Isocyanide Insertion in Alkyl– and Vinyl–Metal Bonds of Square-planar Palladium(II) and Platinum(II): Mechanisms and Stereochemistry

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Reaction of $\mathrm{CNBu^t}$ with *trans*-$[\mathrm{PdX(R')(CNBu^t)_2}]$ ($\mathrm{R'}$ = Me or $\mathrm{PhCH_2}$) in the presence of a nucleophile L ($\mathrm{CNBu^t}$ or $\mathrm{PPh_3}$) gives the mono-insertion product, $[\mathrm{PdX(CR'{:}NBu^t)(CNBu^t)L}]$, and in the absence of L gives a dimer $[\{\mathrm{PdX(CR'{:}NBu^t)(CNBu^t)}\}_2]$. The insertion reaction in the presence of L occurs unimolecularly, being independent of the nature of L. This contrasts to the insertion reaction of CNR (R = $\mathrm{Bu^t}$ or *p*-$\mathrm{MeC_6H_4}$) into *trans*-$[\mathrm{MX(R')(PPh_3)_2}]$ (M = Pd or Pt) which depends on the nature of CNR, suggesting an associative mechanism. The intramolecular insertion reaction of *trans*-$[\mathrm{MBr}(\textit{cis}\text{-}\mathrm{CH{:}CH{\cdot}CO_2Me)(CNBu^t)_2}]$ gives $[\{\mathrm{MBr[C}(\textit{trans}\text{-}\mathrm{CH{:}CH{\cdot}CO_2Me){:}NBu^t](CNBu^t}\}_2]$, indicating isomerisation of the vinyl group, while insertion of $\mathrm{CNC_6H_4Me}$-*p* into *trans*-$[\mathrm{MBr}(\textit{cis}\text{-}\mathrm{CH{:}CH{\cdot}CO_2Me)(PPh_3)_2}]$ yields *trans*-$[\mathrm{MBr\{C}(\textit{cis}\text{-}\mathrm{CH{:}CH{\cdot}CO_2Me){:}NC_6H_4Me\}(PPh_3)_2}]$ with retention of the vinyl geometry. Rapid multi-insertion of $\mathrm{CNBu^t}$ occurs with $[\mathrm{PdX(R)(Ph_2PCH_2CH_2PPh_2)}]$. In contrast to $\mathrm{CNC_6H_4Me}$-*p*, $\mathrm{CNBu^t}$ does not insert into *trans*-$[\mathrm{PtX}(\textit{cis}\text{-}\mathrm{CH{:}CH{\cdot}CO_2H)(PPh_3)_2}]$. Various factors which influence the reaction rate and stereochemistry are described and interpretations accommodating all these features are discussed.

INSERTION reactions of isocyanide have received considerable attention in recent years.[1,2] Insertion into carbon–molybdenum,[3] –iron,[4] –cobalt,[5] and –nickel[6-8] bonds has been reported. Various facets of the nature of the reaction were disclosed from these studies. However, no kinetic data are available, and the reaction mechanism remains to be elucidated. During the course of our studies[9,10] on oxidative addition of alkyl halides to low-valent Group 8 metals, it was necessary to establish the mechanism of insertion into, in particular, square-planar complexes of $\mathrm{Pd^{II}}$ and $\mathrm{Pt^{II}}$. There are two reports[6,7] on insertion into Pt–C bonds in *trans*-$[\mathrm{PtX(R)L_2}]$ (L = phosphines) complexes. Treichel and Hess[7] proposed a mechanism which involves rate-determining nucleophilic attack of $\mathrm{X^-}$ in an ionic intermediate $[\mathrm{M(R)(CNR')L_2}]\mathrm{X}$ leading to a transition complex $[\mathrm{MX(R)(CNR')L_2}]$. If this is valid, the relative rate should increase in the order of nucleophilicity, *i.e.* $\mathrm{Cl} < \mathrm{Br} < \mathrm{I}$. We found the reverse of this order for the reaction with *trans*-$[\mathrm{PdX(R)L_2}]$. More sophisticated studies are therefore necessary.

Although there are reports on the oxidative addition of vinyl halides such as perchloroethylene[11] or trichloroethylene,[12] the insertion of isocyanide into a metal–vinyl bond has not been reported. We are interested in the stereochemistry of the oxidative addition and of the insertion because of the bearing on the mechanisms. The oxidative addition of *cis*- and *trans*-$\mathrm{CHCl{:}CHCl}$ to palladium(0) complexes occurs with retention of configuration.[12] However, the resulting stable complexes failed to show insertion reactions. We found that *cis*-carboxyvinylmetal complexes are moderately reactive toward insertion reactions. Unexpectedly, insertion into the metal–*cis*-carboxyvinyl bond in *trans*-$[\mathrm{MX(CH{:}CH{\cdot}CO_2Me)L_2}]$ occurs with either retention of configuration or isomerisation depending on the nature of the ligand L. In this paper we report features of the isocyanide insertion reaction as revealed by kinetic and stereochemical studies on pertinent systems.

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[6] Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Japan*, 1970, **43**, 2653; 1971, **44**, 1876.

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[10] S. Otsuka and K. Ataka, 6th Internat. Conf. on Organometallic Chemistry, University of Massachusetts, Amherst, 1973.

[11] W. J. Bland, J. Burgess, and R. D. M. Kemmitt, *J. Organometallic Chem.*, 1968, **14**, 201.

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

RESULTS AND DISCUSSION

Addition of alkyl halides to ' $Pd(CNBu^t)_2$ ' occurred yielding *trans* adducts, *e.g.* yellow *trans*-$[Pd(CH_2Ph)(CNBu^t)_2I]$, (Ia),[8] the beige bromo-analogue, (Ib), and $[PdMe(CNBu^t)_2I]$, (Id).[8] Addition of $PhCH_2Cl$ to ' $Pd(CNBu^t)_2$ ' in chlorobenzene (no reaction in n-hexane) was followed by a rapid alkyl migration (insertion reaction) leading to the complex $[\{Pd[C(CH_2Ph){:}NBu^t](CNBu^t)Cl\}_2]$ in low yield (21%). In the preparation of these adducts we observed a qualitative sequence of $PhCH_2I > PhCH_2Br > PhCH_2Cl$ for the rate of oxidative addition. The addition was faster in aromatic solvents than in saturated hydrocarbons, which may be due partly to a solubility effect. In the presence of a free nucleophile such as $CNBu^t$ or PPh_3, the reaction of RX with ' $Pd(CNBu^t)_2$ ' yields monomeric complexes, *trans*-$[PdX\{C(CH_2Ph){:}NBu^t\}(CNBu^t)_2]$, (IIa, X = I; IIb, X = Br; IIc, X = Cl), or *trans*-$[Pd(CMe{:}NBu^t)(CNBu^t)_2I]$, (IId).

As described later, $[PdX(R)(dppe)]$ [$R = CH{:}CH{\cdot}CO_2Me$; dppe = 1,2-bis(diphenylphosphino)ethane] readily undergoes a multi-insertion reaction. Apparently, an intramolecular alkyl migration to an isocyanide ligand requires *cis* disposition of the two ligands. Ready multi-insertion in a *trans* complex must involve either incipient *trans–cis* rearrangement or a process which brings an isocyanide ligand to a position adjacent to the alkyl group. The rearrangement could occur through an associative or a dissociative ligand exchange, and the latter process through an associative mechanism involving five-co-ordinate species, *e.g.* $[MX(R')(CNR)(PR''_3)_2]$, as intermediates or transients.

In order to obtain insight into the mechanism, insertion rates were measured for two systems, an intramolecular alkyl migration of *trans*-$[PdX(CH_2Ph)(CNBu^t)_2]$ to give the dimer $[\{PdX[C(CH_2Ph){:}NBu^t](CNBu^t)\}_2]$ and an intermolecular reaction of *trans*-$[PdMe(CNBu^t)_2I]$ with nucleophiles. These rates could be followed conveniently by ^1H n.m.r. spectroscopy. However, the study of the former system was somewhat hampered by an unavoidable side-reaction of the reactive benzyl complexes, namely the thermal decomposition to the palladium(I) complex $[\{PdX(CNBu^t)_2\}_2]$.[13] Consequently only the initial rates were compared qualitatively and the sequence Cl > Br > I was found, in parallel to the thermal stability of the Pd–R bond in *trans*-$[PdX(R)L_2]$. This result is rather perplexing, because we expected an increase in alkyl-migration rate with increase in the *trans* effect of the halide ions. It appears that polarisation of the metal–halogen bond plays an important role in the rate-determining alkyl-migration step. This view is supported as described later.

The kinetic study of the second system, (Id) + nucleophile L [L = $CNBu^t$, PPh_3, or $P(OPh)_3$], indicated a first-order dependence of the rate on the complex concentration. The reaction obeyed the rate equation (1) for 80% completion. The rate was independent of the nature of the nucleophile (Table 1). Solvent effects

$$\text{Rate} = k_{\text{obs.}}[PdMe(CNBu^t)_2I] \qquad (1)$$

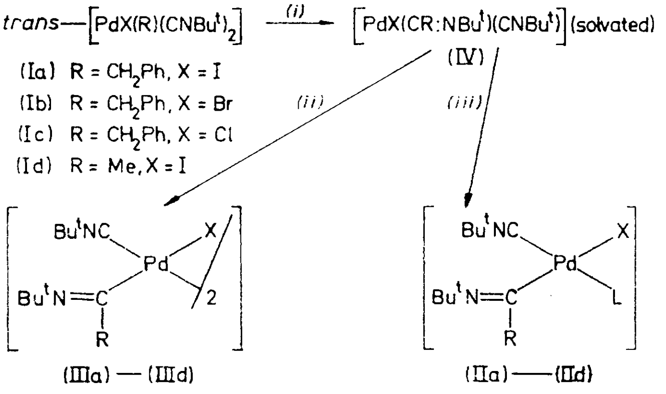
were observed. In n-hexane the rate of insertion was very slow at 0 °C, while the rate was fast in polar aromatic solvents. Similar solvent effects were observed for insertion of carbon monoxide into $[MnMe(CO)_5]$,[14] $[FeMe(\eta\text{-}C_5H_5)(CO)_2]$,[15] and $[MoMe(\eta\text{-}C_5H_5)(CO)_3]$.[16]

TABLE 1

First-order rate constants for the reaction between $[PdMe(CNBu^t)_2I]$ and nucleophiles L at 0 °C

L	$[L]_0$/mol dm^{-3}	Solvent	$10^{-4}k_{\text{obs.}}$/s^{-1}
$CNBu^t$	0.106	PhCl	1.05
	0.177	PhCl	1.03
	0.264	PhCl	1.10
	0.636	PhCl	1.10
PPh_3	0.110	PhCl	1.0
$P(OPh)_3$	0.107	PhCl	1.0
$CNBu^t$	1.106	PhMe	0.47

A toluene solution of (Id) prepared below 0 °C, without the presence of additional $CNBu^t$, showed three singlet resonances at δ 0.60, 1.62, and 2.25 p.p.m. at 11 °C (intensity ratio, 3 : 3 : 1) in addition to the resonances (δ 0.58 and 1.01 p.p.m.; 6 : 1) of (Id) and the resonances (δ 0.87, 1.32, and 2.10 p.p.m.; 3 : 3 : 1) due to (IIId; R = Me, X = I). The intensities of the 3 : 3 : 1 resonances of (IIId) increased at the expense of the resonances of (Id) and of the unassigned 3 : 3 : 1 resonances. On raising the temperature to 19 °C (from 11 °C in 40 min) the latter 3 : 3 : 1 peaks and those of (Id) disappeared almost simultaneously. This behaviour, and the chemical shift and constant-intensity ratio, seems to justify an assignment of the resonance to a highly co-ordinatively unsaturated species having an iminoalkyl



SCHEME 1 (*i*), solvent, slow; (*ii*), fast; (*iii*), L, fast

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[14] F. Calderazzo and K. Noack, *Co-ordination Chem. Rev.*, 1966, **1**, 188, and refs. therein.

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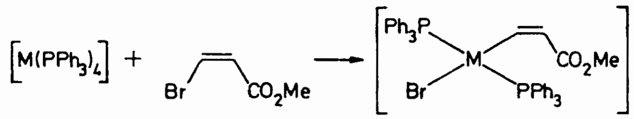
[16] I. S. Butler, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1967, **6**, 2074.

ligand. Although an unambiguous structural assignment was not possible, this species is probably the three-co-ordinate solvated complex (IV; R = Me). In support of this formulation, the spectrum of (IV) was not observed when (Id) and a nucleophile were mixed, due to rapid formation of (IId) (Scheme 1).

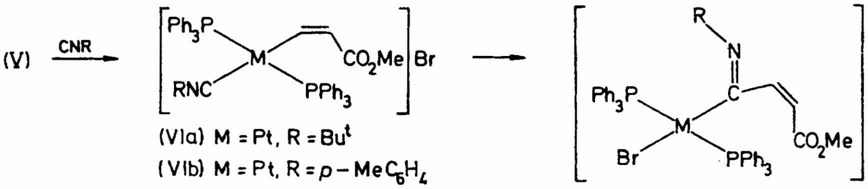
The first-order rate constants, 1.05×10^{-4}, 1.98×10^{-4}, and $3.51 \times 10^{-4}\ \mathrm{s}^{-1}$, obtained at 0, 10, and 20 °C, respectively (in PhCl), afford an activation energy of 9.4 ± 0.5 kcal mol^{-1} and an activation entropy of -22 ± 1 cal $\mathrm{K}^{-1}\ \mathrm{mol}^{-1}$.* The large negative entropy value may be associated with a solvent-assisted alkyl-migration mechanism similar to that proposed for carbonylation of $[\mathrm{MnMe(CO)_5}]$ [14] and $[\mathrm{MoMe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3]$, [16] which obey a similar rate law with comparable energetics.[12] However, the observed independence of rate on the nature of the nucleophile L excludes the possibility of co-ordination of a solvent molecule to the metal. Hence the role of solvent molecules is to assist polarisation of the Pd–X bond rather than to act as nucleophiles. We conclude that the reaction involves rate-determining alkyl migration to form (IV) and subsequent rapid reactions to form (II) or (III) (Scheme 1).

The rate of insertion increases with increasing nucleophilicity of the migrating carbon (as evidenced by the relatively slow rate found for the carboxyvinylmetal complex, see below) and with increasing electrophilicity of the recipient isocyanide ligand (aryl > alkyl isocyanide [17]). A self-consistent picture emerges from the various results, and it seems reasonable to assume that any effect which increases the nucleophilicity of the alkyl carbon and/or the electrophilicity of the isocyanide group would lower the energy of the transition state. Such an effect can be expected in a solvent-participated charge separation $\mathrm{M^+X^-}$; it would increase the effective negative charge on the alkyl carbon atom bonded to the metal and simultaneously decrease the electron density on the isocyanide carbon. Complete ionisation of an M–X bond occurs in platinum(II) complexes [equation (3)], whereas for $\mathrm{Pd^{II}}$ the halogen dissociation to the outer sphere has not been observed as a discrete step. The insertion rate into *trans*-$[\mathrm{PtX(R)L_2}]$ is generally lower than that of the palladium(II) analogue. It appears that extensive ionisation of a M–X bond is not necessarily associated with ready insertion. However, a rationale for the relatively slow insertion into the platinum(II) complexes may be found in the enhanced stability of the $\mathrm{Pt^{II}}$–R bond and/or the decreased electrophilicity of the CNR group. The sequence Cl > Br > I observed for the insertion into *trans*-$[\mathrm{PdX(R)L_2}]$ reflects the electronegativity effect which is exerted bilaterally on the alkyl carbon atom and the isocyanide ligand.

Studies on insertion into σ-vinyl–metal bonds are important, since the moderate nucleophilicity of the vinyl carbon atom slows down the insertion rate so that the reaction sequence can be followed in detail by means of ^{1}H n.m.r. spectroscopy. In addition, the stereochemistry provides further insight into the mechanism.


(2)

(Va) M = Pd
(Vb) M = Pt


(3)

(VIa) M = Pt, R = Bu^t
(VIb) M = Pt, R = p-MeC$_6$H$_4$

(VIIa) M = Pd, R = p-MeC$_6$H$_4$
(VIIb) M = Pt, R = p-MeC$_6$H$_4$

The oxidative addition of methyl *cis*-β-bromoacrylate to $[\mathrm{M(PPh_3)_4}]$ (M = Pd or Pt) gave the corresponding *trans*-(*cis*-methoxycarbonylvinyl) complexes, (V). Insertion of $\mathrm{CNC_6H_4Me}$-*p* into (V) occurs, producing the corresponding monoimino-complex with retention of the geometry of the double bond. *cis* Geometry is deduced for (VII) from the small coupling constants of the olefinic protons ($^3J_{\mathrm{ab}}$ 2.6—3.7 Hz) compared to those observed for (IX) ($^3J_{\mathrm{ab}}$ *ca.* 16 Hz). Addition of isocyanide to (Va) occurred at low temperature to give the ionic adducts (VI). However, use of CNBu^t did not produce the insertion product even when an excess of the isocyanide was employed. The difference in reactivity between $\mathrm{CNC_6H_4Me}$-*p* and CNBu^t may be accounted for by steric and electronic effects. Thus the steric bulk would be unfavourable for formation of a five-co-ordinate transition state [(A), see below]. However, if the insertion proceeds according to a unimolecular mechanism, as is the case for $[\mathrm{PdX(R)(CNBu^t)_2}]$, this

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* 1 cal = 4.184 J.

[17] A. Nakamura, Y. Tatsuno, and S. Otsuka, *Inorg. Chem.*, 1972, **11**, 2058.

steric effect will not operate or will be insignificant. This view is borne out as described later [reaction (6)].

Addition of the bromoacrylate to the labile tetrahedral complex $[Pt(CNBu^t)_2(PPh_3)_2]$ [18] occurred readily giving solely (VIa) without an insertion product. Possibly the addition is preceded by dissociation of one $CNBu^t$ molecule followed by concerted addition of the vinyl halide, an S_N2 type reaction, as manifested in the retention of configuration of the double bond.

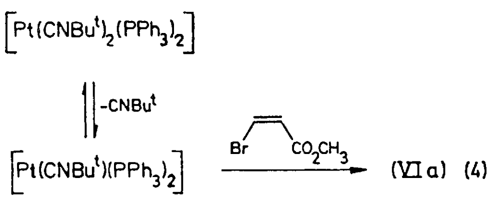
TABLE 2

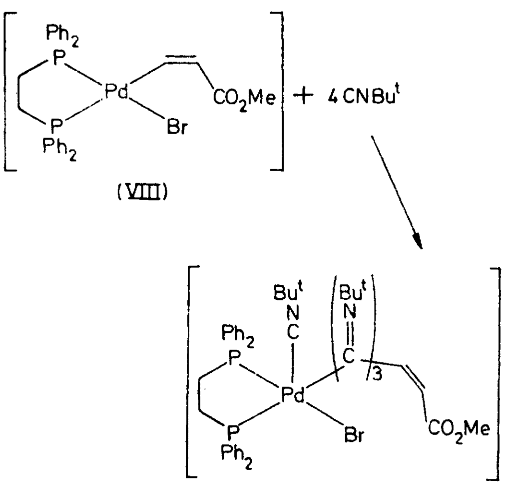
I.r. (recorded in Nujol) and n.m.r. data (in $CDCl_3$)

Complex	I.r. bands (cm^{-1}) (C≡N)	(C=N)	(CO)	(C=C)	N.m.r.[a]
$[PdBr(CH{:}CH{\cdot}CO_2Me)(PPh_3)_2]$ (Va)			1 695	1 570	3.46 (s, OMe), 5.03 [d/t, (–CH=), J_{ab} 7.9, J(PH) 0.5], 7.4—7.7 (m, C_6H_5)
$[PtBr(CH{:}CH{\cdot}CO_2Me)(PPh_3)_2]$ (Vb)			1 700	1 570	3.38 (s, OMe), 5.43 [d/t, (–CH=), J_{ab} 10.5, J(PtH) 136], 7.3—7.7 (m, C_6H_5)
$[Pt(CH{:}CH{\cdot}CO_2Me)(CNBu^t)(PPh_3)_2]Br$ (VIa)	2 250		1 690	1 570	3.37 (s, OMe),[b] 5.83 [d(H_b), J_{ab} 11.8 ,J(PH) 1.3, J(PtH) 90.5], 0.66 (s, Bu^t), 7.55 (m, C_6H_5)
$[PdBr\{C(CH{:}CH{\cdot}CO_2Me){:}NC_6H_4Me\}(PPh_3)_2]$ (VIIa)		1 620	1 705	1 550	3.57 (s, OMe), 2.37 (s, $C_6H_4CH_3$) 6.43, 6.96 [d, (–CH=), J_{ab} 3.7], 7.3 (m, C_6H_5)
$[PtBr\{C(CH{:}CH{\cdot}CO_2Me){:}NC_6H_4Me\}(PPh_3)_2]$ (VIIb)		1 630	1 715	1 545	3.58 (s, OMe), 2.35 (s, $C_6H_4CH_3$), 6.52, 7.17 [d, (–CH=), J_{ab} 2.6], 7.3 (m, C_6H_5)
$[PtBr(CH{:}CH{\cdot}CO_2Me)(CNBu^t)_2]$ (Xa)	2 200[c]		1 695		7.18 [d (H_b), J(PtH_b) 144], 8.42 (H_a), J_{ab} 9.5] [d]
$[\{PtBr[C(CH{:}CH{\cdot}CO_2Me){:}NBu^t](CNBu^t)\}_2]$ (IXb)	2 180 (sh)				6.76, 9.12 [d, (–CH=), J_{ab} 16], 1.04 (s, Bu^t) [d]
$[\{PdBr[C(CH{:}CH{\cdot}CO_2Me){:}NBu^t](CNBu^t)\}_2]$ (IXa)	2 200	1 625	1 705	1 565	3.60 (s, OMe), 6.59, 7.82 [d, (–CH=) J_{ab} 15.8], 0.92, 1.55 (s, Bu^t)

[a] P.p.m. from $SiMe_4$ as internal reference; the multiplicity and assignment are indicated in parentheses. J_{ab} (in Hz) refers to $CH_a{:}CH_b{\cdot}CO_2Me$. [b] Recorded in C_6D_6. [c] Unassignable to either (IXb) or (Xa). [d] In addition, there were signals at 3.58, 3.56 (s, OMe) and 0.76 p.p.m. (two, s Bu^t) unassignable to either (IXb) or (Xa).

Multi-insertion of $CNBu^t$ occurred with the complex $[PdBr(CH{:}CH{\cdot}CO_2Me)(dppe)]$, (VIII). Substitution of the bromo-ligand in (VIII) with $CNBu^t$ is facile, and may be rationalised in terms of the *cis* alignment of the vinyl and isocyanide ligands. However, this may be an oversimplification. For reactions (4) and (5), it is possible to assume five-co-ordinate transition states, (A) and (B), with a similar *cis* alignment of the vinyl and $CNBu^t$ groups. [We postulate that *trans*-configuration (A) is more stable than the *cis*-isomer (A′). In the absence of detailed information about the structure of the transition state, it is meaningless to consider the isomer (B′) with a presumably distorted trigonal-bipyramid structure.] It is not possible to account for the reluctance of (VIa) to undergo the insertion in terms of the *trans* geometry. We believe that the dominant factor governing the susceptibility for the insertion reaction is either the propensity to five-co-ordination or the electronic effect exerted on the migrating carbon and the isocyanide ligand in the transition state. The electronic effect is in turn influenced by the stereochemical disposition of the auxiliary ligands. [In (B), either the vinyl or the isocyanide group cannot avoid being positioned coplanar with one of the P atoms, while this is not true in (A).]





(5)

On treating ' $Pd(CNBu^t)_2$ ' with the bromoacrylate at room temperature, a dimeric insertion product with a *trans* double bond was obtained. Similar treatment of

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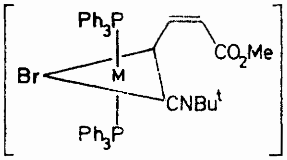
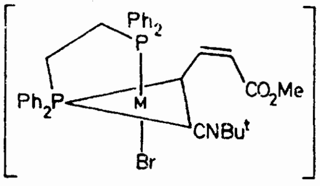
[18] G. A. Larkin, R. Mason, and M. G. Wallbridge, *Chem. Comm.*, 1971, 1054.

[19] M. Green, J. A. Haward, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 3.

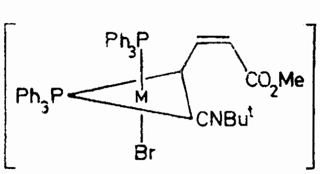
[{Pt(CNBu^t)$_2$}$_3$] [19] with the bromoacrylate gave pale yellow crystals, the ^{1}H n.m.r. spectrum (in C$_6$D$_6$) of which showed two Bu^t proton singlets assignable to the terminal CNBu^t of (Xa) and (IXb) and another singlet (δ 1.04 p.p.m.) due to the imino-group of (IXb). The spectrum also contained two ester methyl singlets, two vinyl proton doublets [*J*(*trans*) 16 Hz] at δ 6.76 and 9.12 p.p.m., and another two vinyl proton doublets [*J*(*cis*) 9.5 Hz] at δ 7.18 and 8.42 p.p.m. The doublet at δ 7.18 p.p.m. was accompanied by platinum satellites [^3J(PtH) 144 Hz] indicating the presence of a *cis*-vinyl group σ bonded to Pt^{II}. Thus the product is a mixture of the simple adduct (Xa) with retention of the geometry of the double bond and the insertion product (IXb) with inversion of the double bond as was the case for the palladium complex (IXa). The result indicates qualitatively a slower insertion rate of the Pt^{II} complex compared to that of Pd^{II}.



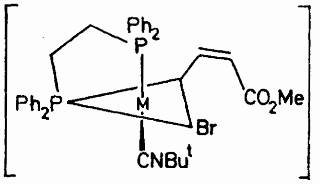
(A)



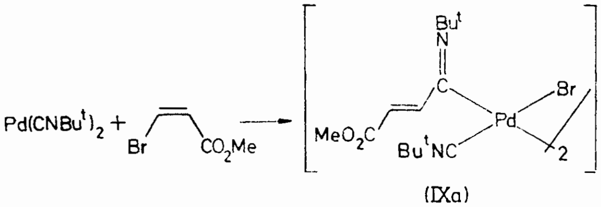
(B)



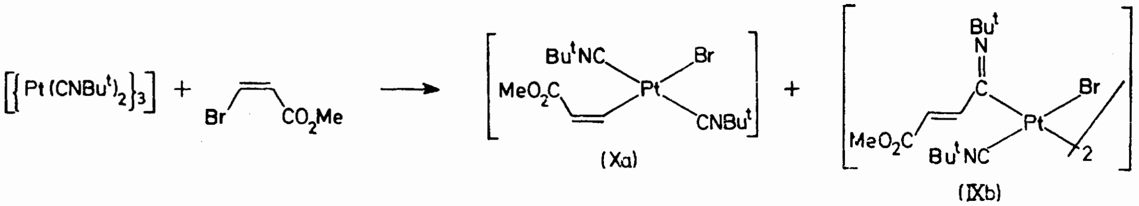
(A′)



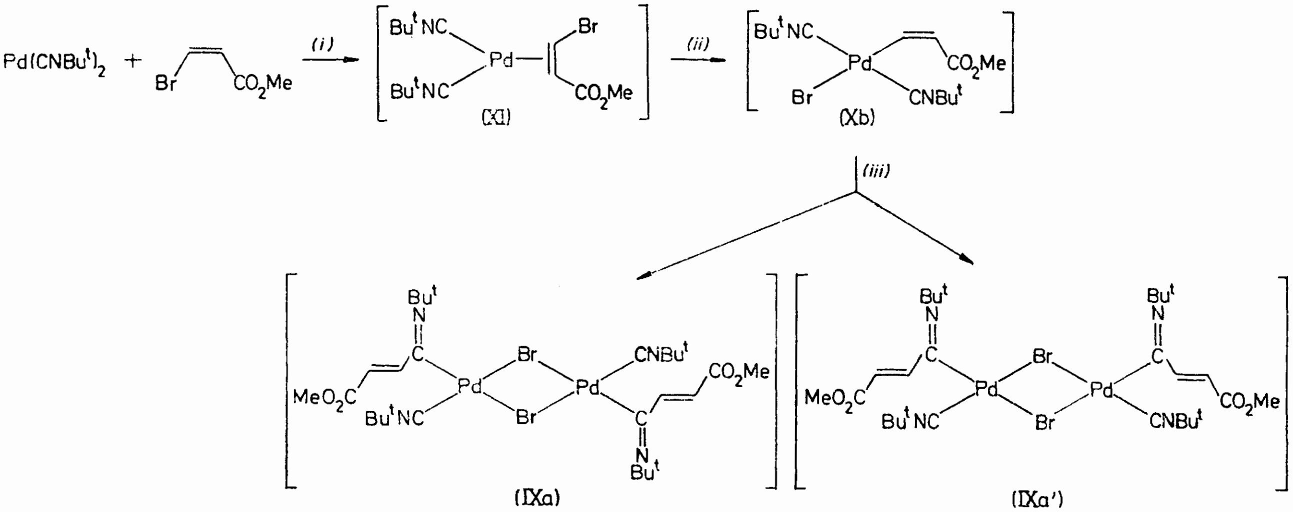
(B′)



(6)



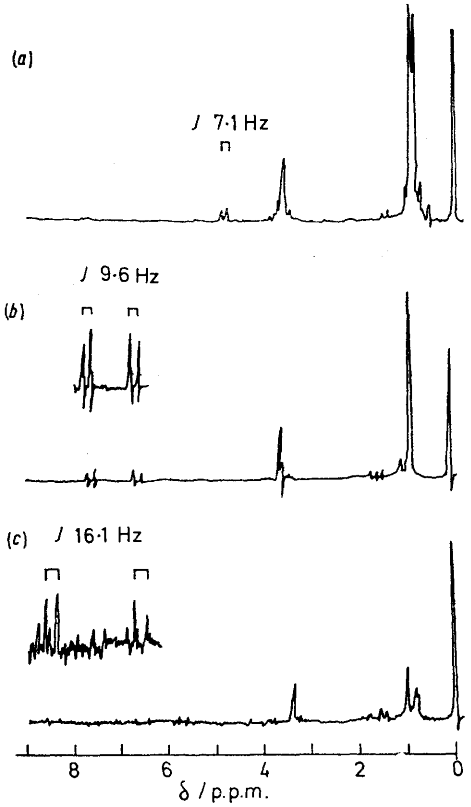
(7)



SCHEME 2 (*i*), −62 °C; (*ii*), 1 °C; (*iii*), 24 °C

The whole sequence of reaction (6) was followed by recording the ^{1}H n.m.r. spectrum of a solution (in [^{2}H$_8$]toluene) containing 'Pd(CNBu^t)$_2$' and BrCH:CH·CO$_2$Me in a 1 : 2.6 mol ratio (Scheme 2, Figure). At −62 °C in [^{2}H$_8$]toluene, signals assignable to the olefin complex (XI) were observed {δ 0.96 and 0.78 [C(CH$_3$)$_3$, s, 18 H], 3.50 [CH$_3$OC(:O), s, 3 H], and 4.75 p.p.m. [–CH=, d, 1 H, *J*(HH) 7.1 Hz]}. One of the doublets of the vinyl protons overlapped with the ester methyl proton signals centred at δ 3.50 p.p.m. The spectrum also contained signals due to the unchanged acrylate at δ 3.15 [CH$_3$OC(:O), s, 3 H] and 6.03 and 6.24 p.p.m.

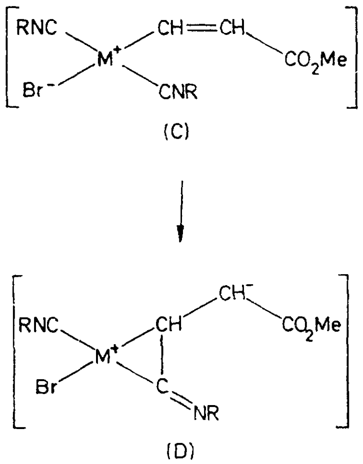
[–CH=, d, 1 H each, *J*(HH) 8.6 Hz]. On slowly increasing the temperature, the spectrum at −30 °C showed broadening of the co-ordinated and free vinyl proton signals, suggestive of an olefin ligand-exchange reaction. The two Bu^t proton signals coalesced into a slightly broad singlet at δ 0.92 p.p.m., indicating equivalence of the two $CNBu^t$ ligands. A new set of signals of very low intensities appeared above −30 °C, and at 1 °C they became sharp peaks at δ 7.57 and 6.57 [=CH–, d, 2 H, *J*(HH) 9.6 Hz], 3.53 [$CH_3OC(\dot{:}O)$, s, 3 H], and 0.86 p.p.m. [$C(CH_3)_3$, s, 9 H], corresponding to the adduct (Xb) in which the geometry of the double bond is retained. When the temperature reached 24 °C, the spectrum consisted essentially of resonances assignable to (IXa) and (IXa′) {δ 1.00 and 0.92 [$C(CH_3)_3$, s], 6.58, 8.48, and 8.66 (=C*H*–, d, *J* 16.1 Hz), and 3.53 p.p.m. [$CH_3OC(\dot{:}O)$, s]}. The olefin proton-coupling constant of 16 Hz indicates a *trans*-olefin configuration in the product, and the two Bu^t proton signals and the three olefin proton signals suggest a mixture of the geometric isomers (IXa) and (IXa′).



^1H N.m.r. spectra (60 MHz) of a mixture of $Pd(CNBu^t)_2$ and *cis*-$CHBr\dot{:}CH{\cdot}CO_2Me$ at −61 (*a*), 1 (*b*), and 24 °C (*c*). Resonances due to the free bromoacrylate are not shown for clarity

The *cis–trans* isomerisation in the course of the insertion reaction deserves comment. In the unimolecular insertion reaction of *trans*-$[PdX(R)(CNBu^t)_2]$ an important process is, as described, the polarisation of the palladium–alkyl bond to facilitate nucleophilic attack of the alkyl carbanion on the isocyanide carbon atom. In the transition state, a contribution of dipolar structure (D) would lead to ready isomerisation to the *trans* double bond. The fact that the insertion reaction into *trans*-$[PtX(R)(PPh_3)_2]$ [reaction (3)] is not accompanied by isomerisation of the double bond is also consistent with this mechanism. Thus the effective positive charge of the central metal co-ordinated to two electron-donating phosphorus atoms is well neutralised compared to that co-ordinated to isocyanide molecules.[20] Hence the extent of charge separation is much reduced so that the double-bond character is retained during the insertion. Isomerisation of co-ordinated olefins could occur by a dipolar mechanism.[21,22] In the *cis*-methoxycarbonylvinyl complexes (V) the α-carbon atom (from the methoxycarbonyl carbon) should carry a partial negative charge. The fact that the geometry of the double bond is retained for adducts (V) indicates that the polarisation of the double bond in (C) is insufficient to cause rotation of the double bond. A radical mechanism cannot rationalise the difference in this isomerisation behaviour.

From the above discussion it is possible to draw several conclusions. Important factors facilitating the insertion reaction into square-planar complexes of the type $[MX(R)L_2]$ are: (*i*) the carbon atom of the migrating group should be of considerable nucleophilicity; (*ii*) the isocyanide ligand should be electrophilic; and (*iii*) the auxiliary ligands X and L are effective in assisting the reaction if they elicit electronic effects in favour of conditions (*i*) and/or (*ii*). It should also be noted that the nature of the ligand L exerts a decisive influence on the reaction mechanism and that steric effects would be more significant in an associative mechanism than in a unimolecular one.



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EXPERIMENTAL

All reactions and manipulations involving organometallic complexes were made under a pure nitrogen atmosphere. N.m.r. spectra were recorded on JEOL JNM-4H-100 or JNM-C-60 HL spectrometers, and i.r. spectra on a Hitachi–Perkin-Elmer 225 spectrometer. The starting materials, [Pd(PPh$_3$)$_4$],[23] [Pt(PPh$_3$)$_4$],[24] [Pt(CNBu^t)$_2$(PPh$_3$)$_2$],[18] Pd(CNBu^t)$_2$,[25] [{Pt(CNBu^t)$_2$}$_3$],[19] and methyl *cis*-β-bromoacrylate [26] were prepared according to known methods.

Additions.—Alkyl halides to Pd(CNBu^t)$_2$. To a suspension of Pd(CNBu^t)$_2$ (560 mg, 2.0 mmol) in n-hexane (30 cm^3) was added PhCH$_2$X (X = Br or I) (2.3 mmol) at −78 °C. After stirring for 2 h and allowing the temperature to reach ambient, the precipitates formed were isolated, washed with n-hexane, and dried *in vacuo* to give *trans*-[PdX(CH$_2$Ph)(CNBu^t)$_2$] [(Ia; X = I), yellow, 94%, m.p. 73—74 °C (decomp.); (Ib; X = Br), beige, 50%, m.p. 149—150 °C (decomp.)] [Found: C, 49.6; H, 6.3; N, 7.0. C$_{17}$H$_{25}$IN$_2$Pd, (Ia), requires C, 49.4; H, 6.2; N, 6.8. Found: C, 44.2; H, 5.6; N, 6.3. C$_{17}$H$_{25}$BrN$_2$Pd, (Ib), requires C, 46.0; H, 5.7; N, 6.3%]. Under the same conditions, benzyl chloride gave no adduct; however, prolonged stirring for 4 h at room temperature gave an insertion product, [{Pd[C(CH$_2$Ph):NBu^t](CNBu^t)Cl}$_2$], (IIIc), m.p. 100—102 °C (Found: C, 54.9; H, 7.2; N, 8.8. C$_{34}$H$_{50}$Cl$_2$N$_4$Pd$_2$ requires C, 54.4; H, 7.7; N, 8.7%). The initial rate of addition of PhCH$_2$X to Pd(CNBu^t)$_2$ in PhCl was compared for X = Br and Cl by means of ^{1}H n.m.r. spectroscopy and a faster rate was found than for the iodide.

Methyl cis-β-*bromoacrylate to* M(CNBu^t)$_2$ (M = Pd *or* Pt). Methyl *cis*-β-bromoacrylate (90 µl, 0.5 mmol) was added to a suspension of Pd(CNBu^t)$_2$ (120 mg, 0.4 mmol) in diethyl ether (10 cm^3) at −65 °C. The mixture was stirred for several hours, the temperature being allowed to reach that of the room. The solvent was removed by decantation, and the residue was washed with n-hexane and dried *in vacuo* to give a pale yellow *powder* (150 mg, 80%), m.p. 118—121 °C(decomp.). This was a mixture of two geometrical isomers of insertion products, [{PdBr[C(*trans*-CH:CH·CO$_2$Me):NBu^t](CNBu^t)}$_2$], (IXa, a′) (Found: C, 38.4; H, 5.3; N, 6.2. C$_{28}$H$_{46}$Br$_2$N$_4$O$_4$Pd$_2$ requires C, 38.4; H, 5.3; N, 6.4%). The reaction of Pd(CNBu^t)$_2$ (50 mg, 0.18 mmol) with the bromoacrylate (50 µl, 0.47 mmol) was monitored with ^{1}H n.m.r. spectroscopy over a range of temperature in order to follow the whole sequence of the reaction (see Figure and text). A similar treatment of [{Pt(CNBu^t)$_2$}$_3$] (265 mg, 0.24 mmol) with methyl *cis*-β-bromoacrylate (150 µl, 1.0 mmol) in diethyl ether at room temperature gave pale yellow *crystals* of formula [PtBr(CH:CH·CO$_2$Me)(CNBu^t)$_2$] (95 mg, 40%), m.p. 129—131 °C (from dichloromethane–n-hexane) (Found: C, 31.6; H, 4.4; Br, 15.1; N, 5.4. C$_{14}$H$_{23}$BrN$_2$O$_2$Pt requires C, 31.9; H, 4.4; Br, 15.2; N, 5.3%). This product was an approximately equimolar mixture of the simple adduct [PtBr(*cis*-CH:CH·CO$_2$Me)(CNBu^t)$_2$], (Xa), and the dimeric insertion product [{PtBr[C(*trans*-CH:CH·CO$_2$Me):NBu^t](CNBu^t)}$_2$], (IXb) (see text).

Methyl cis-β-*bromoacrylate to* [M(PPh$_3$)$_4$] (M = Pd *or* Pt). To a suspension of [Pd(PPh$_3$)$_4$] (680 mg, 0.6 mmol) in toluene (10 cm^3) was added methyl *cis*-β-bromoacrylate (200 µl, 1.2 mmol) at room temperature. After stirring for 2 h, the colourless solution was chilled and treated with n-hexane to give 370 mg (78%) of *trans*-[PdBr(*cis*-CH:CH·CO$_2$Me)(PPh$_3$)$_2$] (Va) as a colourless powder, m.p. 132—133° (decomp.) (Found: C, 62.7; H, 4.7; Br, 9.6. C$_{40}$H$_{35}$BrO$_2$P$_2$Pd·0.5MeC$_6$H$_5$ requires C, 62.1; H, 4.7; Br, 9.5%). The presence of the crystallisation solvent was detected by means of ^{1}H n.m.r. spectroscopy. Similarly obtained from [Pt(PPh$_3$)$_4$] were colourless crystals (80%) of *trans*-[PtBr(*cis*-CH:CH·CO$_2$Me)(PPh$_3$)$_2$], (Vb), m.p. 105 °C (decomp.) (Found: C, 54.4; H, 3.9. C$_{40}$H$_{35}$BrO$_2$P$_2$Pt requires C, 54.3; H, 4.0%).

Methyl cis-β-*bromoacrylate to* [Pt(CNBu^t)$_2$(PPh$_3$)$_2$]. To a solution of [Pt(CNBu^t)$_2$(PPh$_3$)$_2$] (240 mg, 0.3 mmol) in benzene (5 cm^3) was added methyl *cis*-β-bromoacrylate (75 µl, 0.4 mmol) at room temperature. The mixture gave, after stirring for 1 h, an insoluble colourless powder (150 mg, 53%) of *trans*-[Pt(*cis*-CH:CH·CO$_2$Me)(CNBu^t)(PPh$_3$)$_2$]Br, (VIa), m.p. 112—114 °C (decomp.) (Found: C, 58.9; H, 4.9; N, 1.4. C$_{50}$H$_{53}$BrN$_2$O$_2$P$_2$Pt·C$_6$H$_6$ requires C, 58.5; H, 4.8; N, 1.3%).

Reactions.— trans-[PtBr(cis-CH:CH·CO$_2$Me)(PPh$_3$)$_2$] *with* CNBu^t. On addition of CNBu^t (1.2 mmol) to *trans*-[PtBr(*cis*-CH:CH·CO$_2$Me)(PPh$_3$)$_2$] (0.23 mmol) in toluene at room temperature, 0.15 g (65%) of the colourless ionic bromide complex (VIa) was isolated. When complex (VIa) was heated under reflux in toluene for 3 h the original complex was obtained.

trans-[MBr(cis-CH:CH·CO$_2$Me)(PPh$_3$)$_2$] (M = Pd *or* Pt) *with* CNC$_6$H$_4$Me-p. Addition of CNC$_6$H$_4$Me-*p* (1.7 mmol) to *trans*-[PtBr(*cis*-CH:CH·CO$_2$Me)(PPh$_3$)$_2$] (0.34 mmol) in toluene at 40 °C gave a colourless *powder* of the adduct *trans*-[Pt(*cis*-CH:CH·CO$_2$Me)(CNC$_6$H$_4$Me-*p*)(PPh$_3$)$_2$]Br, (VIb). The crude adduct was washed with n-hexane to remove free CNC$_6$H$_4$Me-*p* and heated in hot stirred toluene at 100 °C for 30 min. Treating the chilled reaction mixture with n-hexane gave 85 mg (25%) of an insertion product, *trans*-[PtBr{C(*cis*-CH:CH·CO$_2$Me):NC$_6$H$_4$Me}(PPh$_3$)$_2$], (VIIb), as pale yellow *crystals*, m.p. 133—134 °C (decomp.) (from toluene–n-hexane) (Found: C, 57.6; H, 4.1; N, 1.3. C$_{47}$H$_{42}$BrNO$_2$PPt requires C, 57.6; H, 4.2; N, 1.4%). Similar treatment of *trans*-[PdBr(*cis*-CH:CH·CO$_2$Me)(PPh$_3$)$_2$] with CNC$_6$H$_4$Me-*p* in toluene at room temperature produced an insertion product, *trans*-[PdBr{C(*cis*-CH:CH·CO$_2$Me):NC$_6$H$_4$Me}(PPh$_3$)$_2$], (VIIa), as yellow *crystals*, m.p. 131—132 °C (decomp.) (43%) (Found: C, 65.1; H, 4.9; N, 1.2. C$_{48}$H$_{42}$BrNO$_2$PPd·MeC$_6$H$_5$ requires C, 65.7; H, 5.0; N, 1.3%).

[PdBr(cis-CH:CH·CO$_2$Me)(dppe)] *with* CNBu^t. To a suspension of 400 mg (0.6 mmol) of [PdBr(*cis*-CH:CH·CO$_2$Me)(dppe)], prepared from *trans*-[PdBr(*cis*-CH:CH·CO$_2$Me)(PPh$_3$)$_2$] and Ph$_2$PCH$_2$CH$_2$PPh$_2$ in toluene (10 cm^3), was added CNBu^t (0.2 cm^3, 2 mmol). The mixture, after stirring for 5 h at 80 °C, was chilled and treated with n-hexane to precipitate an orange-yellow powder. Purification of the powder by alumina column chromatography gave 80 mg (15%) of a multi-insertion product of formula [PdBr{(CNBu^t)$_4$(CH:CH·CO$_2$Me)}(dppe)] as orange-red *crystals*, m.p. 180 °C (decomp.) (from chloroform–diethyl ether) (Found: C, 54.2; H, 6.0; N, 4.9. C$_{50}$H$_{65}$BrN$_2$O$_2$P$_2$Pd·CHCl$_3$ requires C, 54.0; H, 5.9; N, 4.9%), δ 0.48, 1.36, 1.44, and 1.60 [C(CH$_3$)$_3$, s, 9 H] and 3.16 p.p.m. (OCH$_3$, s, 3 H).

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Measurement of Insertion Rates.—A chlorobenzene or a toluene solution containing *trans*-[PdMe(CNBu^t)$_2$I] and a nucleophile L [CNBu^t, PPh$_3$, or P(OPh)$_3$] was prepared below −40 °C and aliquot portions were transferred to n.m.r. tubes. The reaction rate can be conveniently followed at 0, 10, or 20 °C by the variation in intensities of the methyl and Bu^t proton resonances [*e.g.* C(CH$_3$)⁚N of the product]. Typical runs at 0—20 °C with initial concentrations of 0.0056 mol dm^{-3} for the complex and 0.106—0.636 mol dm^{-3} for CNBu^t showed, over 80% completion, a first-order dependence on the complex concentration and a zero-order dependence on the CNBu^t concentration (Table 1).

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