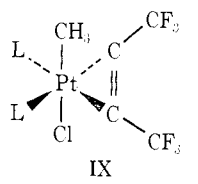
Acetylene	Reaction[a]
$CF_3C{\equiv}CCF_3$	$PtQ_2(CF_3C{\equiv}CCF_3) + Pt(CH_3)_2Q_2Cl_2$
$CH_3O_2CC{\equiv}CCO_2CH_3$[b]	$PtCl_2Q_2 + PtCl_2Me_2Q_2 + CH_4$ + (methyl transfer) *trans*-$PtClQ_2\{C(COOCH_3){=}C(Cl)COOCH_3\}$
$C_6H_5C{\equiv}CCO_2CH_3$	Disproportionation
$CH_3C{\equiv}CCO_2CH_3$	Disproportionation
$HOCH_3C{\equiv}CCH_2OH$	Disproportionation
$C_6H_5C{\equiv}CC_6H_5$	Slow disproportionation
$C_6H_5C{\equiv}CCH_3$	No reaction
$CH_3C{\equiv}CCH_3$	No reaction
$C_6H_5C{\equiv}CH$	$PtCl_2Q_2 + PtCl_2Me_2Q + CH_4$ + *trans*-$PtCl(C{\equiv}CC_6H_5)Q_2$
$HC{\equiv}CCH_2CH_2OH$	$PtCl_2Q_2 + PtCl_2Me_2Q_2 + CH_4$ + *trans*-$PtCl(C{\equiv}CCH_2CH_2OH)Q_2$

[a] Followed by the nmr spectra at room temperature without deaeration, in the absence of an initiator. [b] For this acetylene, formation of the π-complex was observed.

The $CHCl_3$ solution of Ia is very stable and its ^1H nmr spectrum does not show any change even in the presence of air. Addition of acetylenes having electron-withdrawing substituents causes methyl transfer, which is inhibited by addition of an inhibitor. The effect of the substituents suggests that an interaction between an acetylene and Ia also may be involved in initiating the methyl transfer. In the limiting case, this methyl transfer reaction is equivalent to disproportionation. Thus, disproportionation giving V and *cis*-$PtQ_2(CF_3C{\equiv}CCF_3)$ has been observed[6] at room temperature in the reaction of Ia with $CF_3{\equiv}CCF_3$. Uv irradiation of the $CHCl_3$ solution of Ia and $CF_3C{\equiv}CCF_3$ caused only disproportionation while irradiation of the C_6H_6 solution gave only the insertion products. The methyl transfer reaction may thus well be of a radical nature.

Significance of π-Complex Formation. Formation of the 1:1 adduct IIa is rather slow, equilibrium being attained after several hours. The equilibrium constant in $CHCl_3$ is 5.2 mol^{-1} l. (30°), the value decreasing in polar solvents in the order of their dielectric constant ($C_6H_5NO_2 > CH_3COCH_3 > CH_2Cl_2 > CHCl_3$); in benzene no 1:1 adduct formation was observed. The conductivity measurement in nitrobenzene apparently shows IIa is a nonelectrolyte under these conditions. Although solid IIa could not be isolated from such a solution, the analogous 1:1 dma adduct (VIII) of *trans*-$PtCl(C_6H_5)Q_2$ has been isolated as a crystalline solid containing a small amount of *trans*-$PtCl(C_6H_5)Q_2$. The nmr spectra of VIII and IIa each showed two different CO_2CH_3 signals, one of which had ^{195}Pt satellites, J_{PtH} = 1.5 Hz, two overlapping triplets in the P–CH_3 region, and Pt–CH_3 in IIa a triplet with ^{195}Pt satellites, J_{PtH} = 57.0 Hz, which is close to the values expected for platinum(IV) complexes, and thus indicate the stereochemistry II.





As previously reported, $CF_3C{\equiv}CCF_3$, C_2F_4,[6] and $C_2(CN)_4$[15] form 1:1 adducts of stereochemistry IX with *trans*-$PtCl(CH_3)L_2$, and this has also been established[16] for $PtClMe(AsMe_3)_2{\cdot}(C_4F_6)$ by an X-ray crystallographic structure determination. The adduct from tetrachloro-*o*-quinone and Ia also has this stereochemistry. It is not clear why stereochemistry II should be preferred for the dma adduct, although obviously relative trans influences, and steric and solvation effects may all be important.

Experimental Section

Infrared spectra, proton nmr, and mass spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer (samples prepared as Nujol mulls), Varian T-60 and HA-100 spectrometers using $CDCl_3$ as solvent, and a Varian M-66 mass spectrometer, respectively. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz., and Alfred Bernhardt, Mulheim, W. Germany.

Benzoyl peroxide, diphenylpicrylhydrazyl, galvinoxyl, and $CH_3O_2CC{\equiv}CCO_2CH_3$ were obtained from Aldrich Chemical Co., Inc.; $PhC{\equiv}CCO_2CH_3C{\equiv}CCO_2CH_3$ and $HC{\equiv}CCO_2CH_3$ were prepared by the literature methods.[17-19]

Ia, *trans*-$PtClCH_3(PPh_2Me)_2$, and *trans*-$Pt(C_6H_5)Q_2$ were prepared as previously reported.[20,21]

Preparation of IVa (Reaction 2a). Ia (0.194 g) and dma (0.044 g) in 0.7 ml of chloroform were placed in an nmr tube. The gradual formation of IIa over several hours was observed from the nmr spectra. After 10 hr, 0.08 g of BPO was added and the re-

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action was followed by observing changes in the nmr spectrum. After the solution had stood for 4 days at room temperature, the solvent was evaporated under reduced pressure and the orange oily residue was dissolved in *ca.* 3 ml of benzene. The solution was chromatographed through a Florisil column (1 × 5 cm), which on elution with benzene followed by evaporation and addition of diethyl ether gave white needles, V. The mother liquid was again chromatographed with benzene and from the diethyl ether eluate 0.04 g of IVa was obtained as white crystals, mp 124–125°. From the fraction eluted with benzene–dichloromethane (1 : 1), VI was obtained.

Reaction 2b. To the equilibrium solution (orange) of IIa formed from 0.102 g of Ia and dma (0.03 g) in 0.2 ml of chloroform, hydrogen chloride gas was passed for 1 min; the solution immediately turned yellow with the evolution of a gas identified as methane. After standing for 1 hr, the mixture was diluted with 20 ml of dichloromethane, washed twice with water, and dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography on Florisil with benzene followed by evaporation of the benzene and addition of diethyl ether gave IVa (0.09 g). Similarly, IVb and IVc were obtained using gaseous hydrogen bromide or aqueous hydrogen iodide.

Preparation of IVb and IVc from IVa. To an acetone (20 ml) solution of IVa (0.1 g), excess LiBr (or LiI) was added with stirring, and the solution was allowed to stand for 4 hr. After evaporation of the solvent, the residue was extracted with benzene and chromatographed on Florisil. Evaporation of the solvent and addition of diethyl ether gave IVb or IVc in good yield. Similar treatment of IVb obtained in reaction 2b with LiBr also gave IVb.

Preparation of IIIa. To a solution of *trans*-$[CH_3Pt(acetone)Q_2]^+PF_6^-$ in 40 ml of dichloromethane, from Ia (0.51 g) and 0.25 g of $AgPF_6$ in acetone, 0.132 g of dma was added and stirred for 0.5 hr at room temperature. The solvent was evaporated and the yellow oily residue was dissolved in 20 ml of acetone and excess LiCl was added. After 3 hr of stirring, the solvent was evaporated and the residue was dissolved in 5 ml of benzene and washed with water. After being dried over magnesium sulfate, the solution was passed through a Florisil column and was reduced in volume. Addition of diethyl ether gave IIIa (0.17 g).

Preparation of VIIb. To a solution of Ia (0.153 g) in 10 ml of methanol at 40° under N_2, 0.05 g of $PhC{\equiv}CCO_2CH_3$ was added and the solution was stirred for 5 hr. After evaporation of the solvent to *ca.* 2 ml, addition of 5 ml of diethyl ether and of 2 ml of pentane gave white crystals, which were recrystallized from dichloromethane–diethyl ether to give VIIb (0.13 g).

Preparation of the $PtClCH_3Q_2$·tetrachloro-*o*-quinone Adduct. Ia (0.24 g) and tetrachloro-*o*-quinone (0.126 g) were mixed together in *ca.* 1 ml of chloroform. The solution immediately turned dark brown and after about 5 minutes dark brown crystals separated, which were orange-brown when dry (0.164 g) (dec pt >230°). *Anal.* Calcd for $C_{23}H_{25}Cl_5O_2P_2Pt$: C, 36.0; H, 3.3; Cl, 23.1. Found: C, 36.1; H, 3.0; Cl, 23.5.

The nmr spectrum (in CD_2Cl_2) shows the phosphine methyl signals at δ 2.00 as a doublet with ^{195}Pt satellites, J_{PH} = 12.8 Hz, J_{PtH} = 20.0 Hz, and the platinum methyl at δ 1.10 as a triplet, J_{PH} = 4.0 Hz, J_{PtH} = 68.0 Hz.

1:1 Adduct (II). The ^1H nmr spectrum of IIa was measured in $CDCl_3$ solution containing a mixture of Ia and excess dma. A nitrobenzene solution *ca.* 0.04 *M* in IIa showed, after equilibrium had been established, a molar conductivity of $1.4 \times 10^{-2}\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 23° (Ia showed a conductivity of $4.2 \times 10^{-3}\ \Omega^{-1}\ cm^2\ mol^{-1}$ under the same conditions). The peak height ratio of the ^1H nmr spectra of the mixture of *trans*-$PtXCH_3Q_2$ and dma showed that the formation of the 1:1 adduct decreased in the order (Cl > I ≫ Br ~ O) in chloroform. *trans*-$PtClCF_3Q_2$ did not form a 1:1 adduct with dma, while *trans*-$PtClC_6H_5Q_2$ showed only a very slow rate of formation of the 1:1 adduct.

1:1 Adduct between *trans*-$PtClC_6H_5Q_2$ and dma, VIII. *trans*-$PtClC_6H_5Q_2$ (0.057 g) and dma (0.06 g) in 0.5 ml of chloroform were placed in an nmr tube. After 4 days two peaks corresponding to VIII had begun to appear in the nmr spectrum. After 3 weeks the solvent was evaporated and the residue was chromatographed on a Florisil column (0.4 × 1.0 cm) using dichloromethane as an eluent. After concentration of the eluted solution, addition of diethyl ether gave pale yellow crystals (0.032 g), which, from the ^1H nmr spectrum, were contaminated with small amounts of *trans*-$PtClC_6H_5Q_2$. Purification was not possible since chromatography without excess dma caused decomposition to give *trans*-$PtClC_6H_5Q_2$ in yields greater than 65%; the mass spectrum of the impure adduct showed the same fragmentation pattern as pure *trans*-$PtClC_6H_5Q_2$. Reaction of VIII with hydrogen chloride again afforded IVa with elimination of benzene.

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