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SOME REACTIONS OF ALLENE AND ACETYLENES WITH VINYLPLATINUM AND METHYLPALLADIUM COMPLEXES

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Summary

The reactions of cationic vinylplatinum complexes, $Pt(R^1C{=}CHR^2)(PEt_3)_2(acetone)^+ PF_6^-$, with allene and activated acetylenes yield π-allyl and σ-butadienyl products, respectively. Similar reactions of $Pd(CH_3)X(Diphos)$ (X = Cl, NO_3, solvent, Diphos = 1,2-bis(diphenylphosphino)ethane) with acetylenes are also described. Factors affecting these insertion reactions are discussed.

Introduction

The formation of σ-vinylic complexes and their subsequent reactions are of interest because of their potential importance in transition metal-catalyzed oligomerization of olefins and acetylenes [1—3]. However, vinylic complexes are generally relatively inert toward further reaction. Although it has been possible in some cases to cleave metal—vinyl bonds using acids [4], there are few cases where controlled stepwise insertions can be achieved. Thus, in the reaction of $IrHCl_2(PEt_3)_3$ with hexafluorobut-2-yne (C_4F_6) and dimethyl acetylenedicarboxylate (DMA), although two molecules of acetylene are incorporated into the complex, only one acetylenic unit is contained in the vinylic group, the other acetylene being π-bonded to iridium [5] (eq. 1).

$$IrHCl_2(PEt_3)_3 + 2\ DMA \rightarrow IrCl(DMAH)(DMA)(PEt_3)_2 + PEt_3 \qquad (1)$$

While $CpRu(CO)_2(CF_3C{=}CHCF_3)$ has been found [6] to react with C_4F_6 to give a bis-inserted product (eq. 2), a similar complex, $CpRu(PPh_3)_2(CH_3OOC)C{=}CH(COOCH_3)$, reacts with C_4F_6 to give a σ-butadienyl complex by the insertion of the C_4F_6 molecule into the vinylic C—H bond, rather than the ruthenium—vinyl

$$CpRu(CO)_2(CF_3C{=}CHCF_3) \xrightarrow{C_4F_6} CpRu(CO)_2[CF_3C{=}C(CF_3C{=}CHCF_3)CF_3] \qquad (2)$$

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bond [7]. Recently, the insertion reaction of DMA with $PdBr(CH{=}CPh_2)(PBu_3)_2$ was reported [8], but no details of the reaction nor of the characterization of the products were given.

It has been demonstrated that the removal of the halide ligand, X, from the complexes of the type $PtRXQ_2$ (R = alkyl or H, Q = phosphine) using Ag^+ enables the complex to undergo insertion reactions readily with olefins and acetylenes (eq. 3) [9].

$$PtRXQ_2 \xrightarrow[Un]{Ag^+} PtR'Q_2^+ \xrightarrow{X^-} PtR'XQ_2 \qquad (3)$$

(R = H, Un = Olefin, R′ = Alkyl, Q = phosphine; R = Alkyl, H; Un = Acetylene, R′ = vinyl, Q = phosphine)

We have now succeeded in extending this method to facilitate the reactions of relatively inert vinylic complexes with unsaturated organic compounds. This paper reports the reactions of vinyl-platinum and -palladium complexes with allene and acetylenes.

Results

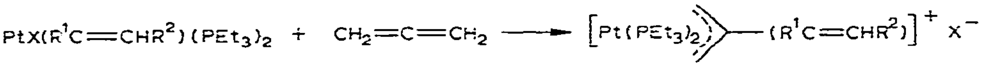
Reactions with allene

Vinylplatinum (II) derivatives can be conveniently prepared by the reactions of acetylenes with hydridoplatinum(II) complexes (eq. 4) [10]. Although the

$$PtHX(PEt_3)_2 + R^1C{\equiv}CR^2 \rightarrow \underset{(I)}{PtX(R^1C{=}CHR^2)(PEt_3)_2} \qquad (4)$$

X = Cl, NO_3, solvent (as PF_6^- salt)

chloro complex (I: X = Cl, $R^1 = R^2 = CH_3$), undergoes no reaction with a saturated methanolic solution of allene over 15 h, the corresponding cation I (X = acetone, $R^1 = R^2 = CH_3$) reacts with allene readily. Thus, after 2 h, IIa can be isolated from the reaction mixture as a white, crystalline solid. Other vinylplatinum complexes also undergo similar reactions (eq. 5).



(5)

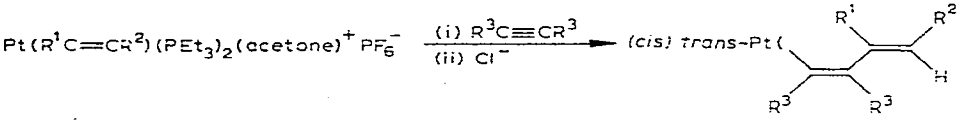
(IIa) $R^1 = R^2 = CH_3$, X = PF_6
(IIb) $R^1 = CH_3$, R^2 = cyclo-C_6H_{11} (Cy), X = PF_6
(IIc) $R^1 = CH_3$, R^2 = Ph, X = NO_3
(IId) $R^1 = R^2 = COOCH_3$, X = PF_6
(IIe) $R^1 = R^2 = CF_3$, X = PF_6

The ^1H NMR spectra of II (Table 1) in chloroform or acetone exhibit the static η^3-allyl pattern [11] at room temperature, as opposed to $Pt(C_3H_5)(PPh_3)_2Cl$ [12] and $Pt(CH_2CH{=}CHMe)Cl(PPh_3)_2$ [13] which show rapid *syn—anti* proton-(methyl) exchanges. This is probably due to the inability of the PF_6^- or NO_3^- to stabilize the σ-allylplatinum(II) intermediate in the exchange reaction [11,13], although the choice of the solvent could also be a factor [13]. Our ^1H NMR spectra are, however, not sufficiently resolved to indicate an AA′BB′ pattern for the allylic protons [14]. Generally, the two *syn*-protons appear as a broad resonance in the region δ 4.1 to 4.4 ppm. Because of the proximity of the *anti*-protons to the metal centre [15], they resonate at higher field (δ 2.4 to 3.0 ppm) and are coupled to both phosphorus (^3J(PH) 8—9 Hz) and platinum nuclei (^2J(PtH) ~40 Hz). The vinylic proton normally appears at around δ 6 ppm, except in IIc, in which it resonates at δ 7.22 ppm. This low field shift could be due to anisotropic shielding caused by the geminal phenyl ring. The vinylic proton is also coupled to platinum (J(PtH) ~8—14 Hz). This coupling constant is much smaller than those reported for olefinic complexes [16] so that the C=C bond of the vinylic group cannot be coordinated to platinum. Whether there is an isomerization of the vinylic double bond during insertion is difficult to determine except for IIe, where the magnitude of the ^5J(FF) value allows a possible determination of the arrangement of the olefinic substituents. For IIe, the ^{19}F NMR spectrum shows two unsymmetrical resonances at δ −59.48 and −58.63 ppm. An isomer with a *cis* arrangement of the two CF_3 groups can be detected (^5J(FF) 11 Hz). However, because the signals are unsymmetrical and broad, it is possible that a minute quantity of the *trans* isomer is also present.

Although reaction 5 works well in acetone, the same reaction in methanol with the platinum complex containing the more electron-withdrawing vinylic group, $CF_3C{=}CH(CF_3)$, resulted in the isolation of a metallocyclic product *cis*-$[Pt(PEt_3)_2(C_4F_6HC_3H_4MeOH)]PF_6$ in high yield (81%). The presence of the CF_3 groups on the vinylic ligand may well be sufficient to increase the electrophilicity of the complex and thus enhance the induced carbonium character of the coordinated allene, resulting in methoxide attack. The characterization and crystal structure of this complex will be reported elsewhere.

Reactions with acetylenes

The reaction between $CF_3C{\equiv}CCF_3$ (C_4F_6) and I ($R^1 = R^2 = CH_3$, X = acetone) afford III in high yield (eq. 6). The formation of *trans*-IIIa or *cis*-IIIb depends on the reaction conditions, with high reaction temperature favouring the thermodynamically more stable *trans* isomer. At room temperature, IIIb was the major product (IIIb/IIIa ~4/1). IIIa can be more conveniently prepared by allowing the reaction to proceed at room temperature and then warming the reaction mixture to 55°C for 1 h before quenching the reaction with sodium chloride.



(6)

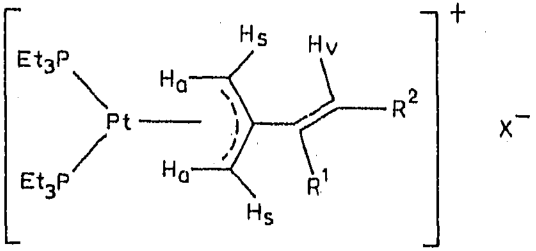
(IIIa) *trans*, $R^1 = R^2 = CH_3, R^3 = CF_3$
(IIIb) *cis*, $R^1 = R^2 = CH_3, R^3 = CF_3$
(IVa) *trans*, $R^1 = CH_3, R^2 = Cy, R^3 = CF_3$
(IVb) *cis*, $R^1 = CH_3, R^2 = Cy, R^3 = CF_3$
(Va) *trans*, $R^1 = R^2 = CH_3, R^3 = COOCH_3$

In the ^{1}H NMR spectrum of IIIb (Table 2), the $PCH_2\underline{CH_3}$ protons exhibit two sets of quintets with the characteristic 1/2/2/2/1 pattern of two *cis*-PEt_3 groups. The two sets of resonances possibly arise from the difference in chemical shifts of the 2 $PCH_2\underline{CH_3}$ groups because of the difference in *trans* influences of the Cl and σ-butadienyl ligands in IIIb. The two CH_3 groups appear at δ 1.61 and 1.88 ppm. The higher field signal is a doublet (J = 7 Hz) which collapses into a broad

(continued on p. 270)

TABLE 1

NMR data (δ, ppm ; J, Hz)[a] of

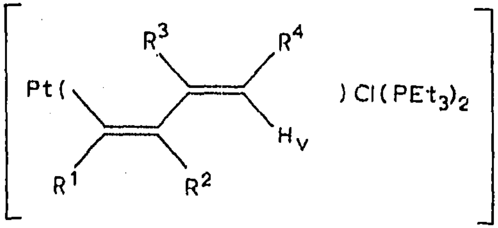


Compound	R^1	R^2	X	NMR data						
				H_a	H_s	H_v	R^1	R^2	$PC\underline{H}_2CH_3$	$PCH_2C\underline{H}_3$
IIa	CH_3	CH_3	PF_6	2.43td ^2J(PtH) 43.2 ^3J(PH) 8.8	4.20(br)	6.28qq ^4J(PtH) 13.4 ^3J(HH) 6.8 ^4J(HH) 1.2	1.62m	1.77dq ^3J(HH) 6.8 ^4J(HH) 0.9	2.1m	1.10qu
IIb	CH_3	Cy	PF_6	2.42td ^2J(PtH) 42.4 ^3J(PH) 9.2	4.18(br)	5.94tdd ^4J(PtH) 13.6 ^3J(HH) 9.2 ^4J(HH) 1.3	1.63td ^4J(PtH) 5.6 ^4J(HH) 1.3	~1.6(br)	2.07m	1.06qu
IIc	CH_3	Ph	NO_3	2.66td ^2J(PtH) 42.0 ^3J(PH) 8.7	4.40(br)	7.22t ^4J(PtH) 12.5 ^4J(HH) NR	1.87td ^4J(PtH) 6.0 ^4J(HH) 1.3	~7.48m	2.15m	1.10qu
IId	$COOCH_3$	$COOCH_3$	PF_6	2.69td ^2J(PtH) 41.8 ^3J(PH) 8.0	4.21(br)	6.36t ^4J(PtH) 14.4	3.80	3.76(br)	2.06m	1.07qu
IIe	CF_3	CF_3	PF_6	2.96td ^2J(PtH) 39.8 ^3J(PH) 8.0	4.13(br)	6.06qt ^3J(FH) 8.1 ^4J(PtH) 8.1	−59.48 ^5J(FF) 11 ^4J(PtF) 10	−58.63 ^3J(FH) 8.5 ^5J(PtF) 6.5	2.10m	1.08qu

[a] d, doublet; t, triplet; q, quartet; qu, quintet; m, multiplet; (br), broad; NR, not resolved.

TABLE 2

NMR data of (δ, ppm ; J, Hz) of



Compound	Configuration at Pt	R^1,R^2	R^3	R^4	NMR data				
					H_v	R^1	R^2	R^3	R^4
IIIa	*trans*	CF_3	CH_3	CH_3	6.28q ^3J(HH) 7	48.79tq ^3J(PtF) 166 ^5J(FF) 16.5	56.81q	1.96(br)	1.67d(br)
IIIb	*cis*	CF_3	CH_3	CH_3	6.28qq ^3J(HH) 7.0 ^4J(HH) 1.4	—47.61tqd ^3J(PtF) 109 ^5J(FF) 16.5 ^4J(PF) 8.5	—57.63q	1.88(br)	1.61d(br)
IVa	*trans*	CF_3	CH_3	Cy	5.60d ^3J(HH) 8.4	—48.83tq ^3J(PtF) 158.8 ^5J(FF) 16.0	—56.78q ^4J(PtF) 4.6	2.04	~1.7
IVb	*cis*	CF_3	CH_3	Cy	5.70d ^3J(HH) 8.4	—47.50tqd ^3J(PtF) 107.3 ^5J(FF) 16.2 ^4J(PF) 8.7	—58.08q	2.03	~1.7
Va	*trans*	$COOCH_3$	CH_3	CH_3	6.75q ^3J(HH) 6.6	3.74s	3.72s	1.90(br)	1.68d(br)

singlet on irradiation of the vinylic proton; no coupling between the two CH_3 groups can be resolved. The resonance for the vinylic proton consists of a quartet of quartets (^3J(HH) 7.0 Hz, ^4J(HH) 1.4 Hz) centred at δ 6.28 ppm. A simple decoupling experiment with irradiation of the two CH_3 signals reduces the quartet into a broad singlet; there is therefore very little or no coupling with the Pt or P nuclei. The normal position of the vinylic proton resonance is in contrast with that of $Pd(PPh_3)_2(DMA_2H)Br$ ($\delta(H_v)$ 8.54 ppm) the crystal structure of which shows that the vinylic hydrogen occupies the fifth coordination site on the metal at a distance rather less than the sum of the Van der Waals radii [3]. Hence, in the platinum compound, neither the double bond nor the vinylic proton has any interaction with the metal centre. In the ^{19}F NMR spectrum, the CF_3 signal at lower field (δ —48.79 ppm from $CFCl_3$) consists of the characteristic triplet of quartet of doublets due to coupling with the ^{195}Pt nucleus, with the other CF_3 groups and with the phosphorus atom *trans* to the σ-butadienyl group. The other CF_3 group causes a resonance at δ —57.63 ppm as a simple quartet with no coupling to the CH_3 group or the vinylic proton. The large ^5J(FF) value of 16.5 Hz implies that the two CF_3 groups are *cis* to each other. The NMR data are, therefore, consistent with the conclusion that the C_4F_6 molecule inserts into the Pt—vinyl bond. It is, however, impossible to tell from these data whether isomerization about the double bond of the $CH_3C{=}CH(CH_3)$ unit has occurred.

The ^1H and ^{19}F NMR spectra of the *trans* isomer IIIa are similar to those of IIIb, except of course for the 1/4/6/4/1 pattern of the PCH_2CH_3 group and the absence of a large ^4J(PF) coupling in the ^{19}F NMR spectrum.

C_4F_6 also reacts with I ($R^1 = CH_3$, R^2 = Cy, X = acetone) to give the insertion products IVa and IVb. The resonances of the vinylic protons of IIIa and IVb appear as broad doublets at δ 5.60 and 5.70 ppm, respectively, with no observable Pt or P coupling. That the C_4F_6 cleaves the platinum—vinyl bond is evidenced by the large value of ^3J(Pt—F) for the α-CF_3 group. Again, the two CF_3 groups are *cis* to each other (^5J(FF) 16 Hz).

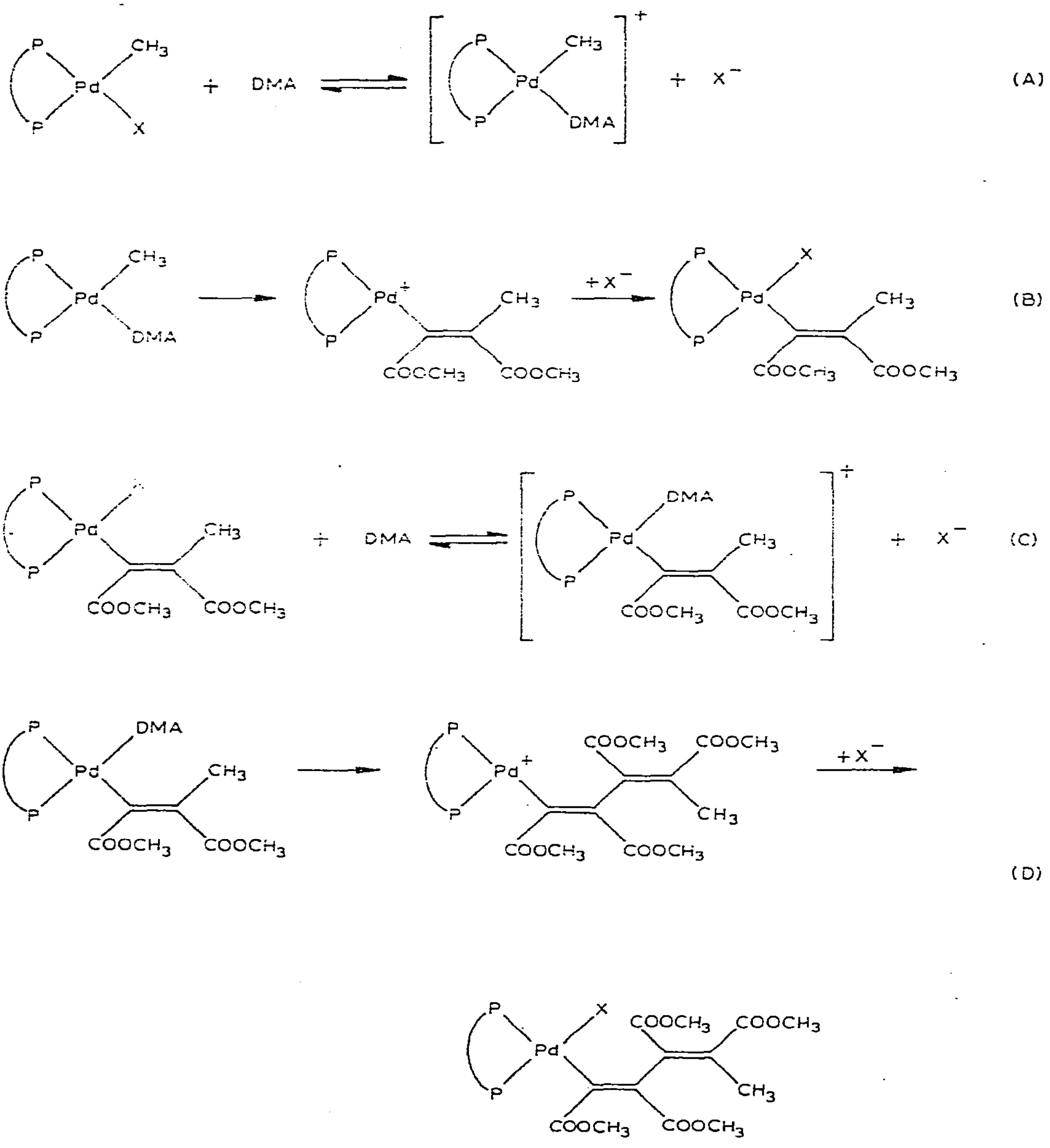
The reaction of DMA with I ($R^1 = R^2 = CH_3$, X = acetone or $R^1 = CH_3$, R^2 = Cy, X = acetone) in acetone, however, does not afford V and the reaction mixture exhibits complicated $COOCH_3$ signals in the ^1H NMR spectrum. Elution of the reaction mixture with ether through a florisil column (after quenching with NaCl) yields complex X. The structure *trans*-$Pt[CH_3OOCC{=}C(OH)COOCH_3]Cl(PEt_3)_2$, was assigned to X based on the following spectroscopic data. The IR spectrum of X in nujol shows two strong bands at 1697 and 1711 cm^{-1} which are assigned to ν(CO) of two non-coordinated ester groups. The medium intensity band at 1608 cm^{-1} is assigned to ν(C=C). In addition, there is also a broad signal at 3400 cm^{-1} and a weaker sharp band at 3574 cm^{-1}. These two signals are shifted to 2520 and 2670 cm^{-1} respectively after X is recrystallized from MeOD. They are therefore assigned as ν(OH).

The ^1H NMR spectrum of X exhibits the characteristic pattern for a platinum(II) complex with two triethylphosphine groups arranged in a *trans* manner. There are two peaks at δ 3.84 (3H) and 3.78 ppm (3H) assignable to $COOCH_3$ groups, with the high field signal coupled to Pt (J(PtH) 3.4 Hz). The resonance at δ 5.56 ppm (1H) shows a coupling constant with Pt of 4.8 Hz. This signal disappears after the complex has been recrystallized from MeOD, therefore it is assigned as an OH group.

The mass spectrum of X contains a parent ion 626 (calcd. 626) and fragmentation occurs by loss of Cl, $CH_3OOCC{=}C(OH)COOCH_3$ and PEt_3, so that $Pt(PEt_3)_2[CH_3OOCC{=}C(OH)COOCH_3]^+$, $Pt(PEt_3)_2Cl^+$ and $Pt(PEt_3)Cl[COOCH_3C{=}C(OH)COOCH_3]^+$ are observed. Elemental analytical data also agreed with the proposed structure.

Compound Va can, however, be prepared in reasonable yield by treating I ($R^1 = R^2 = CH_3$, X = acetone) with DMA in chloroform. The ^1H NMR spectrum of the product shows that the insertion of the DMA molecule occurs at the platinum—vinyl bond. The vinylic proton resonance is at δ 6.75 ppm and appears as

SCHEME 1. Reaction of $Pd(CH_3)X(Diphos)$ with DMA.

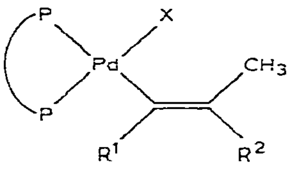


a broad quartet because of the coupling to the geminal CH_3 group ($^3J(HH)$ 6.6 Hz). The two $COOCH_3$ resonances appear very close to each other at δ 3.74 and 3.72 ppm. The two CH_3 resonances are observed at δ 1.90 and 1.68 ppm with the high field one split into a doublet due to coupling with the vinylic proton. Because of the small coupling between the CH_3 groups, it is impossible to tell whether there is isomerization about the original double bond, nor is it possible to assign the geometry of the $CH_3OOCC{=}CR(COOCH_3)$ group. However, by analogy with the C_4F_6 insertion reactions, it is reasonable to assume that the two carbomethoxy groups are *cis* to each other.

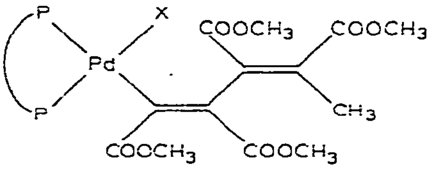
The reaction of DMA with $Pd(CH_3)X(Diphos)$, VI, (VIa, X = Cl; VIb, X = NO_3; VIc, X = solvent as PF_6^- salt) in CH_2Cl_2 yields the mono- or bis-insertion products depending on the nature of X and the amount of acetylene used. When X = NO_3 or solvent, only the mono-insertion product is formed provided that one equivalent of acetylene is used. However, when X = Cl, both the mono- and bis-insertion products are produced even in the presence of only one equivalent of acetylene. This seems to suggest that the displacement of X by acetylene from the methylpalladium complex plays an important role in the reaction. Presumably, when X = NO_3, or solvent, the displacement of X occurs readily so that the rate-

TABLE 3

NMR DATA OF PALLADIUM INSERTION PRODUCTS (δ, ppm; *J*, Hz)



(VIIb) $R^1 = R^2 = COOCH_3$, X = NO_3
(VIIc) $R^1 = R^2 = COOCH_3$, X = PPh_3, as PF_6^- salt
(VIIIa) $R^1 = R^2 = CF_3$, X = Cl



(IXa) X = Cl
(IXb) X = NO_3
(IXc) X = PPh_3, as PF_6^- salt

Compound	NMR data		
	CH_3	$COOCH_3(CF_3)$	PCH_2CH_2P
VIIb	1.80	3.39, 3.42	2.40(br)
VIIc	0.96	2.89, 3.32	2.24(br)
VIIIa	1.56	−59.06(F(1)), −47.41(F(2))	~2.3(br)
	J(HF(1) 1.8	*J*(F(1)F(2) 13.6 *J*(F(1)P) 13.6 *J*(F(2)P) 2.0 *J*(HF(1) 1.8	
IXa	δ = 1.44	3.07, 3.54, 3.56, 3.69	2.45(br)
IXb	δ = 1.56	3.11, 3.40, 3.49, 3.69	2.40(br)
IXc	δ = 0.67	2.92, 3.22, 3.52, 3.69	2.30(br)

determining step is likely to be the actual insertion reaction. Thus the formation of mono- and bis-insertion products depends on the relative rates of steps B and D in Scheme 1. Since the palladium—methyl bond is weaker than the palladium—vinyl bond, step B predominates, resulting in the formation of the mono-insertion product. When X = Cl, however, the relative rates of the displacement of Cl (A and C) and the actual insertion (B and D) may be comparable. The displacement of the anion Cl^- then becomes more important so that there is less distinction between reaction B and D, consequently both mono- and bis-insertion products are obtained.

Further addition of DMA into a CH_2Cl_2 solution of VI, however, does not yield the expected tris-insertion product; only the bis-insertion product is detected.

The cationic insertion products (X = solvent) are isolable as PPh_3 adducts (VIIc, IXc). The ^1H NMR spectrum of VII (Table 3) shows only two peaks in the $COOCH_3$ region, while that of IX exhibits four distinct peaks. Since their chemical shifts are quite variable, it is difficult to assign these resonances unambiguously.

C_4F_6 also reacts with VI (X = Cl) to give only the mono-inserted product, VIII. The ^{19}F NMR spectrum has only two resonances corresponding to two CF_3 groups, with a mutual coupling constant of 13.6 Hz; they are therefore *cis* to each other.

Discussion

The present results show that reaction 3 can be extended to vinylic complexes. When Un = allene, a π-allylic complex is formed; when Un = acetylene, a σ-butadienyl complex is produced, the formation of which occurs by insertion of the acetylene into the metal—vinyl bond rather than the cleavage of the C—H bond in the vinylic moiety as has been observed for ruthenium complexes [7].

As for the reactions of allene and acetylenes with hydrido- and methyl-platinum derivatives, the reactions with the vinylic complexes are sensitive to the type of ligand present. When X = Cl, I is inactive towards both allene and acetylene; with X = NO_3, I ($R^1 = CH_3$, R^2 = Ph) reacts with allene, but the reactions proceeds much more slowly than with the corresponding cationic complex (X = acetone). For the more reactive palladium complex (VI) a second insertion reaction with DMA is possible even for the chloro complex; in fact the presence of the chloride ligand makes the reaction of the vinylpalladium complex comparable to that of the methyl complex making the isolation of the mono-insertion product difficult. Even with the more reactive palladium complexes, we have no evidence for the formation of a tris-inserted product. This may be attributed to both the electronic and the steric hindrance of the σ-butadienyl group.

When reaction 6 is carried out in acetone, both the *trans* and the thermodynamically less stable *cis* isomers can be isolated. This is in accordance with the earlier observation [17] that the *cis* isomer is the kinetically controlled product in this type of insertion reaction. All the available evidence shows that the substituents R^3 of the incoming acetylene remain *cis* in the resulting σ-butadienyl products. The geometry of the second double bond is difficult to determine. The only case in which a determination is possible is in IIe, where the majority of the product has *cis*-CF_3 groups, with the original geometry retained.

Although Maitlis observed Pd—H interaction in $Pd(PPh_3)_2(DMA_2H)Br$ [3], we find no interactions between the platinum atom and either the vinylic proton or the olefinic double bond in all of our σ-butadienyl complexes. This is probably a consequence of the greater reluctance of platinum towards achieving pentacoordination [18].

It has been found that the reactions of acetylenes with methylplatinum complexes depend very much on the type of acetylenes used and on the reaction conditions, such as the choice of solvents and the presence of other nucleophiles [9]. Insertions of acetylenes into methyl—platinum bonds are only possible for highly activated acetylenes such as C_4F_6 [19,20] and DMA [20,21], while reactions with non-activated or less-activated acetylenes lead only to the formation of π-acetylene complexes or their subsequent reaction products such as alkoxycarbenes or vinyl ether derivatives (in the presence of alkoxy-nucleophile) [9]. Similarly, the formation of σ-butadienyl complexes can be achieved only in reactions of the vinylic complexes with strongly-activated acetylenes. Thus in reaction 4 ($R^1 = R^2 = CH_3$, X = acetone), only the mono-inserted product can be isolated (as the chloro complex) even with excess 2-butyne [10]. Interestingly, reaction 4 ($R^1 = R^2 = CF_3$, X = acetone) also leads to the isolation of the mono-inserted product, whereas reaction 6 ($R^1 = R^2 = CH_3$, $R^3 = CF_3$) proceeds smoothly to give III in high yield. It therefore, appears that electron-withdrawing groups on the vinylic ligand have a stabilizing effect on the complex and tend to inhibit further reaction. On the other hand, when they are present in the incoming acetylene, they can provide an additional driving force for the reaction. The formation of a bis-inserted product between DMA and $Pd(CH_3)X$(Diphos) is probably due to the greater reactivity of the palladium complexes as compared with the platinum analogs. The effect of electron-withdrawing groups on the reactivity of metal—vinyl bonds towards cleavage by acids has been described previously [4b]. Thus, $Pt(HC{=}CClH)X(PPh_2Me)_2$ is readily cleaved by HCl, while the reaction with $Pt(ClC{=}CCl_2)X(PPh_2Me)_2$ only leads to the formation of the oxidative addition product with the platinum—vinyl bond still intact.

Also, as for the platinum—alkyl compounds, platinum—vinyl derivatives undergo reactions with acetylenes to yield either the insertion or nucleophilic attack product. With the stronger platinum—vinyl bond the insertion reaction is energetically less favorable, while nucleophilic attack is made easier by the electronic-withdrawing property of the vinylic ligand. The formation of $Pt(DMA\text{-}OH)Cl(PEt_3)_2$ in the reaction of DMA with I ($R^1 = R^2 = CH_3$; or $R^1 = CH_3$, R^2 = Cy) in acetone could be attributed to the nucleophilic attack of traces of H_2O on the coordinated DMA. One possible mechanism is depicted in Scheme 2.

Further support of the mechanism comes from the detection of the olefinic product. Vacuum distillation of the reaction mixture of DMA and I ($R^1 = CH_3$, R^2 = Cy, X = PF_6) at 60°C affords a distillate, the NMR and mass spectra of which show the presence of $CH_3CH{=}CHCy$.

In view of the reluctance of phosphinevinyl-platinum and -palladium complexes to undergo insertion reactions, it seems unlikely that the oligomerization of acetylenes proceed via stepwise insertion (as those observed for non-phosphine containing palladium complexes [3]). Other mechanisms such as ionic polymerization [22] may seem more probable.

SCHEME 2. Possible mechanism for the formation of *trans*-Pt[CH$_3$OOCC=C(OH)COOCH$_3$]Cl(PEt$_3$)$_2$.

$$\mathrm{Pt(R^1C{=}CHR^2)(PEt_3)_2(acetone)^+ + DMA}$$
$$\downarrow$$
$$\mathrm{Pt(R^1C{=}CHR^2)(PEt_3)_2(DMA)^+ + acetone}$$
$$\downarrow \mathrm{OH^-}$$
$$\mathrm{Pt(R^1C{=}CHR^2)[CH_3OOCC{=}C(OH)(COOCH_3)](PEt_3)_2}$$
$$\downarrow \mathrm{H^+}$$
$$\mathrm{Pt[CH_3OOCH{=}C(OH)(COOCH_3)](PEt_3)_2^+ + R^1HC{=}CHR^2}$$
$$\downarrow \mathrm{Cl^-}$$
$$\mathrm{Pt[CH_3OOCC{=}C(OH)(COOCH_3)]Cl(PEt_3)_2}$$

Experimental

All reactions were performed with "spectro-analyzed" solvents without further purification. Dimethyl acetylenedicarboxylate was obtained from Aldrich Chemical Company and was purified by distillation under partial vacuum. Hexafluorobut-2-yne was obtained from P.C.R. Inc., and allene from Matheson Co. Inc.; both gaseous compounds were used without further purification. The ^{1}H and ^{19}F NMR spectra were recorded on a Varian HA 100 spectrometer, IR spectra on a Perkin—Elmer grating spectrometer 2, and mass spectra on a Varian M66. Elemental analyses were done by Chemalytics, Inc. and Midwest Microlab Ltd. The results are reported in Table 4.

Alkenylplatinum complexes were prepared by insertion reactions of acetylenes with platinum(II) hydrides as described previously [10].

Preparation of IIa and IIb

To a solution of 117 mg of *trans*-PtHCl(PEt$_3$)$_2$ in ca. 2 ml of acetone, 62 mg of AgPF$_6$ in acetone was added. The solution was then treated with 2 to 3 equivalent of acetylene (CH$_3$C≡CCH$_3$ for IIa, CH$_3$C≡CCy for IIb). The AgCl precipitate was separated by centrifuge. After 30 min allene gas was passed into the solution. After 2 h, the solution was evaporated to dryness and recrystallized in acetone/ether/pentane (IIa, acetone/ether for IIb). Yield 60% of IIa and 65% of IIb.

Preparation of IIc

200 mg of *trans*-Pt(CH$_3$C=CHPh)(NO$_3$)(PEt$_3$)$_2$ was dissolved in 20 ml of methanol. The solution was then saturated with allene. After 17 h, the solution was evaporated to dryness, dissolved in acetone and passed through a short florisil column. Addition of ether to the acetone solution (ca. 1 ml) yielded white crystals of IIc (160 mg, 75%).

Preparation of IId and IIe

To a solution of 145 mg *cis*-Pt(DMAH)Cl(PEt$_3$)$_2$ for IId or 150 mg *cis*-Pt-(C$_4$F$_6$H)Cl(PEt$_3$)$_2$ for IIe in 10 ml of acetone was added an acetone solution of AgPF$_6$ (60 mg). The AgCl precipitate was separated by centrifuge, the solution

TABLE 4

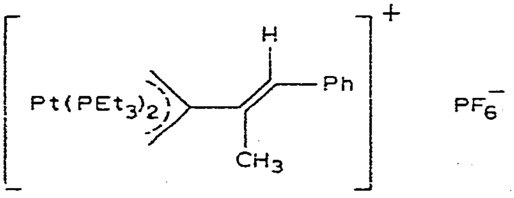
ANALYTICAL DATA OF THE COMPOUNDS OBTAINED

Compound	Elemental analysis (Found (calcd.) (%))			M.p. (°C)	Yield (%)
	C	H	X		
IIa	34.25	6.37	17.27(F)	129—132	60
	(33.98)	(6.15)	(16.97)		
IIb	39.70	6.87		111—112	65
	(38.97)	(6.68)			
IIc	44.48	6.88		103—105	75
	(44.30)	(6.66)			
IId	33.83	5.71		122—123	72
	(33.21)	(5.44)			
IIe	29.52	4.49		193—195	78
	(29.28)	(4.52)			
IIIb	35.22	5.27		152—154	70
	(35.12)	(5.45)			
IVa	40.43	6.13		98.5—100	65
	(39.92)	(6.03)			
IVb	40.01	6.19		150—152	15
	(39.92)	(6.03)			
Va	39.66	6.32		101—106	40
	(39.79)	(6.53)			
VIIb	54.82	4.44		98—100	75
	(54.75)	(4.59)		(dec.)	
VIIc	57.23	4.40		140—141	80
	(57.29)	(4.53)		(dec.)	
VIIIa	51.97	3.71		198—200	65
	(51.91)	(3.79)		(dec.)	
IXa	56.78	4.51		124—127	69
	(55.80)	(4.68)		(dec.)	
IXb	54.10	4.56		170—171	70
	(54.08)	(4.54)		(dec.)	
IXc	56.60	4.31		130—131	70
	(56.52)	(4.49)		(dec.)	
X	34.93	6.10	5.64(Cl)	158—160	50
	(34.54)	(5.96)	(5.66)		

was then saturated with allene and maintained at a slight positive pressure of allene throughout the reaction. After 5 h, the reaction mixture was filtered, evaporated to dryness under vacuo and recrystallized in MeOH/ether to give 130 mg of IId (72%) or in acetone/ether for IIe (Yield 145 mg, 78%).

Reaction of trans-Pt($CH_3C{=}CHPh$)(PEt_3)$_2$(acetone)$^+$ PF_6^- with allene

Allene gas was passed into a solution of *trans*-Pt($CH_3C{=}CHPh$)(PEt_3)$_2$(acetone)$^+$ PF_6^- (prepared by treating 150 mg of *trans*-Pt($CH_3C{=}CHPh$)Cl(PEt_3)$_2$ with 1 equivalent of $AgPF_6$). After 90 min the solution was evaporated to dryness and recrystallized from MeOH/ether to yield 120 mg (74%, m.p. 136—138°C) of:



Reaction of allene with trans-Pt(C_4H_7)Cl(PEt_3)$_2$

A solution of 70 mg of *trans*-Pt(C_4H_7)Cl(PEt_3)$_2$ in 10 ml of methanol was saturated with allene. After 15 h, the solution was evaporated to dryness. The NMR spectrum in $CDCl_3$ showed the *trans*-Pt(C_4H_7)Cl(PEt_3)$_2$ had undergone no reaction.

Preparation of III

234 mg of *trans*-PtHCl(PEt_3)$_2$ and 100 μl 2-butyne were dissolved in 12 ml of acetone. 126 mg of $AgPF_6$ in 3 ml acetone was added dropwise. The AgCl precipitate was separated by centrifuge. The liquid was warmed to drive off the excess 2-butyne. Acetone was added so that the total volume of the solution was ca. 30 ml. The solution was then saturated with C_4F_6 and left overnight. The reaction mixture was evaporated to dryness under vacuo and quenched with NaCl in aqueous methanol. After evaporation, the product was extracted with CH_2Cl_2, passed through florisil and recrystallized in methanol, yielding 230 mg of IIIb (70%).

IIIa was prepared by a similar method but the reaction mixture was warmed to 55°C for 1 h before quenching with NaCl. The complex was recrystallized from hexane.

Preparation of IV

The same procedure, except that the stoichiometric amount of $CH_3C{\equiv}CCy$ replaced 2-butyne, was employed. After quenching with NaCl and extraction with CH_2Cl_2, the extract was evaporated and recrystallized in ether/hexane yielding 58 mg (15%) of the *cis* product IIIb. The filtrate was evaporated and recrystallized in methanol to give 240 mg of the *trans* isomer IIIa (65%).

Preparation of Va

234 mg of *trans*-PtHCl(PEt_3)$_2$ was allowed to react with 100 μl of $CH_3C{\equiv}CCH_3$ and 125 mg $AgPF_6$ in acetone. After separation of the AgCl, the solution was evaporated to dryness to give a light yellow oil which was then dissolved in $CDCl_3$ and 70 μl of DMA was introduced. After 1 h, the solution was quenched with NaCl in aqueous methanol. After removal of the solvent, the residue was passed through a florisil column, in ether, and then recrystallized from hexane. Yield 120 mg (40% based on *trans*-PtHCl(PEt_3)$_2$).

Preparation of VIa

To 2.10 g of Pd(CH_3)Cl(PEt_3)$_2$ in 20 ml of dichloromethane was added a solution of 2.12 g of Diphos (1,2-bis(diphenylphosphino)ethane) in 5 ml of dichloromethane. The resulting pale-yellow solution which smelled strongly of triethylphosphine was stirred for half an hour. The solvent was removed to give a sticky off-white oil. Triethylphosphine was removed from this oil by heating to 80°C for 48 h while maintaining a vacuum with a rotatory pump. The resulting fluffy white solid was recrystallized from dichloromethane/ether to give white crystals in 75% yield, m.p. 186—188°C, dec. ^{1}H NMR: $\delta(CH_3)$ 9.27 (dd), $\delta(CH_2)$ 7.74(t) ppm.

Preparation of VIb

To a suspension of 300 mg of VIa in 20 ml of acetone was added one equivalent of silver nitrate in 2 ml of water. The resulting pale-yellow solution was filtered and the filtrate evaporated to dryness to give the nitrate as a white powder (yield 95%).

Preparation of mono-insertion palladium complexes

(i) VIIb: 250 mg of $Pd(CH_3)(NO_3)$(Diphos) (VIb) and one equivalent of DMA in 10 ml of acetone or CH_2Cl_2 were stirred for 30 min at room temperature. On addition of ether, off-white crystals of VIIb precipitated in 75% yield.

(ii) VIIc: To a suspension of VIa in 20 ml of THF at −30°C under nitrogen, was was added one equivalent of $AgPF_6$ in 10 ml of THF. An immediate precipitate of AgCl was noticed. The mixture was filtered under nitrogen through a cold frit containing celite to give a pale-yellow solution. The solution was warmed to 10°C and one equivalent of DMA added. After 10 min one equivalent of triphenylphosphine was added and the volume of the solution was taken down to 10 ml. Addition of ether gave white microcrystals of VIIc in 80% yield.

(iii) VIIIa: Two equivalents of C_4F_6 were condensed into a thick-walled Carius tube containing a solution of 300 mg of VIa in 10 ml of CH_2Cl_2. The tube was sealed and placed in a hot water bath at 80°C. After 3 h, the tube was cooled, opened and the contents filtered. Removal of the solvent followed by recrystallization from CH_2Cl_2/ether gave white crystals of VIIa in 65% yield.

Preparation of di-insertion palladium complexes

(i) IXa: 250 mg of VIa and two equivalents of DMA in 5 ml of CH_2Cl_2 were placed in a thick-walled Carius tube. The sealed tube was heated to 80°C for 3 h. White crystals of IXa precipitated out on addition of ether in 69% yield.

(ii) IXb: 250 mg of VIb and two equivalents of DMA in 10 ml of CH_2Cl_2 were stirred for 8 h. Addition of ether gave white crystals of IXb in 70% yield.

(iii) IXc: The solvated cation was prepared as for VIIc and two equivalents of DMA were added. The solution was stirred for 15 min at −10°C and then at 20°C for a further 15 min. Addition of one equivalent of triphenylphosphine followed by the addition of ether gave IXc in 70% yield as white crystals.

Reaction of VIa with DMA

(i) At room temperature. 200 mg of VIa and one equivalent of DMA were stirred in 5 ml of CH_2Cl_2 for 12 h at room temperature. The ^1H NMR spectrum showed only unreacted starting materials.

(ii) At 80°C. 100 mg of VIa and one equivalent of DMA in 0.5 ml of CD_2Cl_2 were placed in a sealed NMR tube. The reaction mixture was heated to 80°C and the ^1H NMR spectrum monitored periodically. After 30 min peaks due to the starting compounds and the di-insertion product were present as well as peaks at δ 1.17, 3.45, 3.49 ppm ascribable to the mono-inserted species. After 3 h the resonances of free DMA had disappeared completely and only those of the mono- and di-inserted product remained.

Preparation of X

200 mg of *trans*-$Pt(C_4H_7)Cl(PEt_3)_2$ were treated with 1 equivalent of $AgPF_6$ in 3 ml of acetone. The AgCl precipitate was separated by centrifuge and one equivalent of DMA was added. After 2 h the reaction was quenched by the addi-

tion of NaCl in aqueous methanol. The reaction mixture was then evaporated to dryness, extracted with CH_2Cl_2 and then eluted through a florisil column in ether. Recrystallization from ether/hexane yield light yellow crystals of X (120 mg).

The use of $Pt(PEt_3)_2(CH_3C{=}CHCy)Cl$ gave the same complex.

Identification of the organic product in the reaction of trans-$Pt(CH_3C{=}CHCy)(PEt_3)_2(acetone)^+PF_6^-$ *with DMA in acetone*

300 mg of *trans*-$Pt(CH_3C{=}CHCy)Cl(PEt_3)_2$ were treated with 1 equivalent of $AgPF_6$ in 3 ml of acetone. The AgCl was separated by centrifugation and the volume of the reaction was reduced to about 0.5 ml by distillation under partial vacuum. 50 μl of DMA was then introduced. After 3 h, the organic portion was separated by distillation at 70°C, 0.3 mmHg. The mass spectrum of the distillate shows the presence of peaks at 124 (M^+, $CH_3CH{=}CHCy$), 109 ($M - CH_3^+$) and 41 ($M - Cy^+$).

For NMR study, CD_3COCD_3 was used as the reaction medium and the spectrum was measured in $CDCl_3$: δ 5.30 m, ~1.60 (br) m, ~1.30 (br) ppm.

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