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Reactions of Alkynylplatinum(II) Compounds with Aprotic Substrates

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Reactions of alkynylplatinum(II) compounds *trans*-$PtX(C{\equiv}CR)L_2$, where R = H, Me, or CF_3, X = $C{\equiv}CR$ or Cl, and L = PMe_2Ph or $AsMe_3$, with a number of inorganic and organic substrates A–B are reported. Four types of reactions have been observed: (i) oxidative addition to give platinum(IV) alkynyl compounds (A–B = I_2, IBr, ICN, CF_3I, and MeI) where the ease of oxidative addition followed the order R = Me > H > CF_3, X = $C{\equiv}CR$ > Cl and L = $AsMe_3$ > PMe_2Ph; (ii) insertion into the Pt–C(alkynyl) bond (A–B = $(CN)_2C{=}C(CN)_2$); (iii) attack at the C–C triple bond either to give vinylplatinum(II) compounds (A–B = CF_3COCl, *o*-tetrachloroquinone, and NOCl) or to generate a new alkynyl moiety ($PtC{\equiv}CH + (CF_3)_2CO \rightarrow PtC{\equiv}CC(OH)(CF_3)_2$); and (iv) formation of 1:1 π complexes (A–B = $(CF_3)_2CO$). These reactions are compared with previously reported reactions of methylplatinum(II) compounds. Platinum(II) is shown to activate the σ-bonded alkynyl ligand toward addition reactions.

Introduction

Platinum has played a prominent role in the development of organometallic chemistry.[1,2] Studies involving alkyl- and hydridoplatinum compounds have elucidated many of the fundamental aspects of oxidative addition,[3-8] reductive elimination,[9-12] β-hydrogen elimination,[13-16] π-complex formation,[17-19] and ligand migration (insertion–deinsertion) reactions.[6,17,20-25] Alkynyl- and alkenylplatinum compounds of the type $Pt(un)_2L_2$ and $PtX(un)L_2$ (where un = a σ-bonded alkynyl or alkenyl ligand, X = a univalent anionic ligand, e.g., Cl^-, and L = a neutral donor ligand such as a tertiary phosphine or arsine), although readily synthesized,[26] have not been extensively studied. Since these compounds contain both inorganic[27] and organic sites of unsaturation their reactions pose many interesting synthetic and mechanistic possibilities. Prior to this work we have proposed that their reactions with protic acids and the solvolysis and elimination reactions of α-chlorovinylplatinum(II) compounds involve platinum-stabilized carbonium ion intermediates.[26,28,29] In this paper we describe the reactions of alkynylplatinum(II) compounds of the type *trans*-$Pt(C{\equiv}CR)_2L_2$ and *trans*-$PtCl(C{\equiv}CR)L_2$ with a number of inorganic and organic substrates. (1) Qualitatively we define the relative reactivity of the alkynylplatinum(II) compounds as a function of R (R = H, Me, and CF_3) and L (L = PMe_2Ph and $AsMe_3$) for a given substrate. (2) For a given platinum compound we note certain trends in the reactivity of A–B substrate molecules. (3) We make a comparison with the reactivity patterns of methylplatinum(II) compounds of the type $PtMe_2L_2$ and $PtMe(Cl)L_2$.

Results and Discussion

Four types of reactions have been observed: (1) oxidative addition to give platinum(IV) alkynyl compounds; (2) attack at the carbon–carbon triple bond either to give vinylic platinum(II) compounds containing a $PtC(A){=}C(B)R$ moiety or to generate a new alkynyl moiety, $PtC{\equiv}CR'$; (3) insertion into the platinum–carbon bond to give $Pt(AB)C{\equiv}CR$; (4) π complexation of an unsaturated AB substrate molecule to platinum.

Since elemental analyses cannot distinguish between the above, we comment first on our methods of product analyses which are based predominantly on NMR and infrared spectroscopy. In the previous paper[29] we reviewed the generally accepted criteria that exist for the assignment of stereochemistry in $PtR(X)L_2$ compounds (in particular for L = PMe_2Ph), based on ^1H NMR data. These same arguments hold for stereochemical assignments in the platinum(IV) compounds $PtR(X)(A)(B)L_2$ and a distinction between Pt(II) and Pt(IV) derivatives is readily apparent from the magnitude of platinum-195 to hydrogen coupling constants. For the L methyl protons $^4J_{Pt(II)-H}$ is ca. 50% larger than $^4J_{Pt(IV)-H}$. A similar change is observed for the $PtC{\equiv}CR$ moiety, $J_{Pt(II)-H} > J_{Pt(IV)-H}$. These changes in J_{Pt-H} may be correlated with the change in hybridization of platinum which accompanies oxidative addition, Pt(II)–dsp^2 to Pt(IV)–d^2sp^3, and the relative Pt 6s character in the Pt–L bond.[30] We have also noted that $\nu_{str}(C{\equiv}C)$ increases in going from Pt(II) to Pt(IV). This may be indicative of the relative degree of Pt to $C{\equiv}C$ π* backbonding, Pt(II) > Pt(IV).

Addition of A–B across the carbon–carbon triple bond leads to the loss of $\nu_{str}(C{\equiv}C)$ in the infrared spectrum and the appearance of a lower energy band, ca. 1600 cm^{-1}, associated with the C=C moiety. The coupling constant $^4J_{Pt-H}$ to the L methyl protons remains essentially unchanged in magnitude but J_{Pt-H} to the R protons of the acetylenic substituent is diminished. The latter is consistent with the change from sp to sp^2 hybridization in the carbon atom directly bonded to platinum: $PtC{\equiv}CR + AB \rightarrow PtC(A){=}C(B)R$.

Insertion into the Pt–C(acetylide) bond leads to a loss, or diminuation, of J_{Pt-H} to the R protons of the acetylide. $^4J_{Pt-H}$ to the L methyl protons and $\nu_{str}(C{\equiv}C)$ are little changed.

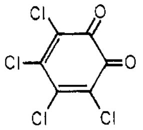
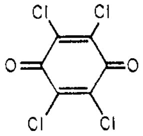
Finally π complexation to platinum, which is only possible for A–B unsaturated molecules, causes changes in J_{Pt-H} and $\nu_{str}(C{\equiv}C)$; the magnitude of these changes is determined largely by the stereochemistry of the adduct.

trans-$Pt(C{\equiv}CR)_2(PMe_2Ph)_2$, where R = H, Me, and CF_3, *trans*-$Pt(C{\equiv}CMe)_2(AsMe_3)_2$, and *trans*-$PtCl(C{\equiv}CMe)(AsMe_3)_2$ were reacted with the following substrates: CH_3I, CF_3I, I_2, ICN, CH_3COCl, CF_3COCl, CF_3CN, $CH_2{=}CH_2$, $CH_2{=}C{=}CH_2$, $CF_2{=}CF_2$, $PhC{\equiv}CH$, $PhC{\equiv}CPh$, $MeC{\equiv}CMe$, $MeO_2CC{\equiv}CCO_2Me$, $MeC{\equiv}CCOOH$, $CF_3C{\equiv}CH$, $CF_3C{\equiv}CCF_3$, CO, CO_2, SO_2, ethylene oxide, Me_2SO, NOCl, *o*- and *p*-tetrachlorobenzoquinone, tetracyanoethylene (TCNE), PhSSPh, and H_2 in the presence of palladium black. The various reactions studied are noted in Table I. Although all combinations of reactants were not examined we believe our studies are sufficient to note general and comparative trends in reactivity.

Analytical and other characterization data for a representative sample of the new compounds are given in Table II. The products obtained from a number of reactions were not subjected to elemental analyses. This was either because the compound was not isolated in a spectroscopically pure state or because spectroscopic data were considered unequivocal with regard to the nature of the product. Pertinent ^1H NMR data are recorded in Table III and infrared data are given in Table IV.

Oxidative Addition. Only I_2, IBr, ICN, CF_3I, or MeI has been found to react with the alkynylplatinum(II) compounds to give isolable alkynylplatinum(IV) compounds. The relative ease of oxidative addition of these substrates follows the order I_2, IBr, ICN > CF_3I > CH_3I. Significantly CH_3COCl was unreactive, although it readily oxidatively adds to alkylplatinum(II) compounds. CF_3COCl, which also very readily

Table I. Some Reactions of Alkynylplatinum(II) Compounds[a]

Substrate	$Pt(C\equiv CH)_2(PMe_2Ph)_2$	$Pt(C\equiv CMe)X(AsMe_3)_2$		$Pt(C\equiv CMe)_2$-$(PMe_2Ph)_2$	$Pt(C\equiv CCF_3)_2$-$(PMe_2Ph)_2$
		X = C≡CMe	X = Cl		
CH_3I	Slow ox addn	Ox addn		Ox addn and red elimn	NR
CF_3I	Ox addn	Ox addn	Slow ox addn		Slow ox addn
I_2	Ox addn	Ox addn	Ox addn		Ox addn
ICN	Ox addn	Ox addn			
CH_3COCl		NR			
HCl	Addn[26,28]	Addn[26]	Addn to C≡C	Addn[26,28]	Addn[26]
HPF_6/MeOH	Alkoxycarbene formn[26]	Alkoxycarbene formn[26]	Alkoxycarbene formn	Alkoxycarbene formn[26]	NR[26]
CF_3CN	NR	NR			
$CH_2{=}CH_2$	NR				
$CF_2{=}CF_2$	NR	NR			
$CF_3C\equiv CCF_3$	Polymerizn	Polymerizn			
$CF_3C\equiv CH$	NR	NR			
$CH_3C\equiv CCOOH$		NR	Complicated NMR		
$CH_3OOCC\equiv CCOOCH_3$	Polymerizn of RC≡CR	NR	NR		
PhC≡CH		NR			
PhC≡CPh		NR			
MeC≡CMe	NR				
SO_2	Dec	Dec			
CO_2	NR			NR	
CO	NR				
$CH_2{=}C{=}CH_2$	NR				
	NR				
Me_2SO	NR				
CF_3COCl	Addn to C≡C and ox addn	Addn to C≡C	Addn to C≡C	Addn to C≡C	Slow ox addn
NOCl	Reaction	Ox addn and addn to C≡C		Ox addn and addn to C≡C	Slow ox addn
	Addn to C≡C	Addn to C≡C		Addn to C≡C	NR
	NR				
CF_3COCF_3	Insertion at β carbon	π adduct	π adduct		NR
TCNE	Insertion at Pt-C≡	Insertion at Pt-C≡	Insertion at Pt-C≡		NR
PhSSPh	NR				
H_2(Pd on carbon, $MeOH/CH_2Cl_2$)	NR				

[a] Key: ox addn = oxidative addition; red elimn = reductive elimination; NR = no reaction.

Table II. Analytical and Other Characterization Data for Alkynylplatinum(II) Compounds and Some of Their Derivatives

Compd[a]	% C		% H		% other		Mp, °C	Color
	Calcd	Found	Calcd	Found	Calcd	Found		
$Pt(C\equiv CMe)_2A_2$	28.08	29.98	4.71	4.80			146-148 dec	White
$Pt(C\equiv CMe)_2(CH_3)IA_2$	23.81	25.05	4.12	4.14	19.37 (I)	18.95	128 dec	Yellow
$Pt(C\equiv CMe)_2(CF_3)(I)A_2$	22.02	22.16	3.39	3.38	17.90 (I)	16.87	169 dec	Yellow
$Pt(C\equiv CMe)_2(I)_2A_2$	18.79	19.36	3.13	2.98	33.10 (I)	32.80	146-148	Red
$Pt(C\equiv CMe)_2(CN)(I)A_2$	23.44	23.44	3.60	3.49			200 dec	Yellow
$Pt(C\equiv CMe)ClA_2$	21.22	22.16	4.12	4.11			107-109	Off-white
$Pt(C\equiv CH)_2(CF_3)(I)P_2$	35.16	34.86	3.35	3.41	17.70 (I)	17.81	192-194	Yellow
$Pt(C\equiv CH)_2(I)_2P_2$	30.98	29.69	3.09	3.06	32.55 (I)	31.93	120	Red
$Pt(C\equiv CMe)_2(C_6Cl_4O_2)A_2$	28.48	28.72	3.16	2.94	18.68 (Cl)	21.59	158 dec	Yellow
$Pt(C\equiv CH)_2(C_6Cl_4O_2)_2P_2$	37.93	38.06	2.39	2.57	27.99 (Cl)	28.05	143	Yellow
$Pt[C(Cl){=}C(COCF_3)Me]_2A_2$	24.70	24.50	3.08	3.08	9.11 (Cl)	9.11	140-142	Yellow
$Pt(C\equiv CMe)_2(TCNE)A_2$	33.72	33.68	3.74	3.66	8.74 (N)	8.76	148-152	Yellow
$Pt(C\equiv CH)_2(TCNE)P_2$	48.01	47.81	3.69	3.72	8.62 (N)	8.55	191	Yellow
$Pt(C\equiv CMe)(CCl{=}C(NO)Me)(NO)(Cl)A_2$	22.38	22.47	3.73	3.61			136-140	Pink
$Pt(C\equiv CH)_2(CF_3COCF_3)_2P_2$	36.59	37.08	2.81	2.62			171-173	White

[a] Key: A = $AsMe_3$; P = PMe_2Ph.

oxidatively adds to alkylplatinum(II) compounds, always reacted to give products of addition to the carbon–carbon triple bond (see later).

For *trans*-$Pt(C\equiv CR)_2L_2$ compounds we observed the following relative order of ease of oxidative addition: R = Me > H > CF_3 and L = $AsMe_3$ > PMe_2Ph. Thus, while I_2 readily

Table III. ^1H NMR Data[a] for Alkynylplatinum(II) Compounds and Their Derivatives

		Ligand A or P methyls			Acetylide R			Other		
Compd[b]	Solvent	δ	$^2J + ^4J$	$^3J_{Pt-H}$	δ	J_{P-H}	J_{Pt-H}	δ	J_{P-H}	J_{Pt-H}
$Pt(C{\equiv}CMe)_2A_2$	Benzene	1.37		24.0	2.00		15.2			
$Pt(C{\equiv}CMe)_2(CH_3)(I)A_2$	Benzene	1.54		16.6	2.10		14.6	1.61		70.4 (Me)
$Pt(C{\equiv}CMe)_2(CF_3)(I)A_2$	Benzene	1.71		16.4	2.10		14.6			
$Pt(C{\equiv}CMe)_2(I)_2A_2$	Benzene	1.87		16.0	2.46		15.0			
$Pt(C{\equiv}CMe)_2(CN)(I)A_2$	Benzene	1.74		17.3	2.13		14.5			
$Pt(C{\equiv}CMe)ClA_2$	Benzene	1.27		23.6	2.12		22.8			
$Pt(C{\equiv}CMe)Cl(CF_3)(I)A_2$	Benzene	1.57		15.8	1.95		20.8			
$Pt(C{\equiv}CMe)Cl(I_2)A_2$	Benzene	1.71		15.2	2.33		20.4			
$Pt(C{\equiv}CMe)_2P_2$	$CDCl_3$	2.02	7.5	33.0	1.83	1.9	16.4			
$Pt(C{\equiv}CH)_2P_2$	CD_2Cl_2	2.05	7.8	33.0	2.13	2.3	45			
$Pt(C{\equiv}CH)_2I_2P_2$	$CDCl_3$	2.62	7.4	17.6	1.56	3.6	33.0			
$Pt(C{\equiv}CH)_2(CF_3)IP_2$	$CDCl_3$	2.47	8.6	20.2	1.86	3.8	36.4			
$Pt(C{\equiv}CCF_3)_2P_2$	CH_2Cl_2	1.93	8.0	32.8						
$Pt(C{\equiv}CCF_3)_2I_2P_2$	Benzene	2.23	8.4	20.4						
		1.12		23.5						
$Pt(C(Cl){=}C(COCF_3)Me)_2A_2$	Benzene	1.06		25.5	2.08					
$Pt(C(Cl){=}C(COCF_3)Me)ClA_2$	Benzene	1.12		23.4	2.10		15			
$Pt(C{\equiv}CMe)_2A_2(o\text{-}O_2C_6Cl_4)$	Benzene	0.98		24.7	2.00		15	2.12		10 (vinyl R)
		0.93		25.0						
$Pt(C{\equiv}CH)_2P_2(o\text{-}O_2C_6Cl_4)_2$	Benzene	1.5–1.0		c				5.1	2.5	39 (vinyl H)
$Pt(C{\equiv}CMe)(CCl{=}C(NO)Me)(NO)(Cl)A_2$	CH_2Cl_2	1.53		15.0	1.98		14	2.15		6 (vinyl R)
					2.09		14			
$Pt(C{\equiv}CMe)_2((CF_3)_2CO)A_2$	Benzene	1.28		23.4	1.72		10			
$Pt(C{\equiv}CMe)Cl((CF_3)_2CO)A_2$	Benzene	1.20		23.0	1.69		13.6			
$Pt(C{\equiv}CMe)_2((CF_3)_2CO)P_2$	CH_2Cl_2	1.91	7.8	33.8	1.63	2.3	14	1.28	1.8	10
$Pt(C{\equiv}CC(CF_3)_2OH)_2P_2$	Acetone-d_6	1.18	8.0	32.6	2.07	d				
$Pt(C{\equiv}CMe)_2(TCNE)A_2$	Benzene	1.13		25.0	1.94		15	1.91		None
$Pt(C{\equiv}CMe)Cl(TCNE)A_2$	CH_2Cl_2	1.47		24.0				1.74		None
		1.44		24.0						
$Pt(C{\equiv}CH)_2(TCNE)P_2$	Acetone-d_6	1.47	8.2	30.0						

[a] δ in ppm relative to Me_4Si; J in Hz. [b] Key: A = $AsMe_3$; P = PMe_2Ph. [c] Very complicated. [d] Singlet.

Table IV. Characteristic Infrared Absorptions for Some Alkynylplatinum(II) Compounds and Their Derivatives

Compd[a]	$\nu(C{\equiv}C)$[b]	Other[b]
$Pt(C{\equiv}CMe)_2A_2$	2122	
$Pt(C{\equiv}CMe)_2(CH_3)(I)A_2$	2160	
$Pt(C{\equiv}CMe)_2(CF_3)(I)A_2$	2170	
$Pt(C{\equiv}CMe)_2(I)_2A_2$	2166	
$Pt(C{\equiv}CMe)_2(CN)(I)A_2$		2165, 2150
$Pt(C{\equiv}CMe)ClA_2$	2122	
$Pt(C{\equiv}CH)_2P_2$	1968	
$Pt(C{\equiv}CH)_2I_2P_2$	1998	
$Pt(C{\equiv}CH)_2(CF_3)IP_2$	2005, 2030	
$Pt(C{\equiv}CCF_3)_2P_2$	2130	
$Pt(C{\equiv}CCF_3)_2I_2P_2$	2160	
$Pt(C(Cl){=}C(COCF_3)Me)_2A_2$		1720 $\nu(C{=}O)$, 1575, 1560, 1540 $\nu(C{=}C)$
$Pt(C(Cl){=}C(COCF_3)Me)ClA_2$		1710 $\nu(C{=}O)$, 1580, 1520
$Pt(C(Cl){=}C(COCF_3)Me)_2P_2$		1728 $\nu(C{=}O)$, 1678, 1550
$Pt(C{\equiv}CMe)_2A_2\text{-}o\text{-}O_2C_6Cl_4$	2130	1738, 1575, 1540
$Pt(C{\equiv}CH)_2P_2{\cdot}2o\text{-}O_2C_6Cl_4$		1760, 1570
$Pt(C{\equiv}CMe)(CCl{=}C(NO)Me)(NO)(Cl)A_2$	2180	1660, 1620, 1500
$Pt(C{\equiv}CMe)_2((CF_3)_2CO)A_2$		1875, 1640 1625
$Pt(C{\equiv}CMe)(Cl)((CF_3)_2CO)A_2$		1880, 1640
$Pt(C{\equiv}CC(CF_3)_2COH)_2P_2$	2105	3525 $\nu(OH)$, 2620 $\nu(OD)$
$Pt(C{\equiv}CMe)_2(TCNE)A_2$		2225, 1560
$Pt(C{\equiv}CMe)Cl(TCNE)A_2$		2210, 1550
$Pt(C{\equiv}CH)_2(TCNE)P_2$		2220, 1980

[a] Key: A = $AsMe_3$, P = PMe_2Ph. [b] ±2 cm^{-1}.

reacted with all the alkynylplatinum compounds, MeI only slowly reacted with *trans*-$Pt(C{\equiv}CMe)_2(AsMe_3)_2$ to give *trans*-$Pt(Me)(I)(C{\equiv}CMe)_2(AsMe_3)_2$. Under comparable conditions *trans*-$Pt(C{\equiv}CMe)_2(PMe_2Ph)_2$ and MeI do not react. However, under reflux and in the presence of a large excess of MeI, *trans*-$Pt(C{\equiv}CMe)_2(PMe_2Ph)_2$ reacted to give *trans*-$PtI(C{\equiv}CMe)(PMe_2Ph)_2$. This reaction could well proceed via an oxidative addition/reductive elimination sequence, but this has not been demonstrated.

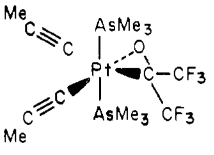
trans-$PtCl(C{\equiv}CMe)(AsMe_3)_2$ did not react with MeI, cf. the reaction with $Pt(C{\equiv}CMe)_2(AsMe_3)_2$ above, but did react slowly with CF_3I to give oxidative addition. The reactivity order *trans*-$Pt(C{\equiv}CMe)_2(AsMe_3)_2$ > *trans*-$PtCl(C{\equiv}CMe)(AsMe_3)$ has a parallel in the reactivity of methylplatinum(II) compounds, $PtMe_2L_2$ > $PtCl(Me)L_2$. However, *trans*-$PtMe(Cl)L_2$ compounds do react with MeI to give oxidative-addition products, e.g., L = PEt_3 and PMe_2Ph.[1]

We conclude that alkynylplatinum(II) compounds are generally less susceptible to oxidative-addition reactions than their methylplatinum analogues. This may well reflect the electron density on platinum which we expect follows the order Me > $C{\equiv}CMe$ > $C{\equiv}CH$ > $C{\equiv}CCF_3$. The reactivity order L = $AsMe_3$ > PMe_2Ph finds a direct parallel in methylplatinum chemistry. We believe this is largely a kinetic effect. The $AsMe_3$ ligand is less sterically demanding than PMe_2Ph and thus their derivatives are more open to attack by substrates.

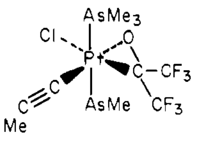
π Complexation. Clark and his co-workers[31-35] have found that a number of substituted acetylenes and ethylenes form π complexes with $PtMe_2L_2$ and $PtMe(Cl)L_2$ compounds. These five-coordinated platinum π complexes are involved in Pt–C(methyl) insertion reactions and in acetylene polymerization reactions. The alkynylplatinum(II) compounds in the present study did not form π complexes in NMR detectable concentrations. In some cases acetylene polymerization was observed, e.g., $CF_3C{\equiv}CH$, $CF_3C{\equiv}CCF_3$, and $MeO_2CC{\equiv}CCO_2Me$. We find no evidence to support the suggestion that this polymerization occurs via insertion into Pt–C(acetylide) bonds. Our results may be interpreted in terms of the reaction sequence discussed by Appleton, Clark, and Puddephatt[33] for the polymerization of $CF_3C{\equiv}CH$ by methylplatinum compounds.

A number of other unsaturated molecules are known to form π complexes with electron-rich group 8 transition metal complexes, e.g., allene,[36] O_2,[37] CO_2,[38] CS_2,[39,40] CF_3CN,[41] SO_2,[42] and $(CF_3)_2CO$.[43-45] Of these only hexafluoroacetone forms π complexes with alkynylplatinum compounds.

We find that *trans*-$Pt(C{\equiv}CMe)_2(AsMe_3)_2$ and *trans*-$PtCl(C{\equiv}CMe)(AsMe_3)_2$ react to form the stable 1:1 adducts I and II. The stereochemistry of I and II is readily deduced from the ^1H NMR data. Both I and II show only one $AsMe_3$ proton resonance with $^3J_{Pt-H} = 23$ Hz. I showed two propynyl methyl resonances with differing values of $^4J_{Pt-H}$. We assign the methyl resonance with $^4J_{Pt-H} = 10$ Hz to the propynyl ligand trans to the Pt–C bond and the methyl resonance with $^4J_{Pt-H} = 14$ Hz to the ligand trans to the Pt–O bond. Similarly for II the magnitude of $^4J_{Pt-H} = 14$ Hz for the propynyl protons leads us to suggest that this is trans to the Pt–O bond. Our proposed stereochemistry for II is that expected from trans-influence theories.[30] Of course the angle O–Pt–C of the Pt–O–$C(CF_3)_2$ moiety must be much smaller than 90°; cf.[46] $PtMe(Cl)(AsMe_3)_2(CF_3C{\equiv}CCF_3)$ where the C–Pt–C angle of the $PtC_2(CF_3)_2$ moiety is 37°. The geometry about platinum in I and II might be described in terms of either a five- or a six-coordinate model. In any event both compounds are stereochemically rigid on the NMR time scale.



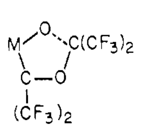
I



II

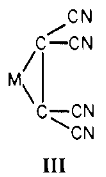
Reaction of $(CF_3)_2CO$ with ethynylplatinum(II) compounds leads to insertion into the $\equiv$C—H bond and is discussed later. The trifluoropropynylplatinum compound *trans*-$Pt(C{\equiv}CCF_3)_2(PMe_2Ph)_2$ did not react with $(CF_3)_2CO$. This observation is consistent with our previously expressed view that the electron density on platinum is sensitive to the acetylenic substituent R and is greater for Me than for CF_3; cf. relative ease of oxidative addition.

When a large excess of $(CF_3)_2CO$ was reacted with *trans*-$Pt(C{\equiv}CMe)_2(AsMe_3)_2$ a platinum-containing compound which was insoluble in benzene and only very sparingly soluble in acetone was formed. This we believe is probably similar to Ni, Pd, and Pt five-membered ringed compounds previously reported[43] which involve

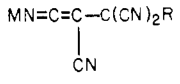


moieties.

Pt–C(acetylide) Insertion Reactions. Tetracyanoethylene (TCNE) is known to react with transition metal complexes (i) to give π complexes, e.g., with *trans*-$PtMe(X)L_2$,[47] (ii) to give insertion products which may be either C or N bonded to the metal, and[48] (iii) to undergo oxidative-addition reactions.[49] These possibilities are shown schematically in III–VI.



III

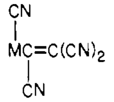


$$MN{=}C{=}\underset{\displaystyle CN}{\underset{|}{C}}{-}C(CN)_2R$$

IV

$MC(CN)_2C(CN)_2R$

V



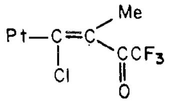
$$\underset{\displaystyle CN}{\underset{|}{\overset{\displaystyle CN}{\overset{|}{M}}}}C{=}C(CN)_2$$

VI

trans-$Pt(C{\equiv}CMe)_2(AsMe_3)_2$ reacts with 1 equiv of TCNE to give a platinum compound in which the $^1J_{Pt-H}$ to the $AsMe_3$ protons remains unchanged. There are two propynyl methyl resonances: one shows $^4J_{Pt-H} = 15$ Hz; the other shows no apparent coupling to ^{195}Pt. These observations rule out π complexation of TCNE to platinum and oxidative addition, i.e., derivatives of type III and VI. Also we discount the formation of an N-bonded ligand, IV, since a marked increase in $^4J_{Pt-H}$ to the propynyl protons would be expected.[30] We believe the only reasonable structure consistent with the ^1H NMR and infrared data is that of *trans*-$Pt(C{\equiv}CMe)(C(CN)_2C(CN)_2C{\equiv}CMe)(AsMe_3)_2$ in which insertion into one Pt–C (acetylide bond) has occurred, i.e., formation of a compound of type V. This is the only example of an insertion into a Pt–C(acetylide) bond that we have observed for a neutral platinum compound.[50] There is a report concerning the insertion of $MeO_2CC{\equiv}CCO_2Me$ into the Pd–C(acetylide) bond in $PdCl(C{\equiv}CPh)(PEt_3)_2$. We believe that the inertness of the Pt–C(acetylide) bond toward insertion reactions, relative to the Pt–C(methyl) bond, is a result of thermodynamic considerations, namely the Pt–C bond strengths.[52] Only the highly electron-withdrawing cyano groups of the $PtC(CN)_2C(CN)_2C{\equiv}CMe$ ligand make the insertion thermodynamically favorable. It seems a similar situation may hold in palladium chemistry where the driving force for the reaction $PdC{\equiv}CPh + MeO_2CC{\equiv}CCO_2Me \rightarrow PdC(CO_2Me){=}(CO_2Me)C{\equiv}CPh$ comes from the electron-withdrawing substituents on the Pd–vinylic ligand.

Addition to the C–C Triple Bond. CF_3COCl,[53] *o*-tetrachloroquinone,[54,55] Br_2,[56] and NOCl[57] are known to oxidatively add to d^8 metal complexes. However, in our study we find products of addition to the carbon–carbon triple bond.

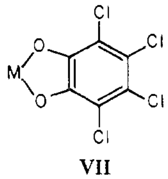
trans-$Pt(C{\equiv}CMe)_2L_2$ reacts quantitatively with 2 equiv of CF_3COCl to give a platinum(II) bisvinyl derivative. A number of isomers could be formed depending on the mode of addition: the CF_3CO moiety could add to either the α or β carbon and the addition could lead to either cis or trans vinylic isomers. Furthermore if there is restricted rotation about the Pt–C(vinyl) bond, then two further sets of stereoisomers are possible. We believe the addition of the CF_3CO moiety occurs exclusively to the β carbon but that in solution both cis and trans vinylic isomers are present. In a crystallographic study the presence of the



$$Pt{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}C\begin{matrix}{}^{\diagup}Me\\{}_{\diagdown}\underset{\displaystyle O}{\underset{\|}{C}}CF_3\end{matrix}$$

isomer was found.[58]

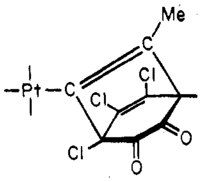
When tetrachloro-*o*-quinone forms 1:1 adducts with group 8 transition metal complexes, a decrease in $\nu_{str}(C{=}O)$ is observed of ca. 200 cm^{-1}.[59] This is indicative of coordination to the metal as shown in VII.



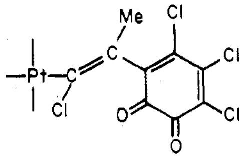
VII

However, upon reaction with alkynylplatinum(II) compounds we observed an increase in $\nu_{str}(C{=}O)$ by ca. 70 cm^{-1}. This we believe rules out complexation to platinum as in VII.

When *trans*-$Pt(C{\equiv}CMe)_2(AsMe_3)_2$ was reacted with 1 equiv of o-$O_2C_6Cl_4$ we obtained a product of addition to one of the propynyl ligands. The exact nature of the product cannot be deduced from ^1H NMR data alone. However, we can reasonably formulate the product either as a 1,4-addition product, VIII, or as a phenyl C–Cl addition product, IX, akin



VIII



IX

to that obtained in the reaction with CF_3COCl.

The evidence in support of VIII or IX may be summarized as follows. (1) There are two $AsMe_3$ resonances (δ 0.98 and 0.93 ppm relative to Me_4Si) in the integral ratio 1:1. Both have similar $^3J_{Pt-H}$ values, 24.7 and 25 Hz, respectively. This is indicative of a Pt(II) complex with As trans to As and an absence of a plane of symmetry containing the $MeC\equiv CPt$-(vinyl) moiety. In VIII such a plane does not exist. For IX such a plane need not exist if there is restricted rotation about the C(vinyl)—$C_6Cl_3O_2$ single bond. (2) The only other two ^1H resonances, δ 2.00 and 2.12 ppm, are readily assigned to $PtC\equiv CMe$ and $PtC{=}CMe$ moieties on the basis of the magnitude of $^4J_{Pt-H}$: $^4J_{PtC\equiv CCH} = 15$ Hz and $^4J_{PtC=CCH} = 10$ Hz. Again the magnitude of these values are consistent with the mutually high trans influence of both the acetylide and vinyl ligands.

If addition had occurred in the manner shown in IX, a number of vinylic isomers might be possible; cf. the sterochemistry of CF_3COCl addition. Only one $PtC{=}CMe$ resonance is observed and only one is expected for VIII. We cannot, however, use this observation to rule out a reaction giving only one isomer of IX.

Further evidence for the formation of vinylic compounds is seen in the reaction between *trans*-$Pt(C\equiv CH)_2(PMe_2Ph)$ and o-$O_2C_6Cl_4$ (2 equiv). Here again reaction occurred at the C–C triple bond; the product showed a ^1H resonance at δ 5.1 ppm, with coupling to both platinum, $^3J_{PtC=CH} = 39$ Hz, and phosphorus, $^4J_{P-H} = 2.5$ Hz. This observation is entirely reconcilable with a 1,4-addition product of type VII. Rather interestingly, p-tetrachloroquinone was found to be unreactive with alkynylplatinum(II) compounds. A 1,4-cycloaddition is, of course, not possible here. We conclude that spectroscopic data are at least consistent with a 1,4 addition of type VIII but that we cannot rule out a product of type IX.

Nitrosyl chloride reacts rapidly with *trans*-$Pt(C\equiv CMe)_2(AsMe_3)_2$ to give both oxidative addition and addition to the C–C triple bond competitively. With 2 equiv of NOCl a compound is formed which, on the basis of ^1H NMR data, we formulate as *trans*-$Pt(NO)(Cl)(C\equiv CMe)(CCl{=}C(NO)Me)(AsMe_3)_2$. A single $AsMe_3$ proton resonance with $^3J_{Pt-H} = 15$ Hz is consistent with the proposed *trans*-$Pt^{IV}(AsMe_3)_2$ moiety. In addition there are two other methyl resonances at δ 1.98 and 2.15 ppm relative to Me_4Si which show $^4J_{Pt-H} = 14$ and 6 Hz, respectively. Nothing can be said concerning the stereochemistry of the vinylic ligand, however. In the infrared spectrum absorptions at 1600, 1620, and 1500 cm^{-1} are probably associated with $\nu_{str}(NO)$ and $\nu_{str}(C{=}C)$ modes.

trans-$Pt(C\equiv CH)_2(PMe_2Ph)_2$ reacts smoothly with hexafluoroacetone to give *trans*-$Pt(C\equiv CC(OH)(CF_3)_2)_2(PMe_2Ph)_2$. This reaction is accompanied by an increase in $\nu_{str}(C\equiv C)$, 1967–2105 cm^{-1}. $\nu_{str}(OH)$ occurs at 3525 cm^{-1} in the infrared spectrum. Upon deuteration (simple dissolution in MeOD) this band shifts to 2620 cm^{-1}.

trans-$Pt(C\equiv CCF_3)_2(PMe_2Ph)_2$ did not react with o-$O_2C_6Cl_4$, CF_3COCl, $(CF_3)_2CO$, and TCNE under comparable conditions. Addition of NOCl led initially to oxidative addition to platinum (as indicated by the change in $^3J_{Pt-H}$ to the phosphine methyl protons). However, further subsequent reactions occurred and no pure compounds were isolated from this reaction.

In blank experiments $MeC\equiv CMe$ was reacted with o-$O_2C_6Cl_4$, TCNE, CF_3COCl, and NOCl in benzene. No reaction was observed.

Experimental Section

K_2PtCl_4 was obtained from Mathey Bishop, Inc. CH_3OD, TCNE, o-$O_2C_6Cl_4$, $PhC\equiv CH$, $MeO_2CC\equiv CCO_2Me$, $MeC\equiv CCO_2H$, $MeC\equiv CMe$ were from Aldrich; $(CF_3)_2CO$, $HC\equiv CCF_3$, $CF_3C\equiv CCF_3$, $CF_2{=}CF_2$ were from PCR, Inc.; $CH_2{=}CH_2$, $CH_3C\equiv CH$, and $HC\equiv CH$ were from Matheson. Analyses were performed by Atlantic Microlabs and Chemalytics, Inc.

cis-$PtCl_2L_2$[4] and *trans*-$Pt(C\equiv CR)(X)L_2$ (where R = H, Me, Ph, CF_3; X = Cl, $C\equiv Cr$; and L = $AsMe_3$, PMe_2Ph) were prepared by methods previously described.[26]

Infrared spectra were obtained from Nujol mulls between CsI or NaCl plates using a Beckman IR-12 spectrophotometer. ^1H NMR were recorded on a Varian A60 or HA100 spectrometer.

$Pt(C\equiv CMe)_2(CF_3)(I)(AsMe_3)_2$. $Pt(C\equiv CMe)_2(AsMe_3)_2$ (0.103 g, 0.2 mmol) was dissolved in benzene (0.5 mL) and CF_3I (1.0 mmol) was condensed into the reaction tube which was sealed. When the tube warmed to room temperature, a yellow compound crystallized from solution. After 3 h, the tube was opened and petroleum ether added, producing more yellow crystals, mp 169 °C dec, 0.05 g (49% yield based on Pt).

Analogous procedures were used for the preparation of the oxidative-addition products using CH_3I, I_2, and ICN with $Pt(C\equiv CMe)Cl(AsMe_3)$, $Pt(C\equiv CH)_2(PMe_2Ph)_2$, $Pt(C\equiv CCF_3)_2(PMe_2Ph)_2$, and $Pt(C\equiv CMe)_2(PMe_2Ph)_2$. However, only 1 equiv of I_2 and ICN was used.

Test for π-Complex Formation. $Pt(C\equiv CR)XL_2$ (R = Me, H; X = $C\equiv CR$, Cl; L = $AsMe_3$, PMe_2Ph) (0.1 mmol) in an appropriate solvent (either benzene or CH_2Cl_2) was reacted with 1 equiv of one of the possible π-complexing agents (listed in Table I) in an NMR tube. NMR spectra were recorded. IR spectra of the residues from these reactions were also taken.

$Pt(C(Cl){=}C(CF_3C(O))Me)_2(AsMe_3)_2$. $Pt(C\equiv CMe)_2(AsMe_3)$ (0.15 g, 0.29 mmol) was dissolved in benzene (2.5 mL) and reacted with $CF_3C(O)Cl$ (8 eq) for 2 h. Addition of petroleum ether to the solution resulted in formation of yellow crystals (0.10 g (ca. 90% yield based on Pt) $Pt(C(Cl){=}C(CF_3C(O))Me)Cl(AsMe_3)_2$, mp 140–142 °C).

$Pt(C\equiv CMe)_2(AsMe_3)_2{\cdot}o$-$O_2C_6Cl_4$. $Pt(C\equiv CMe)_2(AsMe_3)_2$ (0.2 g, 0.4 mmol) was dissolved in benzene (5 mL). A benzene solution (10 mL) containing o-$O_2C_6Cl_4$ (0.2 g, 0.4 mmol) was added. After 3 h workup (as above) yielded a yellow product, 0.10 g (ca. 40% yield based on Pt).

$Pt(C\equiv CH)_2(PMe_2Ph)_2$ was reacted with o-$O_2C_6Cl_4$ (2 equiv) in a similar manner to give yellow crystals of $Pt(C\equiv CH)_2(PMe_2Ph)_2{\cdot}2(o$-$O_2C_6Cl_4)$, mp 143 °C.

$Pt(C(Cl){=}C(NO)Me)(C\equiv CMe)(NO)(Cl)(AsMe_3)_2$. $Pt(C\equiv CMe)_2(AsMe_3)$ (0.1 g, 0.2 mmol) was reacted with excess NOCl (0.5 mmol) in toluene (3 mL) (as above). The platinum bisacetylide selectively reacts with only 2 equiv of NOCl. Within 1 h a pink precipitate came out of solution, mp 140–150 °C, yield 0.06 g (ca. 45% based on Pt). Prolonged exposure to the excess NOCl caused formation of other products, one being *cis*-$PtCl_2(AsMe_3)_2$.

$Pt(C\equiv CMe)_2((CF_3)_2CO)(AsMe_3)_2$. $Pt(C\equiv CMe)_2(AsMe_3)_2$ (0.2 g, 0.4 mmol) was dissolved in benzene (5 mL). $(CF_3)_2CO$ (10 eq) was reacted with the Pt compound. Within 1 h white crystals formed. The benzene solution was pipetted off and evaporated to dryness giving 0.1 g, mp 164–165 °C, $Pt(C\equiv CMe)_2(CF_3)_2CO(AsMe_3)_2$. The benzene-insoluble crystals were dissolved in acetone-d_6 for NMR and gave a similar NMR. IR was identical. When L = PMe_2Ph, the synthesis is the same.

$Pt(C\equiv CC(CF_3)_2OH)_2(PMe_2Ph)_2$. *trans*-$Pt(C\equiv CH)_2(PMe_2Ph)_2$ was reacted with $(CF_3)_2CO$ (2 equiv) as above. *trans*-$Pt(C\equiv CC(CF_3)_2OH)(PMe_2Ph)$ was dissolved in CH_2Cl_2:MeOD (1:1) and stirred for 5 h. The IR spectrum of the dried residue showed ν(OD) 2620 cm^{-1}.

$Pt(C\equiv CMe_2)_2(AsMe_3)_2$ + TCNE. *trans*-$Pt(C\equiv CMe)_2(AsMe_3)_2$ was reacted with TCNE (1 equiv) in a manner directly analogous to that described for reaction with o-$O_2C_6Cl_4$. A similar reaction was carried out with *trans*-$Pt(C\equiv CH)_2(PMe_2Ph)_2$.

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Registry No. $Pt(C{\equiv}CMe)_2A_2$, 61483-32-7; $Pt(C{\equiv}CMe)_2(CH_3)IA_2$, 63230-91-1; $Pt(C{\equiv}CMe)_2(CF_3)(I)A_2$, 63230-92-2; $Pt(C{\equiv}CMe)_2(I)_2A_2$, 63230-93-3; $Pt(C{\equiv}CMe)_2(CN)(I)A_2$, 63250-50-0; $Pt(C{\equiv}CMe)ClA_2$, 61483-33-8; $Pt(C{\equiv}CH)_2(CF_3)(I)P_2$, 63230-94-4; $Pt(C{\equiv}CH)_2(I)_2P_2$, 63230-95-5; $Pt(C{\equiv}CMe)_2(C_6Cl_4O_2)A_2$, 63230-96-6; $Pt(C{\equiv}CH)_2(C_6Cl_4O_2)_2P_2$, 63230-97-7; $Pt[C(Cl){=}C(COCF_3)Me]_2A_2$, 63230-98-8; $Pt(C{\equiv}CMe)_2(TCNE)A_2$, 63230-99-9; $Pt(C{\equiv}CH)_2(TCNE)P_2$, 63231-00-5; $Pt(C{\equiv}CMe)(CCl{=}C(NO)Me)(NO)(Cl)A_2$, 63231-01-6; $Pt(C{\equiv}CH)_2(CF_3COCF_3)_2P_2$, 63231-02-7; $Pt(C{\equiv}CMe)Cl(CF_3)(I)A_2$, 63301-43-9; $Pt(C{\equiv}CMe)Cl(I_2)A_2$, 63230-83-1; $Pt(C{\equiv}CMe)_2P_2$, 52638-03-6; $Pt(C{\equiv}CH)_2P_2$, 60314-10-5; $Pt(C{\equiv}CCF_3)_2P_2$, 38682-79-0; $Pt(C{\equiv}CCF_3)_2I_2P_2$, 63230-84-2; $Pt(C(Cl){=}C(COCF_3)Me)ClA_2$, 63230-85-3; $Pt(C{\equiv}CMe)_2((CF_3)_2CO)A_2$, 63230-86-4; $Pt(C{\equiv}CMe)Cl((CF_3)_2CO)A_2$, 63230-87-5; $Pt(C{\equiv}CMe)_2((CF_3)_2CO)P_2$, 63230-88-6; $Pt(C{\equiv}CC(CF_3)_2OH)_2P_2$, 63269-84-1; $Pt(C{\equiv}CMe)Cl(TCNE)A_2$, 63230-89-7; $Pt(C(Cl){=}C(COCF_3)Me)_2P_2$, 63230-90-0; CF_3I, 2314-97-8; $CF_3C(O)Cl$, 354-32-5; NOCl, 2696-92-6.

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