The Formation of Alkenylplatinum(II) Complexes by Protonation of Platinum(0)–Acetylene Complexes

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Summary In the protonation of acetylene–platinum(0) complexes of type $Pt(ac)(PPh_3)_2$ to give alkenylplatinum(II) complexes, *trans*-$PtX(alkenyl)(PPh_3)_2$, the platinum and the added proton are mutually *cis* on the alkenyl double bond.

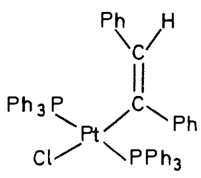
RECENTLY it has been reported that the platinum(0)–diphenylacetylene complex $Pt(PhC{\vdots}CPh)(PPh_3)_2$ reacts with HCl to give the alkenylplatinum(II) complex, $PtCl(CPh{:}CHPh)(PPh_3)_2$, which was given the stereochemistry (I), with the hydrogen *trans* to platinum.[1] We have also studied the protonation of acetylene–platinum(0) complexes of the type $Pt(ac)(PPh_3)_2$ and find it to be an excellent route to some alkenylplatinum(II) complexes of the type $PtX(alkenyl)(PPh_3)_2$, ($X = Cl$ or CF_3CO_2). However, we find that the protonation of the acetylene is *cis* with respect to the platinum, not *trans*; thus from $Pt(PhC{\vdots}CPh)(PPh_3)_2$ and CF_3CO_2H the product, $Pt(OCOCF_3)(CPh{:}CHPh)(PPh_3)_2$, has the stereochemistry (II; $R^1 = R^2 = Ph$, $R^3 = H$). We have assigned the stereochemistry of this and other alkenylplatinum complexes from their ^1H n.m.r. spectra. A key compound for the assignments is $PtBr(CH{:}CH_2)(PPh_3)_2$, prepared from $Pt(PPh_3)_3$ and vinyl bromide. At 90 MHz this compound gives a first-order pattern for the vinyl resonance (with platinum satellites);

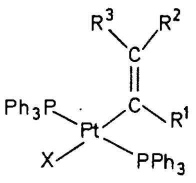
values of J_{HH} are given in the Table. The assignments have been made assuming the relative values J decrease in the order $J^{trans}_{HH} > J^{cis}_{HH} > J^{gem}_{HH}$ (neglecting signs). As can be seen from the Table, values of J_{PtH} parallel those of J_{HH} and are very useful in assigning stereochemistry. We find the following ranges of values for J_{PtH}: *trans*, 122—148 Hz (6 values); *cis*, 63—80 Hz (11 values); *gem*, 8 Hz (1 value only). Our assumptions on the relative values of J_{HH} are almost certainly correct since the ^1H n.m.r. spectra of a very large number of vinyl compounds have been analysed and invariably $J^{trans}_{HH} > J^{cis}_{HH} > J^{gem}_{HH}$.[2] Thus, for Pb(CH:CH$_2$)$_4$ the values are $J^{trans}_{HH} = 19{\cdot}569$, $J^{cis}_{HH} = 12{\cdot}127$, and $J^{gem}_{HH} = 2{\cdot}024$ Hz.[3]

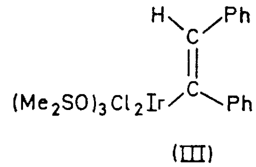
^1H *n.m.r data for complexes of type trans*-PtX(alkenyl)(PPh$_3$)$_2$. *Measured at* 90 *MHz in* CDCl$_3$. *Alkenyl protons numbered as in* (II).

Alkenyl	X	τ_1	τ_2	τ_3	$J_{1,2}$	$J_{2,3}$	$J_{1,3}$	$J_{Pt,1}$	$J_{Pt,2}$	$J_{Pt,3}$	Other τ- and J-values
CH:CH$_2$	Br	3·75	4·79	5·74	10·2	17·75	1·4	8·0	148	78	
CPh:CH$_2$	Cl		4·32	5·21			< 1		134	72·4	
”	Br[a]		4·30	5·21			< 1		140	72	
”	I[a]		4·33	5·18			< 1		146·4	76	
”	OCOCF$_3$		4·29	5·30			< 1		122	69	
C(*p*-tol):CH$_2$[c]	Cl		4·38	5·29			< 1		134	72	
CMe:CH$_2$	OCOCF$_3$		4·90	5·48			< 1		120	63	τ_{Me} 9·05, J_{PtMe} 42·5
CEt:CH$_2$	”		4·97	5·42			< 1		121·2	68·4	
CPh:CHPh	”			4·88						80·8	
C(*p*-tol):CH(*p*-tol)	Cl			4·78						75·2	
CMe:CHPh	OCOCF$_3$			b							τ_{Me} 8·96, J_{PtMe} 45·4
CPh:CHMe	”			5·07						77·1	τ_{Me} 8·96, J_{PtMe} 41·6 J_{HMe} 6·8
CH:CHPh	Br	b		4·54		16·8		b		76·4	

[a] Made by metathesis from the chloride. [b] Masked by Ph resonances. [c] *p*-tol = *p*-MeC$_6$H$_4$


(I)


(II)


(III)

When the complexes Pt(ac)(PPh$_3$)$_2$, ac = PhC⋮CPh, or *p*-MeC$_6$H$_4$·C⋮C·C$_6$H$_4$Me-*p* are treated with one mole of HCl or trifluoroacetic acid in diethyl ether or benzene, the alkenyl complexes *trans*-PtX(CR:CHR)(PPh$_3$)$_2$, R = Ph or *p*-tolyl, are formed in high (>85%) yield. The values of J_{PtH} of 75—81 Hz indicate the stereochemistry to be (II; R^1 = R^2 = Ph or *p*-tolyl, R^3 = H), *i.e.*, the proton has added *cis* with respect to the platinum. (With X = Cl and R^1 = R^2 = Ph the resonance of H^3 is obscured by the phenyl resonances). The *trans*-arrangement of the phosphines follows from the occurrence of only one ^{31}P resonance in the ^{31}P n.m.r. spectrum (with satellites).

When Pt(EtC⋮CEt)(PPh$_3$)$_2$ is treated with hydrogen chloride (1 mol.) some of the alkenyl complex PtCl(CEt:CHEt)(PPh$_3$)$_2$ is formed, together with PtCl$_2$(PPh$_3$)$_2$ and some of the unchanged acetylene complex. Pt(MeC⋮CPh)(PPh$_3$)$_2$ reacts with one mole of trifluoroacetic acid in benzene to give an approximately equimolecular mixture of Pt(OCOCF$_3$)(CMe:CHPh)(PPh$_3$)$_2$ and Pt(OCOCF$_3$)(CPh:CHMe)(PPh$_3$)$_2$. Complexes of monoacetylenes; *e.g.* Pt(HC⋮CR)(PPh$_3$)$_2$ (R = Ph or *p*-tolyl) protonate on the unsubstituted carbon atom giving PtX(CR:CH$_2$)(PPh$_3$)$_2$; *i.e.*, Markownikoff addition occurs. Protonation of the complexes Pt(HC⋮CMe)(PPh$_3$)$_2$ or Pt(HC⋮CEt)(PPh$_3$)$_2$ similarly gives the alkenyl complexes PtX(CR:CH$_2$)(PPh$_3$)$_2$ (X = Cl or OCOCF$_3$) but some PtCl$_2$(PPh$_3$)$_2$ is also formed when X = Cl. The complexes with a vinylidine (:CH$_2$) group show two singlets which are only slightly broadened (*i.e.*, $J_{2,3} < 1$ Hz) together with their Pt satellites, with $J_{PtH^2} = 120$—$146{\cdot}4$ Hz and $J_{PtH^3} = 63{\cdot}0$—$76{\cdot}0$ Hz (data in the Table).

DCl in diethyl ether reacts with Pt(*p*-tolC⋮CH)(PPh$_3$)$_2$ to give PtCl{C(*p*-tol):CHD}(PPh$_3$)$_2$ contaminated with PtCl{C(*p*-tol):CH$_2$}(PPh$_3$)$_2$ (presumably moisture in the apparatus converted some DCl into HCl). The ^1H n.m.r. spectrum shows that the deuterium is exclusively *cis* to platinum, *i.e.*, the configuration is (II; R^1 = *p*-tol, R^2 = H, and R^3 = D). There is a small isotope shift of proton H^2; *i.e.*, in the undeuteriated compound it absorbs at τ 4·379 and in the monodeuteride at τ 4·396 but J_{PtH^2} is the same (134·0 Hz) in each case.

Thus, our work shows that the protonation of complexes of type Pt(ac)(PPh$_3$)$_2$ is *cis* with respect to the platinum. Similarly, Pt(CF$_3$C⋮CCF$_3$)(PPh$_3$)$_2$ reacts with hydrogen chloride to give PtCl{C(CF$_3$):CHCF$_3$}(PPh$_3$)$_2$ on which the two CF$_3$ groups were considered to be *cis*.[4] Probably the reactions go *via* protonation of the platinum to give a hydride followed by addition of Pt–H across the coordinated acetylenic bond. From our work, therefore, the observed formation of *trans*-stilbene by treatment of PtCl(CPh:CHPh)(PPh$_3$)$_2$ with HCl implies either that platinum–carbon bond fission goes with inversion of configuration or that *cis*-stilbene is first formed but isomerizes to the more stable *trans*-stilbene. Diphenylacetylene and IrHCl$_2$(Me$_2$SO)$_3$ form an adduct IrCl$_2$(CPh:CHPh)(Me$_2$SO)$_3$ which on subsequent hydrolysis gives *cis*-stilbene.[5] The authors[5] point out that the formation of *cis*-stilbene indicates configuration (III) for the complex only if solvolysis goes with retention of configuration; our work, coupled with that of Tripathy and Roundhill,[1] suggests that this may not be so.

Our results on the stereochemistry of the protonation of co-ordinated acetylenes are in accord with some features of the hydrocarboxylation of acetylenes by tetracarbonylnickel and aqueous acid. Hydrocarboxylation involves the overall *cis*-addition of $H–CO_2H$ to the triple bond; the addition is in the Markownikoff sense; *e.g.*, phenylacetylene gives $CH_2:C(Ph)CO_2H$ and *cis*-protonation of the co-ordinated triple bond is thought to be a key step.[6,7]

trans-β-Bromostyrene reacts with $Pt(PPh_3)_4$ to give *trans*-$PtBr(CH:CHPh)(PPh_3)_2$ in which the *trans*-configuration of the styryl group is retained, as shown by the ^1H n.m.r. data (Table). $PtBr(CH:CHPh)(PPh_3)_2$ of unknown stereochemistry has been reported previously.[8]

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