Stability of the Metal–Carbon–Halogen System. Part I. The Preparation and Properties of Some Platinum(II)- and Palladium(II)-Vinyl Complexes

By **Brian F. G. Johnson** and **Jack Lewis**,* The University Chemical Laboratory, Lensfield Road, Cambridge
J. David Jones and **Keith A. Taylor**, Imperial Chemical Industries Ltd., The Corporate Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire

A number of chlorovinyl complexes of palladium and platinum have been prepared from the reaction of the zerovalent palladium or platinum complexes $[(Ph_3P)_4M]$ with chlorinated olefins such as tetrachloroethylene, trichloroethylene, and dichloroethylene. ^1H N.m.r. spectroscopic studies of the complexes containing PPh_2Me have allowed the stereochemistry of the new compounds to be established. Oxidation of the Pt^{II} complexes with chlorine yields six-co-ordinate vinyl complexes of Pt^{IV}.

THE stability of metal–carbon bonds in transition metal–alkyl complexes is enhanced by replacement of hydrogen by fluorine. The factors involved have been summarised by Nyholm[1] and basically relate to the effect of the greater electronegativity of the fluorine relative to hydrogen on the nature of the metal–carbon bond. Recent work by other groups on the structures of related fluorine and chlorine substituted metallo-carbon systems has led to the suggestion that, on the basis of metal–carbon bond lengths, the relative stability of the metal–carbon bond does not follow the expected order of electronegativity but is M–C–Cl > M–C–F > M–C–H. This observation has obvious impact on the nature of metal–carbon bonds and as part of an extensive investigation of such systems we report here the general

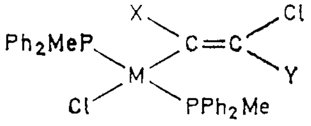
---

[1] R. S. Nyholm, *Quart. Rev.*, 1970, **24**, 1.

chemistry of some platinum(II) and palladium(II)-chlorovinyl derivatives.

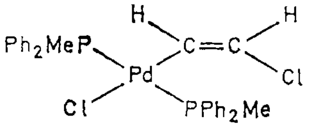
In a preliminary communication[2] we described the reactions of tetrakis(diphenylmethylphosphine)platinum(0) with a range of halogenated olefins. We now report these results in greater detail and present further observations made during the course of this study. The reactivity of zerovalent platinum and palladium complexes of the type [$(Ph_3P)_4M$], where M = Pt and Pd, with chlorinated olefins such as tetrachloroethylene, trichloroethylene, and dichloroethylene to give platinum(II)-chlorovinyl complexes has been reported.[3,4] We find that the complexes containing diphenylmethylphosphine are most convenient to study from a structural viewpoint and a ^1H n.m.r. spectroscopic study of these complexes has established their stereochemistry and has provided information regarding the stereochemical arrangement of the protons on the vinyl group.

Tetrakis(diphenylmethylphosphine)-platinum or -palladium react with the chloro-olefins $Cl_2C{=}CCl_2$, $CHCl{=}CCl_2$, and *trans*-$CHCl{=}CHCl$ in toluene to give the vinyl complexes (I)—(VI) respectively in good yield.



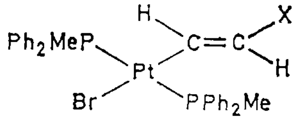
(I) M = Pt, X = Y = Cl
(II) M = Pt, X = Cl, Y = H
(III) M = Pt, X = Y = H
(IV) M = Pd, X = Y = Cl
(V) M = Pd, X = H, Y = Cl
(VI) M = Pd, X = Y = H

Interestingly, no vinyl complex was observed when [$(Ph_2MeP)_4Pt$] was treated with *cis*-1,2-dichloroethylene yet with the zerovalent palladium complex a 40% yield of the chlorovinyl complex (VII) was obtained. Similar observations have been reported previously for the complexes [$(Ph_3P)_4Pt$] and [$(Ph_3P)_4Pd$].[3,4] If zerovalent metal complexes such as [$(Ph_2MeP)_4Pt$] or the co-ordinatively unsaturated species [$(Ph_2MeP)_3Pt$] present in solution,[5] which are electron-rich centres, are regarded as nucleophiles then the reactivity of this nucleophile with *cis*- and *trans*-1,2-dichloroethylene is the reverse of that usually observed. A nucleophile of the type toluene-*p*-thiolate, for example, reacts with the *cis*-isomer of 1,2-dichloroethylene in the presence of base to give *cis*-1,2-bis(*p*-tolylmercapto)ethene, however, no reaction is observed with the *trans* isomer.[6] The presence of a base, ethoxide ions in this case, is a prerequisite for reaction with the nucleophile and suggests that the primary step in the nucleophilic substitution of *cis*-1,2-dichloroethylene involves elimination of hydrogen chloride. The ethoxide ion must initially attack an olefinic hydrogen atom causing elimination which is accompanied by an anionic leaving group (a chloride ion) from the neighbouring carbon atom forming the chloroacetylene ($ClC{\equiv}CH$). The chloroacetylene then adds the nucleophile and a proton to give the product of substitution. As *trans*-elimination of hydrogen chloride is more favourable than *cis*-elimination[7] the observation that no reaction occurs with *trans*-1,2-dichloroethylene is understood. The reaction of *cis*-1,2-dichloroethylene and [$(Ph_2MeP)_4Pt$] was also examined in the presence of a base. In a typical experiment *cis*-1,2-dichloroethylene was treated with [$(Ph_2MeP)_4Pt$] in the presence of ethoxide ions under reflux in ethanol and the ethynyl complex [$(Ph_2MeP)_2PtCl(C{\equiv}CH)$] was produced. The production of this ethynyl complex from *cis*-1,2-dichloroethylene is consistent with the initial formation of chloroacetylene as a prerequisite to nucleophilic substitution of this olefin and establishes that the subsequent reaction with the zerovalent metal nucleophile differs from that of the more conventional organic nucleophiles in that carbon–halogen bond cleavage is favoured rather than addition to the carbon–carbon triple bond.



(VII)

We have observed that both *trans*-1,2-dibromoethylene and vinyl bromide react more readily than the corresponding chloro-olefins with [$(Ph_2MeP)_4Pt$]. *trans*-1,2-Dibromoethylene reacts with [$(Ph_2MeP)_4Pt$] at room temperature to give a 90% yield of the bromovinyl complex (VIII) and vinyl bromide reacts under similar conditions producing a 50% yield of the vinyl complex (IX). In contrast, vinyl chloride did not react with the zerovalent complex even over a prolonged period. This suggests that the increased reactivity of the bromo-olefins can be correlated with the ease of carbon–halogen bond cleavage. In fact, we observed that the bromovinyl complex (VIII) readily decomposes in chloroform to give *cis*-[$(Ph_2MeP)_2PtBr_2$]. The ^1H n.m.r. spectrum of the bromovinyl complex in deuteriochloroform exhibits resonances for the two vinylic protons at τ 3·5 and 5·2 together with the triplet pattern at τ 7·8 associated with the methyl protons of the mutually *trans*-phosphine molecules. After a period of only 30 min the spectrum has changed completely, vinylic proton resonances are no longer evident, and the resonance of the phosphine methyl protons appear as doublets indicating a *cis*-arrangement of the phosphine molecules. In addition, using g.l.c. we identified acetylene as the concomitant organic product of this elimination reaction. The elimination of acetylene from complex (VIII) is also promoted thermally, the bromovinyl complex melts at 148° with a gaseous evolution to give another solid which



(VIII) X = Br
(IX) X = H

---

[2] B. F. G. Johnson, J. Lewis, K. A. Taylor, and J. D. Jones, *J. Organometallic Chem.*, 1971, **32**, C62.

[3] W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1968, 1278.

[4] P. Fitton and J. E. McKeon, *Chem. Comm.*, 1968, 4.

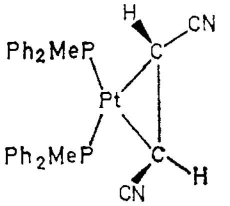
[5] H. C. Clark and K. Itoh, *Inorg. Chem.*, 1971, **10**, 1707.

[6] W. E. Truce, M. M. Boudakian, R. F. Heine, and R. J. McManimee, *J. Amer. Chem. Soc.*, 1956, **78**, 2743.

[7] S. I. Miller and R. M. Noyes, *J. Amer. Chem. Soc.*, 1952, **74**, 629.

subsequently melts at 250°, the melting point observed for *cis*-$[(Ph_2MeP)_2PtBr_2]$.

The cyano-group in *trans*-1,2-dicyanoethylene does not undergo displacement and the reaction of $[(Ph_2MeP)_4Pt]$ with this olefin produces the olefin complex (X) in good yield. This complex is surprisingly inert. Olefin complexes such as $[(Ph_3P)_2Pt(CCl_2{=}CCl_2)]$ have been shown to be precursors in the production of chloro-vinyl complexes, *e.g.* $[(Ph_3P)_2PtCl(CCl{=}CCl_2)]$ by refluxing in a polar solvent such as ethanol.[3] However, the dicyanoethylene complex (X) remains unchanged when refluxed in ethanol. The rearrangement of certain olefin complexes to vinyl complexes has been shown to be accelerated by silver salts.[8] Thus, $[(Ph_3P)_2Pt(CBrF{=}CF_2)]$ can be isomerized in refluxing butanol or more conveniently by the addition of silver acetate to an acetone solution of the olefin complex to give the vinyl complex *trans*-$[(Ph_3P)_2PtOAc(CF{=}CF_2)]$, the bromide ion being removed as silver bromide. In contrast, our attempts to rearrange the dicyanoethylene complex (X) by refluxing the complex in acetone in the presence of silver acetate were unsuccessful and this failure must reflect the increased stability of the carbon-cyanide bond.



(X)

TABLE 1

^{1}H N.m.r. spectroscopic data for phosphine methyl protons

Complex ($L = Ph_2MeP$)	Chemical shift (τ)	$J(^{31}P{-}H)$ * Hz	$J(^{195}Pt{-}H)$ Hz
trans-$[L_2PtCl(CCl{=}CCl_2)]$	7·86 (3t)	7·5	31
trans-$[L_2PtCl(CCl{=}CHCl)]$	7·88 (3t)	8·0	33
trans-$[L_2PtCl($*trans*-$CH{=}CHCl)]$	7·90 (3t)	8·0	29
trans-$[L_2PtBr($*trans*-$CH{=}CHBr)]$	7·80 (3t)	7·0	29
trans-$[L_2PtBr(CH{=}CH_2)]$	7·94 (3t)	7·0	31
trans-$[L_2PdCl(CCl{=}CCl_2)]$	7·93 (t)	7·0	
trans-$[L_2PdCl(CCl{=}CHCl)]$	7·98 (t)	7·0	
trans-$[L_2PdCl($*trans*-$CH{=}CHCl)]$	7·98 (t)	7·0	
trans-$[L_2PdCl($*cis*-$CH{=}CHCl)]$	7·98 (t)	7·0	

* This is given as the separation of the outer peaks of the 1 : 2 : 1 triplet. t = Triplet.

Spectroscopic Studies.—It is now well established [9] that the stereochemical arrangement of phosphine molecules in square planar bisphosphine complexes of platinum and palladium can be determined by ^{1}H n.m.r. spectroscopy providing the phosphine contains a methyl group as substituent. Two mutually *trans*-phosphorus atoms produce an apparent triplet of intensity 1 : 2 : 1 for the protons of the methyl groups. The resonance of the phosphine methyl protons for mutually *cis*-phosphorus nuclei appear as a well defined doublet of intensity 1 : 1. Without exception, the vinyl complexes produced by reaction of $[(Ph_2MeP)_4M]$, where M = Pt and Pd, and halogeno-olefins have a *trans*-configuration of phosphorus molecules, that is the phosphine methyl proton resonance always appears as a well defined 1 : 2 : 1 triplet. Table 1 summarizes the ^{1}H n.m.r. spectroscopic data obtained for the phosphine methyl protons of the platinum and palladium vinyl complexes. The platinum complexes have an additional coupling constant resulting from the coupling of the phosphine methyl protons with the ^{195}Pt isotope which has a spin ½ and abundance *ca.* 33% and appears as a triplet of approximate intensity 1 : 4 : 1.

It can also be shown by ^{1}H n.m.r. spectroscopy that the configuration of the original olefin is retained in the platinum and palladium vinyl complexes. Thus, when *trans*-1,2-dichloroethylene reacts with the platinum and palladium zerovalent complexes to give the chloro-vinyl complexes the coupling constant between the vinylic protons is 14 Hz. This value is of the order expected for *trans*-AB coupling across a double bond. Similarly, reaction of *cis*-1,2-dichloroethylene with $[(Ph_2MeP)_4Pd]$ gives a vinyl complex in which the vinylic protons are coupled to the extent of 5·5 Hz which is consistent with the retained *cis*-arrangement of these protons.

The relative position occupied by a proton on the vinyl group may be deduced from a knowledge of the ^{195}Pt–H coupling constant and the complex (IX) has proved invaluable in this respect. This complex contains three distinct vinylic protons which may be distinguished by observations of the proton–proton coupling constant and since each proton has an associated ^{195}Pt–H coupling the magnitude of this can be related to the position of the proton relative to the metal. These values can be compared to the $J(^{195}Pt{-}H)$ values for vinylic protons in other complexes and hence the relative position of the proton on the vinyl group may be deduced. Table 2 summarizes some of the ^{1}H n.m.r. spectroscopic data of the vinyl complexes which we have prepared. The subscripts *g*, *t*, and *c* relate to the relative position of the vinylic proton with respect to the metal, *geminal*, *trans*, and *cis* respectively. The values of $J(^{195}Pt{-}H)$ for the vinylic protons of complex (IX) are comparable to those published [10] during the course of this work for the analogous complex *trans*-$[(Ph_3P)_2PtBr(CH{=}CH_2)]$ and parallel those of J(H–H) for olefins *viz. trans* > *cis* > *gem*.

Assignment of the ^{1}H n.m.r. spectrum of complex (II)

---

[8] A. J. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 947.

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

[10] B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Comm.*, 1970, 1333.

TABLE 2

^{1}H N.m.r. spectroscopic data for vinylic protons

Complex (L = Ph_2MeP)	Chemical shift (τ) H_g	Chemical shift (τ) H_t	Chemical shift (τ) H_c	$J(^{195}Pt–H)$/Hz H_g	$J(^{195}Pt–H)$/Hz H_t	$J(^{195}Pt–H)$/Hz H_c
trans-[$L_2PtBr(CH=CH_2)$]	3·62	4·70	5·52	~30	158	84
trans-[$L_2PtCl(CCl=CHCl)$]			5·00			31
trans-[$L_2PdCl(CCl=CHCl)$]			5·03			
trans-[L_2PtCl(*trans*-$CH=CHCl$)]	3·74		5·35	30		46
trans-[L_2PdCl(*trans*-$CH=CHCl$)]	4·21		5·51			
trans-[L_2PtBr(*trans*-$CH=CHBr$)]	3·50		5·20	28		46
trans-[L_2PdCl(*cis*-$CH=CHCl$)]	3·93	4·34				

is not simple and may be interpreted in terms of either structure (II) or the alternative isomer, X = H, Y = Cl. The main evidence for the proposed structure (II) stems from ^{13}C n.m.r. studies. The ^{13}C n.m.r. spectrum of the complex in $CDCl_3$ (see Table 5) is consistent only with structure (II) and cannot be rationalized in terms of the alternative form. A more detailed discussion of this ^{13}C n.m.r. study and that of other, related molecules will be given in a subsequent paper.

Two main features of the i.r. spectra of the vinyl complexes are the carbon–carbon double-bond stretching frequency and the metal–halogen stretching frequency and these are summarized in Table 3. The former occurs as a weak band at *ca.* 1500 cm^{-1} and the latter as a strong band *ca.* 300 cm^{-1} for this type of complex.[3,4] In order to confirm the ν(Pt–Cl) assignment we prepared the complex *trans*-[$(Ph_2MeP)_2PtBr(CCl=CHCl)$].

TABLE 3

I.r. spectroscopic data for the vinyl complexes

Complex (L = Ph_2MeP)	(C=C)/cm^{-1}	ν(M=Cl)/cm^{-1}
trans-[$L_2PtCl(CCl=CCl_2)$]	1535w	305s
trans-[$L_2PdCl(CCl=CCl_2)$]	1535w	314s
trans-[$L_2PtCl(CCl=CHCl)$]	1541w	307s
trans-[$L_2PtBr(CH=CCl_2)$]	1536w	
trans-[$L_2PdCl(CCl=CHCl)$]	1537w	312s
trans-[L_2PtCl(*trans*-$CH=CHCl$)]	1550w	290s
trans-[L_2PdCl(*trans*-$CH=CHCl$)]	1542w	297s
trans-[L_2PdCl(*cis*-$CH=CHCl$)]	1555w	290s
trans-[$L_2PtBr(CH=CH_2)$]	1570m	

w = Weak; m = medium; s = strong.

Reactivity of the Chlorovinyl–Metal(II) *Complexes with Chlorine.*—The most reactive centre in these molecules to chlorine is the metal. Treatment of the platinum(II) complexes with one equivalent of chlorine leads to oxidation of the metal yielding six co-ordinated platinum(IV) complexes with the stereochemical configuration shown in (XI).

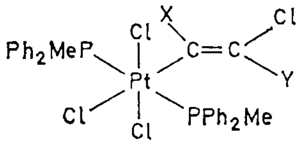
TABLE 4

^{1}H N.m.r. spectroscopic data for the platinum(IV) vinyl complexes

Complex (L = Ph_2MeP)	Phosphine methyl protons: Chemical shift (τ)	Phosphine methyl protons: $J(^{31}P–H)$ * /Hz	Phosphine methyl protons: $J(^{195}Pt–H)$/Hz	Vinylic protons: Chemical shift H_g (τ)	Vinylic protons: $J(^{195}Pt–Hg)$/Hz	Vinylic protons: Chemical shift H_c (τ)	Vinylic protons: $J(^{195}Pt–H_c)$/Hz	Vinylic protons: $J(Hg–H_c)$/Hz
trans-[$L_2PtCl_3(CCl=CCl_2)$]	7·54 (3ot)	8	15					
trans-[$L_2PtCl_3(CCl=CHCl)$]	7·60 (3ot)	8	15			3·95 (3t)	26	
trans-[L_2PtCl_3(*trans*-$CH=CHCl$)]	7·60 (3ot)	8	15	4·05 (2ot)	56	4·76 (2ot)	30	13

* This is given as the separation of the outer peaks of the 1 : 2 : 1 triplet. t = Triplet; ot = overlapping triplet.

Substitution of hydrogen by halogen, reduces the electrophilic nature of the olefin bond, thus increasing the possibility of metal oxidation when reacting with electrophilic reagents. The $^{195}Pt–H$ coupling constant for the phosphine methyl protons is reduced from *ca.* 30 Hz in the platinum(II) complexes to 15 Hz for the platinum(IV) complexes. This marked reduction has been noted previously when platinum(II) alkyls were oxidized to platinum(IV) alkyls[11] and may be attributed to a decrease in the *s*-character of the platinum–phosphorus bond on increasing the co-ordination from four to six. Table 4 summarizes some of the ^{1}H n.m.r. spectroscopic data for the platinum(IV) vinyl complexes.



(XI)

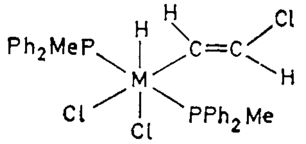
(XI) a; X = Y = Cl
b; X = Cl, Y = H
c; X = Y = H

Thus, treatment of the platinum(II) vinyl complexes with one equivalent of chlorine leads to reaction exclusively at the metal. Subsequent reaction with chlorine appears to depend upon the nature of the substituted groups in the vinyl group. Thus whilst the platinum(IV) complex *trans*-[$(Ph_2MeP)_2PtCl_3(CCl=CCl_2)$] was unaffected when treated with a further equivalent of chlorine treatment of the complex *trans*-[$(Ph_2MeP)_2PtCl_3(CCl=CHCl)$] with 1 mol equiv. of chlorine gave the complex *trans*-[$(Ph_2MeP)_2PtCl_3(CCl=CCl_2)$]; the vinylic proton having been substituted by a chlorine atom. Reaction of the complex *trans*-[$(Ph_2MeP)_2PtCl_3$(*trans*-$CH=CHCl$)] with 1 mol equiv. of chlorine gave an intractable oil which was not examined further.

---

[11] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801.

Reactivity of the Chlorovinyl–Metal(II) *Complexes with Hydrogen Chloride.*—Treatment of the platinum and palladium(II) vinyl complexes with hydrogen chloride emphasises the stability differences between the various complexes. The complexes *trans*-[$(Ph_2MeP)_2MCl(CCl{=}CCl_2)$], where M = Pt and Pd, were unaffected by treatment with hydrogen chloride and this shows the enhanced stability of the metal–vinylic carbon bond when the vinyl group is fully substituted by electron-withdrawing groups. In contrast, treatment of the complexes *trans*-[$(Ph_2MeP)_2MCl$(*trans*-CH=CHCl)], where M = Pt and Pd, with hydrogen chloride leads to cleavage of the metal–carbon bond and removal of the vinyl group. The products obtained in the case of the platinum complex were *cis*-[$(Ph_2MeP)_2PtCl_2$] and vinyl chloride whilst the palladium complex yielded a *cis*/*trans* mixture of [$(Ph_2MeP)_2PdCl_2$] and vinyl chloride. The elimination of the vinyl group probably proceeds *via* the hydrido-intermediate species (XII) which can decompose to the *cis*-bisphosphine dichloride complexes by elimination of the hydrogen atom with the relatively weakly bonded vinyl group. In the case of the palladium complex production of *cis*-[$(Ph_2MeP)_2PdCl_2$] is probably followed by partial rearrangement to the more stable *trans*-isomer thus producing the *cis*/*trans* mixture which is isolated.


(XII)

An interesting reaction occurs when the vinyl complex *trans*-[$(Ph_2MeP)_2PtCl(CCl{=}CHCl)$] (II) is treated with hydrogen chloride. The original complex has an ^1H n.m.r. spectrum showing the vinylic proton at τ 5 and is coupled to the ^{195}Pt nucleus to the extent of 31 Hz. Treatment of the complex with hydrogen chloride had no apparent visual effect, the product having a similar elemental analysis and i.r. spectrum to that of the starting material. However, examination of the product by ^1H n.m.r. spectroscopy revealed that a reaction had occurred.

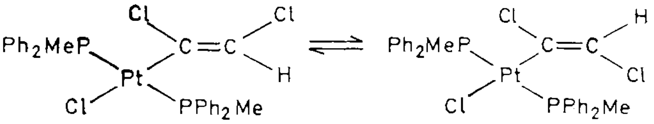
Table 5

^{13}C N.m.r. spectroscopic data for platinum(II) vinyl complexes [a]

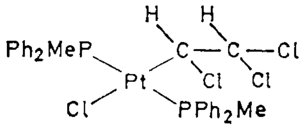
	Phosphine methyl carbons			Vinylic carbons					
Complex (L = Ph_2MeP)	Chemical shift (p.p.m.)	J(P–C)/Hz	J(Pt–C)/Hz	Chemical shift C_α (p.p.m.)	$J(Pt–C_\alpha)$/Hz	$J(P–C_\alpha)$/Hz	Chemical shift C_β (p.p.m.)	$J(Pt–C_\beta)$/C_β (p.p.m.)	$J(P–C_\alpha)$/Hz
trans-$L_2PtCl(CCl{=}CHCl)$	11·7	40		[b]			107·8 (t) [c]	210	
trans-$L_2PtCl(CH{=}CHCl)$	12·3	37	30	124·1 (t)	900	10	108·8 (t)	128	5

[a] Spectra run in $CDCl_3$. [b] α-Carbon lacks any Overhauser enhancement. Unambiguous assignment impossible even with added relaxation reagent. [c] Phosphorus–carbon coupling observed as fine structure of the components of the 1 : 4 : 1 triplet arising from carbon coupling to platinum-195.

Two vinylic proton resonances occur at τ 5 and 4, the former showing a $J(^{195}Pt–H)$ coupling constant of 31 Hz, identical to the vinylic proton of the starting material, and the latter had a $J(^{195}Pt–H)$ coupling constant of 84 Hz. There was no mutual coupling between the two protons. The resonance of the phosphine methyl protons at *ca.* τ 8 appeared complex but examination of an expanded spectrum showed this to consist of two almost coincidental 1 : 2 : 1 triplets. The product of reaction, therefore, consists of a mixture of the starting material and another complex having the same stoicheiometry but a different vinylic proton environment. As only one new vinylic proton resonance is observed the product appears to be exclusively one form and we tentatively suggest that isomerization of the vinyl group has occurred and an equilibrium between the isomerized product and the starting material has been established. The value of 84 Hz for the $^{195}Pt–H$ coupling constant for the vinylic proton in the new environment is more consistent with this proton occupying a position *trans* to the metal rather than geminal and it is concluded that the isomerized product is (XIII) and the equilibrium is presumably as shown:


(II) (XIII)

The mechanism by which the isomerization is established, is a matter for conjecture since no systematic study has been made. One possibility is that the hydrogen chloride adds to the vinylic group to give an intermediate of the type (XIV) which can then eliminate


(XIV)

hydrogen chloride in one of *two ways* to give the starting material or the product. Alternatively, addition of a proton to form a carbonium ion followed by rotation about the carbon–carbon bond and elimination of the proton would produce the same result.

EXPERIMENTAL

The zerovalent metal complexes were prepared by published methods.[12–14]

Platinum(II) *Chlorovinyl Complexes.*—(*a*) trans-*Chlorobis*(*diphenylmethylphosphine*)*trichlorovinylplatinum.* Tetrakis(diphenylmethylphosphine)platinum (1·0 g) in toluene (30 ml) was treated with tetrachloroethylene (3 ml) and the clear yellow solution was heated at 90° for 2 h. The resulting pale yellow solution was filtered and the solvent was removed under reduced pressure to give a yellow oil, addition of light petroleum (b.p. 40—60°) to which gave a white solid which was crystallized from a dichloromethane–ethanol to give colourless crystals of the *product* (0·6 g, 80%) m.p. 167—170° (Found: C, 43·7; H, 3·5; Cl, 17·95. $C_{28}H_{26}Cl_4P_2Pt$ requires C, 44·1; H, 3·44; Cl, 18·60%).

(*b*) trans-*Chlorobis*(*diphenylmethylphosphine*)*dichlorovinylplatinum.* By the method described in (*a*) tetrakis(diphenylmethylphosphine)platinum (1·7 g) and trichloroethylene (3 ml) gave colourless crystals of the *product* (1·2 g, 95%), m.p. 158—160° (Found: C, 46·7; H, 3·8; Cl, 14·25. $C_{28}H_{27}Cl_3P_2Pt$ requires C, 46·3; H, 3·74; Cl, 14·64%).

(*c*) trans-*Chlorobis*(*diphenylmethylphosphine*)-trans-*chlorovinylplatinum.* By the method described in (*a*) tetrakis(diphenylmethylphosphine)platinum (1·5 g) and *trans*-1,2-dichloroethylene (3 ml) gave colourless crystals of the *product* (0·86 g, 83%), m.p. 120—125° (Found: C, 48·5; H, 4·5; Cl, 10·1. $C_{28}H_{28}Cl_2P_2Pt$ requires C, 48·6; H, 4·07; Cl, 10·24%).

(*d*) *Attempted reaction between tetrakis*(*diphenylmethylphosphine*)*platinum and vinyl chloride.* Tetrakis(diphenylmethylphosphine)platinum (0·8 g) in toluene (20 ml) and vinyl chloride (*ca.* 1 ml) in a sealed tube at room temperature for 14 days failed to react and gave only the platinum(0) starting material as revealed by i.r. spectroscopy.

(*e*) *Attempted reaction between tetrakis*(*diphenylmethylphosphine*)*platinum and* cis-*1,2-dichloroethylene.* Tetrakis(diphenylmethylphosphine)platinum (1·2 g) in toluene (20 ml) and *cis*-1,2-dichloroethylene (1 ml) in a sealed tube at 140° for 5 h gave unchanged platinum(0) starting material as revealed by i.r. spectroscopy.

(*f*) *Reaction between tetrakis*(*diphenylmethylphosphine*)*platinum and* cis-*1,2-dichloroethylene in the presence of ethoxide ions.* Tetrakis(diphenylmethylphosphine)platinum (1·5 g) in ethanol (50 ml), containing dissolved sodium (0·05 g), was treated with *cis*-1,2-dichloroethylene (2 ml) and heated under reflux for 1 h, the resulting white solid was filtered, washed with ethanol, and recrystallized from chloroform to give white crystals of the *product* (0·80 g, 81%), m.p. 170°(d) (Found: C, 51·0; H, 4·25; Cl, 5·5. $C_{28}H_{27}ClP_2Pt$ requires C, 51·2; H, 4·15; Cl, 5·41%).

(*g*) trans-*Bromobis*(*diphenylmethylphosphine*)*dichlorovinylplatinum.* *trans*-Chlorobis(diphenylmethylphosphine)dichlorovinylplatinum (0·3 g) in acetone (25 ml) was treated with anhydrous lithium bromide (1·0 g) and heated under reflux for 2 h; the solution was filtered and removal of the the solvent gave a white solid which was filtered off, washed with water, and recrystallized from a dichloromethane–ethanol mixture to give colourless crystals of the *product* (0·3 g, 95%), m.p. 169—172° (Found: C, 43·7; H, 3·85. $C_{28}H_{27}BrClP_2Pt$ requires C, 43·6; H, 3·53%).

Palladium(II) *Chlorovinyl Complexes.*—(*a*) trans-*Chlorobis*(*diphenylmethylphosphine*)*trichlorovinylpalladium.* Tetrakis(diphenylmethylphosphine)palladium (0·4 g) in toluene (20 ml) was treated with tetrachloroethylene (3 ml) and heated at 90° for 1 h; the pale yellow solution was filtered and removal of solvent under reduced pressure from the filtrate gave a pale yellow oil. Addition of light petroleum (b.p. 40—60°) to this gave a white solid which was recrystallized from dichloromethane–ethanol to give colourless crystals of the *product* (0·24 g, 81%), m.p. 165° (Found: C, 50·2; H, 3·65; Cl, 21·1. $C_{28}H_{26}Cl_4P_2Pd$ requires C, 50·0; H, 3·89; Cl, 21·05%).

(*b*) trans-*Chlorobis*(*diphenylmethylphosphine*)*dichlorovinylpalladium.* By the method used in (*a*) tetrakis(diphenylmethylphosphine)palladium (0·7 g) and trichloroethylene (3 ml) gave colourless crystals of the *product* (0·4 g, 81%), m.p. 156° (Found: C, 52·4; H, 4·15; Cl, 17·0%. $C_{28}H_{27}Cl_3P_2Pd$ requires C, 52·7; H, 4·26; Cl, 16·67%).

(*c*) trans-*Chlorobis*(*diphenylmethylphosphine*)-trans-*chlorovinylpalladium.* By the method used in (*a*) tetrakis(diphenylmethylphosphine)palladium (0·7 g) and *trans*-1,2-dichloroethylene (3 ml) gave white crystals of the *product* (0·36 g, 78%), m.p. 120°(d) (Found: C, 55·6; H, 4·8; Cl, 11·25. $C_{28}H_{28}Cl_2P_2Pd$ requires C, 55·7; H, 4·67; Cl, 11·74%).

(*d*) trans-*Chlorobis*(*diphenylmethylphosphine*)-cis-*chlorovinylpalladium.* By the method used in (a) tetrakis(diphenylmethylphosphine)palladium (0·36 g) and *cis*-1,2-dichloroethylene (3 ml) gave white crystals of the *product* (0·1 g, 42%), m.p. 130° (d) which was identified by i.r. and ^1H n.m.r. spectroscopy.

Platinum(II) *Bromovinyl Complexes.*—(*a*) trans-*Bromobis*(*diphenylmethylphosphine*)*vinylplatinum.* Tetrakis(diphenylmethylphosphine)platinum (1·3 g) in toluene (20 ml) was treated with vinyl bromide (1 ml) and stirred at room temperature for 1 h; the clear yellow solution was filtered and the solvent was removed under reduced pressure from the filtrate to give a yellow oil. Addition of ether to this gave a white solvent which was recrystallized from dichloromethane–n-hexane to give white crystals of the *product* (0·45 g, 50%), m.p. 160° (Found: C, 47·3; H, 3·9; Br, 11·75. $C_{28}H_{29}BrP_2Pt$ requires C, 47·8; H, 4·16; Br, 11·38%).

(*b*) trans-*Bromobis*(*diphenylmethylphosphine*)-trans-*bromovinylplatinum.* By the method used in (*a*) above tetrakis(diphenylmethylphosphine)platinum (0·5 g) and *trans*-1,2-dibromoethylene (1 ml) gave white crystals of the *product* (0·35 g, 90%), m.p. 148° [with evolution of gas to give a white solid m.p. 250° (d)] (Found: C, 43·2; H, 3·65; Br, 20·55. $C_{28}H_{28}Br_2P_2Pt$ requires C, 43·0; H, 3·61; Br, 20·45%).

Decomposition of trans-*Bromobis*(*diphenylmethylphosphine*)-trans-*bromovinylplatinum in Chloroform.*—*trans*-Bromobis(diphenylmethylphosphine)-*trans*-bromovinylplatinum (0·1 g) in chloroform (10 ml) was stirred at room temperature for 30 min; removal of solvent under reduced pressure gave a white solid which was recrystallized from dichloromethane–methabol to give colourless crystals of the *product* (0·09 g, 90%), m.p. 250°(d) (Found: C, 41·5; H, 3·35; Br, 21·2. $C_{26}H_{26}Br_2P_2Pt$ requires C, 41·4; H, 3·47; Br, 21·15%).

Examination by g.l.c. Samples of the vinyl complex in chloroform were examined by g.l.c. using a Porapak R column at 70° with a nitrogen carrier gas flow of 15 lb in^{-2}. Acetylene was identified by comparison of elution times with a pure sample of acetylene dissolved in chloroform.

Reactions involving trans-*Dicyanoethylene.*—(*a*) *Bis*(*diphenylmethylphosphine*)-trans-*1,2-dicyanoethyleneplatinum.*

---

[12] L. Malatesta and Miss C. Cariello, *J. Chem. Soc.*, 1958, 2323.

[13] L. Malatesta and Miss M. Angoletta, *J. Chem. Soc.*, **1957**, 1186.

[14] P. Chini and G. Longani, *J. Chem. Soc.* (*A*), 1970, 1542.

Tetrakis(diphenylmethylphosphine)platinum (0·5 g) in toluene (25 ml) was treated with *trans*-1,2-dicyanoethylene (0·1 g) and stirred at room temperature for 1 h; the pale yellow solution was filtered and the solvent was removed under reduced pressure to give a pale yellow oil; addition of ether to this gave a white solid which was recrystallized from dichloromethane–methanol to give white crystals of the *product* (0·3 g, 89%), m.p. 189° (Found: C, 53·0; H, 4·35; N, 4·00. $C_{30}H_{28}N_2P_2Pt$ requires C, 53·4; H, 4·19; N, 4·16%).

(*b*) *Attempted isomerization in ethanol.* Bis(diphenylmethylphosphine)-*trans*-1,2-dicyanoethyleneplatinum (0·2 g) was refluxed in ethanol (50 ml) for 2 h to give the cyano-olefin-platinum starting material (0·19 g, 95%) as identified by i.r. spectroscopy.

(*c*) *Attempted isomerization with silver acetate.* Bis(diphenylmethylphosphine)-*trans*-1,2-dicyanoethylene (0·5 g) in acetone (50 ml) was treated with silver acetate (0·5 g) and heated under reflux for 6 h to give, on work-up, the cyano-olefin-platinum starting material (0·46 g, 92%) as identified by i.r. spectroscopy.

Reactions and Attempted Reactions of Platinum(II) *Vinyl Complexes with a Molar Equivalent of Chlorine.*—(*a*) trans-*Trichlorobis(diphenylmethylphosphine)trichlorovinylplatinum.* trans-Chlorobis(diphenylmethylphosphine)trichlorovinylplatinum (0·404 g) in dichloromethane (10 ml) was treated with a solution of chlorine in carbon tetrachloride (1 ml of a 3·76% solution) and the yellow solution was stoppered and stirred at room temperature for 1 h. Removal of the solvent under reduced pressure gave a yellow oil which was chromatographed on silica gel using a solution of 10% ethyl acetate in toluene. The yellow eluate was filtered and removal of the solvent under reduced pressure gave a yellow oil which on treatment with ether–methanol gave yellow crystals of the *product* (0·38 g, 86%), m.p. 172°(d) (Found: 40·9; H, 3·45; Cl, 25·1. $C_{28}H_{26}Cl_6P_2Pt$ requires C, 40·4; H, 3·15; Cl, 25·56%).

(*b*) trans-*Trichlorobis(diphenylmethylphosphine)dichlorovinylplatinum.* With the method described in (*a*) *trans*-chlorobis(diphenylmethylphosphine)dichlorovinylplatinum (0·193 g) and a solution of chlorine in carbon tetrachloride (0·5 ml of a 3·76% solution) gave yellow crystals of the *product* (0·195 g, 96%) m.p. 174—175°(d) (Found: C, 42·5; H, 3·75; Cl, 21·85. $C_{28}H_{27}Cl_5P_2Pt$ requires C, 42·2; H, 3·41; Cl, 22·23%).

(*c*) trans-*Trichlorobis(diphenylmethylphosphine)*-trans-*chlorovinylplatinum.* With the method described in (*a*) *trans*-chlorobis(diphenylmethylphosphine)-*trans*-chlorovinylplatinum (0·366 g) and a solution of chlorine in carbon tetrachloride (1 ml of a 3·76% solution) gave yellow crystals of the *product* (0·32 g, 80%) m.p. 173°(d) (Found: C, 43·8; H, 3·9; Cl, 17·8. $C_{26}H_{28}Cl_4P_2Pt$ requires C, 44·1; H, 3·69; Cl, 18·58%).

Reaction of Platinum(IV) *Vinyl Complexes with a Molar Equivalent of Chlorine.*—(*a*) trans-*Trichlorobis(diphenylmethylphosphine)trichlorovinylplatinum.* *trans*-Trichlorobis(diphenylmethylphosphine)trichlorovinylplatinum (0·286 g) in dichloromethane (10 ml) was treated with a solution of chlorine in carbon tetrachloride (1 ml of a 2·44% solution) for 24 h. On work-up starting material was recovered.

(*b*) trans-*Trichlorobis(diphenylmethylphosphine)dichlorovinylplatinum.* *trans*-Trichlorobis(diphenylmethylphosphine)dichlorovinylplatinum (0·278 g) and a solution of chlorine in carbon tetrachloride (1 ml of a 2·44% solution) was set aside for 24 h. Removal of solvent gave an oil which on treatment with ether–methanol gave yellow crystals of the *product* (0·26 g, 90%) (Found: C, 40·8; H, 3·3; Cl, 25·45. $C_{28}H_{26}Cl_6P_2Pt$ requires C, 40·4; H, 3·15; Cl, 25·56%).

(*c*) trans-*Trichlorobis(diphenylmethylphosphine)*trans-*chlorovinylplatinum.* By the method described in (*b*) *trans*-trichlorobis(diphenylmethylphosphine)-*trans*-chlorovinylplatinum (0·266 g) and a solution of chlorine in carbon tetrachloride (1 ml of a 2·44% solution) gave an intractable oil which was discarded.

Reaction and Attempted Reactions of Platinum and Palladium(II) *Vinyl Complexes with Hydrogen Chloride.*—(a) trans-*Chlorobis(diphenylmethylphosphine)trichlorovinylplatinum.* *trans*-Chlorobis(diphenylmethylphosphine)trichlorovinylplatinum (0·25 g) in dichloromethane (25 ml) was treated with hydrogen chloride for 3 h. The clear solution was filtered and removal of the solvent under reduced pressure gave a white solid which was recrystallized from a dichloromethane–methanol mixture to give crystals of the starting material.

(*b*) trans-*Chlorobis(diphenylmethylphosphine)dichlorovinylplatinum.*—By the method described in (*a*) *trans*-chlorobis(diphenylmethylphosphine)dichlorovinylplatinum (0·20 g) and hydrogen chloride gave crystals of the product (0·19 g, 95%), m.p. 145—150° (Found: C, 46·3; H, 3·75; Cl, 14·45. $C_{28}H_{27}Cl_3P_2Pt$ requires C, 46·3; H, 3·74; Cl, 14·64%).

(*c*) trans-*Chlorobis(diphenylmethylphosphine)*trans-*chlorovinylplatinum.* By the method described in (*a*) *trans*-chlorobis(diphenylmethylphosphine)-*trans*-chlorovinylplatinum (0·20 g) and hydrogen chloride gave crystals of the *product* (0·185 g, 96%), m.p. 235° (Found: C, 46·7; H, 3·95; Cl, 10·75. $C_{26}H_{26}Cl_2P_2Pt$ requires C, 46·9; H, 3·93; Cl, 10·64%).

Examination by g.l.c. Samples of the reaction solution were examined by g.l.c. using a 10 ft di-2-cyanoethyl ether column at 55° with a nitrogen carrier gas flow of 15 lb in^{-2} to show the presence of vinyl chloride.

(*d*) trans-*Chlorobis(diphenylmethylphosphine)trichlorovinylpalladium.*— *trans*-Chlorobis(diphenylmethylphosphine)trichlorovinylpalladium (0·08 g) and hydrogen chloride gave crystals of the starting material on work-up.

(*e*) trans-*Chlorobis(diphenylmethylphosphine)dichlorovinylpalladium.*— *trans*-Chlorobis(diphenylmethylphosphine)dichlorovinylpalladium (0·08 g) and hydrogen chloride gave crystals of starting material on work up.

(*f*) trans-*chlorobis(diphenylmethylphosphine)*trans-*chlorovinylpalladium.* By the method described in (*a*) *trans*-chlorobis(diphenylmethylphosphine)-*trans*-chlorovinylpalladium (0·1 g) and hydrogen chloride gave yellow crystals of the *product* (0·09 g, 94%), m.p. 190°(d) (Found: C, 53·8; H, 4·75; Cl, 12·0. $C_{26}H_{26}Cl_2P_2Pd$ requires C, 54·0; H, 4·53; Cl, 12·27%).

Examination by g.l.c. Samples of the reaction solution were examined by g.l.c. using a 10 ft di-2-cyanoethyl ether column at 55° with a nitrogen carrier gas flow of 15 lb in^{-2} to show the presence of vinyl chloride.

We thank the Corporate Laboratory (I.C.I., Runcorn) and the S.R.C. for a studentship (to J. D. J.) and Johnson, Matthey Ltd. for the loan of palladium salts.

[3/430 *Received, 23rd February,* 1973]