Mechanism of Migration of Ancillary Ligands in Binuclear Palladium(II) Allyl Complexes

Bruno Crociani *
Istituto di Chimica Generale, Via Archirafi 26, University of Palermo, Italy
Paolo Uguagliati and Umberto Belluco
Centro Chimica Composti Metallorganici Elementi Transizione C.N.R., Facoltà di Ingegneria, University of Padua, Italy
Marino Nicolini
Istituto di Chimica Generale, Facoltà di Farmacia, University of Padua, Italy

The kinetics and mechanism of the reaction between the binuclear cationic complexes $[L_2ClPd\{C(=NR^1)CR^3=NR^2\}Pd(\eta^3\text{-}CH_2CR^4CH_2)]ClO_4$ [1 ; $R^1 = R^2 = C_6H_4OMe\text{-}p$, R^3 = H, Me, or Ph, R^4 = H or Me, L = $P(C_6H_4X\text{-}p)_3$, X = Cl, H, or OMe; $R^1 = C_6H_4OMe\text{-}p$, $R^2 = R^3 = R^4$ = Me, L = PPh_3 or $PMePh_2$] and the anionic allyl derivatives $[NEt_3(CH_2Ph)][PdCl_2(\eta^3\text{-}2\text{-}R^4C_3H_4)]$, (A), leading to the binuclear zwitterionic compounds $[LCl_2Pd\{C(=NR^1)CR^3=NR^2\}Pd(\eta^3\text{-}CH_2CR^4CH_2)]$, (2), together with the neutral palladium–allyl products $[PdCl(\eta^3\text{-}2\text{-}R^4C_3H_4)L]$, (B), have been studied in 1,2-dichloroethane. This reaction, which involves exchange of the ancillary ligands L and Cl^- between the reactants (1) and (A), proceeds *via* two parallel steps with rate constants k_1 and k_2. The faster step consists of a rapid pre-equilibrium association (K) to give the intermediate (1 · · · A), which then rearranges slowly (k_2) *via* opening of the five-membered α-di-imino-cycle in a proposed three-metal transition state. The parallel slower step is formulated as a rate-determining (k_1) intramolecular rearrangement of (1) to a labile intermediate (1*), which reacts rapidly with (A) to yield the final products. For this step, the activation process is proposed to involve unassisted α-di-imino ring opening and dissociative exchange of L. The mechanism proposed is based on the activation parameters and on the rate effects exerted by the α-di-imino-substituents R^2, R^3, by the allyl group substituent R^4, and by the electronic properties of L. In general, the rate constants k_1, k_2 and the pre-equilibrium constant K decrease with increasing electron-releasing abilities of the *C*- and *N*-imino-substituents; k_2 is also depressed by increasing steric demands of the R^3 and R^4 groups. An increase in the electron-donor properties of L will also bring about a decrease in the overall reaction rate. The effects are generally related to the ease of opening and rearrangement of the σ,σ-*N,N*-chelated α-di-imine in (1) together with the lability of the Pd–L bond.

The interaction between different ligands bound to adjacent metal centres is currently believed to play a key role in the ability of polynuclear complexes to act as polyfunctional catalysts. A special type of interaction is the exchange of ancillary ligands that we have observed in binuclear complexes obtained from [1,2-bis(imino)alkyl]palladium(II) derivatives, equations (i) (L = PPh_3, S–S = S_2CNMe_2, R = $C_6H_4OMe\text{-}p$, M = Pd or Pt),[1] (ii) (L = PPh_3, $R^1 = C_6H_4OMe\text{-}p$, $R^2 = C_6H_4OMe\text{-}p$ or Me, cod = cyclo-octa-1,5-diene),[2] and (iii) (L = triarylphosphine, R^1,R^2,R^3 = alkyl or aryl, R^4 = H or Me).[3] Reaction (i) involves intramolecular exchange of the ligands dimethyldithiocarbamate and chloride between the two metal centres in the initially formed binuclear adducts.[1] Although reactions (ii) and (iii) appear formally as intermolecular processes, earlier preliminary studies suggest that the exchange proceeds with an essentially intramolecular mechanism, *via* a trinuclear transient or activated state, which in the case of reaction (iii) arises from interaction between the binuclear cationic and mononuclear anionic species in the ionic intermediate.[2–4] As a follow-up to a previous short communication,[4] we have carried out a systematic study of the mechanism of reaction (iii) aiming at assessing the nature of the steps involved and the factors affecting their relative rates.

Results and Discussion

The system under investigation is represented in the Scheme. The cationic substrates (1) were used as perchlorate salts while the allylic anion (A) (as the benzyltriethylammonium salt) was added in excess in order to provide pseudo-first-order conditions. Kinetic data, $k_{obs.}/s^{-1}$, for the reaction (1a) + (A) (R^4 = Me) at various temperatures are reported in Table 1 and those of the other systems examined are listed in Table 2.

A general feature of these data is a curvilinear dependence of $k_{obs.}$ values on the concentration of (A) with non-zero intercepts, as shown in curve (*a*) of the Figure. Such a depen-

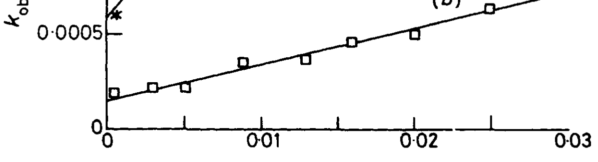
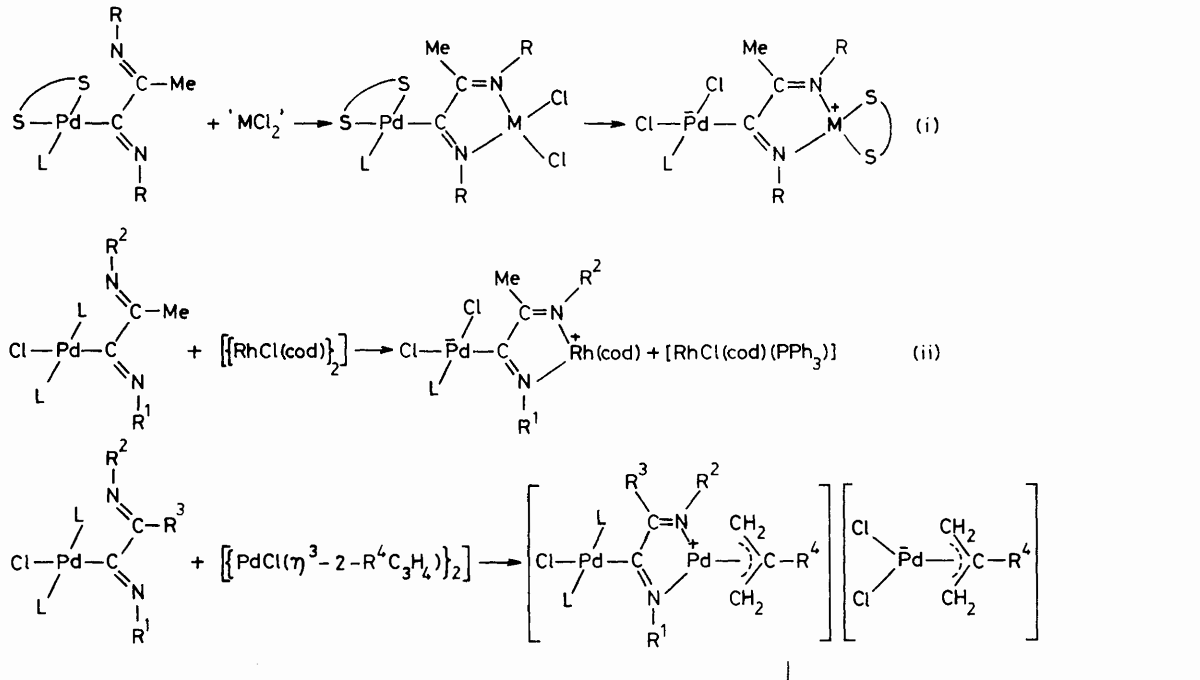
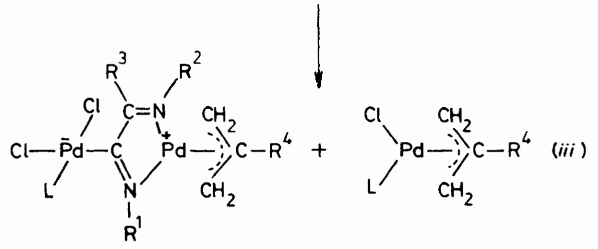
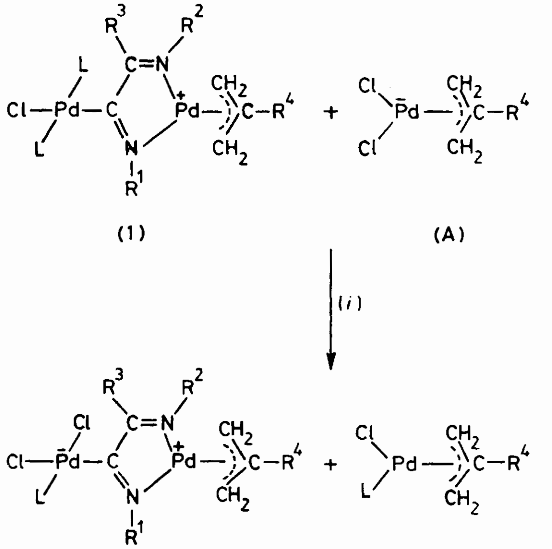


Figure. Dependence of $k_{obs.}$ on [(A)] for the reactions of (1a) [40 °C, curve (*a*)], (1g) [40 °C, curve (*b*)], and (1c) [30 °C, curve (*c*)] with (A; R^4 = Me). Lines (*a*) and (*b*) are the best fits to equations (v) and (vii), respectively; (*c*) represents the average value in equation (viii). Symbols on curves denote experimental data points







(1) (A)

(2) (B)

	L	$R^1 = R^2$	R^3	R^4
(1a)	PPh_3	C_6H_4OMe-*p*	Me	Me
(1b)	PPh_3	C_6H_4OMe-*p*	H	Me
(1c)	PPh_3	C_6H_4OMe-*p*	Ph	Me
(1d)	PPh_3	C_6H_4OMe-*p*	Me	H
(1e)	$P(C_6H_4OMe$-*p*$)_3$	C_6H_4OMe-*p*	Me	Me
(1f)	$P(C_6H_4Cl$-*p*$)_3$	C_6H_4OMe-*p*	Me	Me
(1g)	PPh_3	$R^1 = C_6H_4OMe$-*p* $R^2 = Me$	Me	Me

Scheme. (*i*) 1,2-Dichloroethane as solvent, unless otherwise stated; appropriate amounts of NBu_4ClO_4 were added in order to keep the total concentration of ionic species (F) constant at 3×10^{-2} mol dm^{-3}

dence, combined with electronic and proton n.m.r. spectral evidence to be discussed later, is consistent with the mechanism in equation (iv) with the corresponding rate expression (v).

$$\begin{tikzcd} (1) + (A) \arrow[r, shift left, "K"] \arrow[dr, "k_1"'] & (1\cdots A) \arrow[l, shift left] \arrow[r, "k_2"] & (2) + (B) \\ & (1^*) \arrow[ur, "\text{fast, + (A)}"'] & \end{tikzcd} \qquad \text{(iv)}$$

$$k_{\text{obs.}} = \frac{k_1 + k_2K[(A)]}{1 + K[(A)]} \qquad \text{(v)}$$

The formation of the final products occurs *via* two parallel stages, characterized by the rate-determining terms k_1 and k_2. The k_2 step is preceded by a fast association pre-equilibrium between the cationic binuclear complex (1) and the anion (A). The k_1 step can be envisaged as the limiting case of the general steady-state approach in equation (vi) where $k_3[(A)] \gg k_{-1}$.

$$(1) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (1^*) \xrightarrow{k_3,\ + (A)} (2) + (B) \qquad \text{(vi)}$$

From Table 2 there also emerge two particular cases of the $k_{\text{obs.}}$ *vs.* [(A)] dependence. For the systems (1e) and (1g) + (A) (R^4 = Me) the linear dependence (vii) holds, since

$$k_{\text{obs.}} = k_1 + k_2K[(A)] \qquad \text{(vii)}$$

$K[(A)] \ll 1$ throughout the concentration range of (A) explored [curve (*b*) of Figure]. For the system (1c) + (A)

Table 1. Rate data for the reaction of substrate (1a) with $[NEt_3(CH_2Ph)][PdCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]$, (A), in 1,2-dichloroethane at a total ionic species (F) concentration of 3×10^{-2} mol dm^{-3}. Uncertainties quoted are standard errors of estimate

θ_c/°C	10^3[(A)]/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	θ_c/°C	10^3[(A)]/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
30 [a]	0.5	1.17	40 [b]	0.5	6.10
	3.0	1.52		3.0	8.70
	5.0	1.75		6.0	10.62
	7.5	2.18		9.0	11.65
	10.0	2.40		13.0	13.87
	15.0	2.90		17.0	15.37
	20.0	3.22		22.0	16.67
	25.0	3.57		27.0	18.17
	28.0	3.90			
35 [c]	0.5	2.67	44 [d]	0.5	11.30
	3.0	3.72		3.0	15.83
	5.0	4.28		5.0	18.17
	7.5	4.97		7.5	21.50
	11.0	5.87		11.0	25.00
	16.0	6.72		16.0	27.50
	20.0	7.42		17.0	27.83
	21.0	7.55		20.0	29.67
	25.0	8.20		23.0	32.00
	27.0	8.57		27.0	33.33

[a] $k_1 = (1.08 \pm 0.07) \times 10^{-4}$, $k_2 = (8.0 \pm 1) \times 10^{-4}$ s^{-1}, $K = 23.2 \pm 5$ dm^3 mol^{-1}. [b] $k_1 = (5.9 \pm 0.3) \times 10^{-4}$, $k_2 = (29.3 \pm 2) \times 10^{-4}$ s^{-1}, $K = 39.4 \pm 7$ dm^3 mol^{-1}. [c] $k_1 = (2.55 \pm 0.07) \times 10^{-4}$, $k_2 = (15.8 \pm 0.8) \times 10^{-4}$ s^{-1}, $K = 29.3 \pm 3$ dm^3 mol^{-1}. [d] $k_1 = (10.5 \pm 0.5) \times 10^{-4}$, $k_2 = (49.8 \pm 3) \times 10^{-4}$ s^{-1}, $K = 49.8 \pm 8$ dm^3 mol^{-1}.

Table 2. Rate data for the reaction of substrates (1) with $[NEt_3(CH_2Ph)][PdCl_2(\eta^3\text{-}2\text{-}R^4C_3H_4)]$, (A), in 1,2-dichloroethane at a total ionic species (F) concentration of 3×10^{-2} mol dm^{-3}. Uncertainties quoted are standard errors of estimate

Substrate	R^3	R^4	θ_c/°C	10^3[(A)]/ mol dm^{-3}	$10^4k_{obs.}$/ s^{-1}	Substrate	R^3	R^4	θ_c/°C	10^3[(A)]/ mol dm^{-3}	$10^4k_{obs.}$/ s^{-1}
(1b) [a]	H	Me	30	0.5	2.30	(1e) [b]	Me	Me	45	0.5	0.53
				2.5	3.67					2.0	0.60
				5.0	5.07					5.0	0.73
				7.5	6.03					10.0	0.97
				10.0	7.17					15.0	1.17
				14.0	8.83					19.0	1.38
				18.0	10.00					24.0	1.55
				22.0	11.28					25.0	1.62
				28.0	13.00	(1f) [g]	Me	Me	30	0.5	27.17
(1c) [e]	Ph	Me	30	3.0	16.30					2.0	28.67
				4.0	16.25					4.0	29.67
				9.0	16.10					5.0	30.30
				11.0	17.00					6.0	30.50
				13.0	17.10					7.0	31.00
				15.0	16.40					10.0	31.67
				20.0	17.20					14.0	32.50
(1d) [h]	Me	H	40	0.52	9.83					18.0	33.50
				1.03	10.50					21.0	33.67
				5.12	14.00					24.0	34.00
				10.24	17.17	(1g) [i]	Me	Me	40	0.5	1.77
				13.32	19.67					3.0	2.17
				17.41	21.17					5.0	2.33
				21.51	23.00					9.0	3.37
				25.61	23.67					13.0	3.77
				29.70	25.17					16.0	4.50
										20.0	5.03
										25.0	6.15
										28.0	6.80

[a] $k_1 = (2.1 \pm 0.1) \times 10^{-4}$, $k_2 = (30.9 \pm 2) \times 10^{-4}$ s^{-1}, $K = 21.4 \pm 2$ dm^3 mol^{-1}. [b] $k_1 = (0.51 \pm 0.01) \times 10^{-4}$ s^{-1} (see *c*), $k_2K = (4.41 \pm 0.06) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} (see *d*). [c] Intercept of linear plot of $k_{obs.}$ *vs.* [(A)]. [d] Slope of linear plot of $k_{obs.}$ *vs.* [(A)]. [e] $k_2 = (16.6 \pm 0.5) \times 10^{-4}$ s^{-1} (see *f*). [f] Average value with standard deviation from the mean (see text). [g] $k_1 = (26.8 \pm 0.2) \times 10^{-4}$, $k_2 = (37.0 \pm 0.3) \times 10^{-4}$ s^{-1}, $K = 95.5 \pm 10$ dm^3 mol^{-1}. [h] $k_1 = (9.3 \pm 0.2) \times 10^{-4}$, $k_2 = (39.7 \pm 2) \times 10^{-4}$ s^{-1}, $K = 37 \pm 5$ dm^3 mol^{-1}. [i] $k_1 = (1.57 \pm 0.08) \times 10^{-4}$ s^{-1} (see *c*), $k_2K = (1.82 \pm 0.05) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} (see *d*).

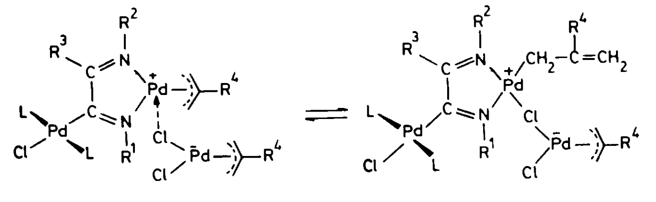
(R^4 = Me) the limiting value (viii) is already reached at the

$$k_{obs.} = k_2 \qquad \text{(viii)}$$

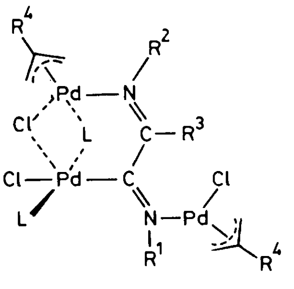
lowest concentration of (A) compatible with pseudo-first-order conditions, since now $K[(A)] \gg 1$ [curve (*c*) of Figure].

The establishment of a fast pre-equilibrium is shown by the marked and sudden change in the electronic spectrum of a solution of (1) upon addition of (A); this initial change is followed by a much slower variation with time corresponding to the progress of the reaction. The fast and reversible conversion (1) + (A) $\rightleftharpoons$ (1 ··· A) is maintained throughout the reaction and is in accord with the fact that we were able to detect the presence of *three* independently absorbing species, (1), (1 ··· A), and (2), in the spectral range 500—460 nm by abstract factor analysis of absorbance data.[5] [In this region, which was generally used for the monitoring of kinetics, the anion (A) and the product (B) do not absorb appreciably.]

Further evidence for the formation of the intermediate species (1 ··· A) is provided by the proton n.m.r. spectra of the equimolar mixtures (1)-(A) in $CDCl_3$ at 35 °C, which show that the allyl system in (1) is undergoing a fast *syn-anti* proton exchange essentially due to a fast $\eta^3 \rightleftharpoons \sigma$ conversion upon interaction with the anion (A).[3] In the absence of (A), the proton n.m.r. spectra of the cationic substrates (1), with ClO_4^- as counter ion, indicate the presence of ' static ' η^3-allyl groups only. The intermediate (1 ··· A) may be simply formulated as resulting from ion pairing *via* chloride bridging. This intermediate subsequently rearranges slowly (k_2) to give the final products *via* opening of the five-membered α-di-imino-ring, as indicated by rate effects of *C*- and *N*-imino-substituents (see below). According to previous reports on the ability of α-di-imines to act as bridging bidentate ligands,[2,6,7] we suggest an activation process for the k_2 step involving a three-metal transition state in which each imino-nitrogen is bound to a palladium allyl unit, as shown below.

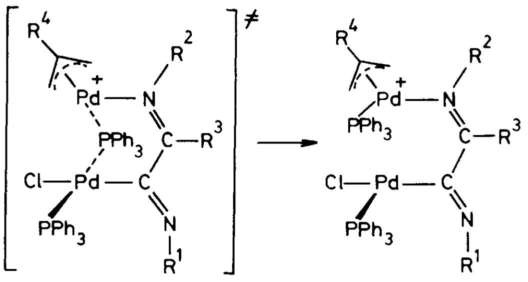


(1 ··· A)



Such an activated complex in which the exchange of the ancillary ligands proceeds in a concerted intramolecular way is in agreement with the rate effects of varying phosphine ligands L (see below) and with the small positive activation entropy for the k_2 step, as determined from the temperature dependence of rate data for the system (1a) + (A) (R^4 = Me) in Table 1 ($\Delta H_2^\ddagger = 100.4 \pm 1$ kJ mol^{-1}, $\Delta S_2^\ddagger = 28.5 \pm 4$ J K^{-1} mol^{-1}). The rearrangement of the intermediate (1 ··· A) implies a small net change in the number of degrees of freedom resulting from a balance of entropic effects in the conversion of a σ,σ-*N*,*N*-chelated α-di-imino group into a bridging system with simultaneous concerted exchange of L and Cl^- ligands.

The parallel step k_1 is likely to involve a slow intramolecular rearrangement of substrates (1) to the highly reactive intermediates (1*) which are then converted rapidly into the final products by the anion (A). Here, the rate effects of both *C*- and *N*-imino-substituents and L, together with the activation parameters for the system (1a) + (A) (R^4 = Me) ($\Delta H_1^\ddagger$ = 127.6 ± 2 kJ mol^{-1}, $\Delta S_1^\ddagger$ = 100.4 ± 6 J K^{-1} mol^{-1}), are consistent with both unassisted ring opening and dissociative exchange of L in which bond breaking predominates over bond making, as shown below.



(1*)

The unassisted α-di-imino five-membered ring opening of this process is reflected in the higher activation enthalpy than that of the parallel k_2 step.

As a general feature, the rate constants k_1 and k_2 and the pre-equilibrium constant *K* decrease with increasing electron-releasing abilities of the *C*- and *N*-imino-substituents. Thus, substitution of the methyl R^3 group in (1a) by a proton, to give (1b), brings about an increase in the reaction rate. When R^3 = Ph the k_2 term at 30 °C is doubled compared to the corresponding value for the (1a; R^3 = Me) at the same temperature. In this case, the *K* term is so high that a rate-limiting plateau is observed [equation (viii)]. Further, when the R^2 group in (1a; R^2 = C_6H_4OMe-*p*) is replaced by a methyl substituent, to give (1g), a marked decrease in the rate is observed and the k_1 term at 40 °C is reduced to about one fourth (see Table 2). This also causes such a drop in the *K* value as to give a linear dependence of $k_{obs.}$ *vs.* [(A)] as in equation (vii), thereby preventing any determination of the k_2 parameter. The electronic substituent effects on k_1 and k_2 fit nicely into our mechanistic picture since the stability of the chelated α-di-imino-cycle, whose opening and rearrangement are involved in the described activation processes, will increase with increasing electron-releasing power of R^2 and R^3, as was confirmed by dissociation-equilibrium studies of σ,σ-*N*,*N*-chelated α-di-imine ligands from complexes of the type $[M(\eta^3\text{-}2\text{-}R^4C_3H_4)(RN{=}CR'{-}CR''{=}NR)]ClO_4$[6] and $[M'X_2(RN{=}CR'{-}CR''{=}NR)]$[5b] (M = Pd or Pt; M' = Zn or Hg; X = Cl or Br; R = C_6H_4-OMe-*p* or CMe_3; R' = R'' = H or Me; R' = H, R'' = Me; R^4 = H or Me).

The drastic substituent effects on the pre-equilibrium constant mentioned above agree with the proposed formulation of the intermediate (1 ··· A), since increasing basicity of the 2-imino-nitrogen is expected to reduce the effective positive charge on the allylic palladium centre of the cation substrate, which will eventually result in a reduced interaction with the anion (A), *i.e.* in a lower *K* value. Consistently, the opposite effect is observed when the R^3 substituent is the electron-withdrawing Ph group. Further, the slight variation of *K* on going from (1a) to (1b) is in line with the small difference of inductive effects between the Me and H groups as R^3 substituents. The reactivity order for the k_2 step appears to be affected by the steric requirements of R^3. In fact, the observed trend (1b) > (1c) > (1a) at 30 °C is not the one expected on purely electronic grounds and originates from the more favourable electronic properties of the phenyl group being counterbalanced by its larger size, which militates against rotation around the C–C single bond of the α-di-imino-moiety following the ring-opening step, through steric interaction with the bulky ancillary ligands L. The influence of steric factors is also borne out by the higher k_1 and k_2 values for the reaction (1d) + (A) (R^4 = H) relative to those for (1a) + (A) (R^4 = Me) at 40 °C, as the steric interaction of the bulkier 2-methylallyl moiety with neighbouring groups will play an adverse role in both the activation processes, even though the pre-equilibrium constant K is hardly affected.

The rate parameters are markedly influenced also by the nature of the ancillary ligands L in substrates (1). When L = $P(C_6H_4OMe\text{-}p)_3$, complex (1e), the reaction proceeds at a much slower rate even at the highest temperature explored (45 °C), compared to the analogous reaction of (1a; L = PPh_3), with a linear kinetic expression of the type (vii), resulting from a strongly depressed K value. By contrast, when L = $P(C_6H_4Cl\text{-}p)_3$, complex (1f), the rates at 30 °C are considerably higher than those for (1a) at the same temperature. The observed increase in the k_1 term is *ca.* 27-fold, while k_2 and K are higher by a factor of *ca.* 4.

The observed reactivity order $P(C_6H_4Cl\text{-}p)_3 > PPh_3 > P(C_6H_4OMe\text{-}p)_3$ is essentially due to electronic factors, since the three phosphorus ligands have very similar steric requirements.[8] In other words, it appears that the exchange of ligands occurs more readily with decreasing electron-donor properties of the phosphines.[9] Such an effect lends further support to the proposed mechanism, as an increased electron density on the metal centre of the *trans*-PdCl(L)$_2$ unit will be transmitted to the α-di-imino-moiety in substrates (1) through the Pd–C_{imino} linkage, thereby stabilizing the five-membered cycle and reducing the effective positive charge on the allyl–palladium reaction site (*cf.* the effects of R^2 and R^3 substituents discussed above). Furthermore, electron-withdrawing *para*-substituents in the phosphine L are likely to enhance the ease of exchange by lowering the σ-donor properties of L, thereby loosening the Pd–L bond in the postulated transition state. (It is currently accepted that the M–P bond in tertiary phosphine complexes has a predominantly σ character.[10]) The latter argument would account for the larger increase experienced by k_1 relative to k_2 when the PPh_3 ligands of (1a) are replaced by $P(C_6H_4Cl\text{-}p)_3$, as in (1f), in view of the higher dissociative component of the activation process of step k_1. Consistently, the reaction of the complex (1; $R^1 = R^2 = C_6H_4OMe\text{-}p$, $R^3 = R^4$ = Me) containing the more loosely bound $AsPh_3$ ligands was too rapid for conventional spectrophotometric techniques, whereas when L was the better σ-donor $PMePh_2$ ($R^1 = C_6H_4OMe\text{-}p$, $R^2 = R^3 = R^4$ = Me) the reaction did not proceed at any detectable rate, even though the latter ligand is sterically less demanding than *para*-substituted triphenylphosphines.[8]

The dependence of the pre-equilibrium constant K on temperature for the reaction (1a) + (A) (R^4 = Me) yielded $\Delta H^\ominus = 44.8 \pm 2$ kJ mol^{-1} and $\Delta S^\ominus = 174 \pm 6$ J K^{-1} mol^{-1}. As can be seen, the reversible formation of intermediate (1 · · · A) is an endothermic process with a highly positive standard entropy, consistent with association of oppositely charged ions, the negative association entropy being more than offset by a highly positive desolvation entropy (defreezing of solvent molecules). However, in a poor dissociating solvent, such as 1,2-dichloroethane, the picture is certainly complicated by a contribution of ion-pairing effects to the thermodynamic parameters. In fact, the K value was found to decrease with increasing total concentration of ionic species (F).[4] The relevance of solvent effects in these systems is borne out by some preliminary results for the reaction (1a) + (A) (R^4 = Me) at 40 °C, wherein a small addition of a protic polar solvent, such as ethanol, to the 1,2-dichloroethane medium causes a striking decrease in the overall reaction rate (*e.g.* for 5% v/v ethanol, $k_1 = 5.2 \times 10^{-5}$ s^{-1}, $k_2 = 3.3 \times 10^{-4}$ s^{-1}, and $K = 50.0$ dm^3 mol^{-1}), to the extent that at ethanol concentrations higher than 10% v/v the reaction is halted altogether. By contrast, the reaction is considerably accelerated on adding increasing amounts of benzene (*e.g.* for 5% v/v benzene, $k_1 = 8.9 \times 10^{-4}$ s^{-1}, $k_2 = 4.0 \times 10^{-3}$ s^{-1}, and $K = 39.4$ dm^3 mol^{-1}). This is also reflected in our previous observation that the ligand-exchange reactions in neat benzene under preparative conditions go to completion much more rapidly.[3] At present, it would be hard to disentangle the factors which relate to the observed solvent effects, in view of the several metal centres involved in the reaction steps and of the scarce experimental information available. However, it appears that solvent polarity and hydrogen-bonding ability depress the reactivity, probably through stabilization of the interacting ionic substrates.

Experimental

Preparation of Complexes.—The preparation of the binuclear cationic substrates (1a)—(1g), as well as the isolation and characterization of the reaction products (2) and (B) of the Scheme, have been described previously.[3] Compound (1; L = $PMePh_2$, $R^1 = C_6H_4OMe\text{-}p$, $R^2 = R^3 = R^4$ = Me) was also prepared in the same way, starting from *trans*-[PdCl{C(=NC$_6$H$_4$OMe-*p*)C(Me)=NMe}(PMePh$_2$)$_2$], which was obtained by a procedure similar to that described for the PPh_3 analogue.[11]

The anionic reactant (A), [NEt$_3$(CH$_2$Ph)][PdCl$_2$(η^3-2-R^{4}C$_3$H$_4$)] (R^4 = H or Me), was prepared as follows. The dimer [{PdCl(η^3-2-R^{4}C$_3$H$_4$)}$_2$] (5 mmol) was dissolved in dichloromethane (*ca.* 50 cm^3) and treated with anhydrous benzyltriethylammonium chloride (10 mmol), obtained by prolonged heating of a commercial sample under vacuum (7—8 h, 80 °C, *ca.* 1.34 Pa). The reaction mixture was concentrated to small volume at reduced pressure and added to excess Et_2O, whereupon an oil formed, which crystallized on stirring. The crude product was purified by recrystallization from CH_2Cl_2–Et_2O (yield 95%, based on the theoretical amount) (Found: C, 47.8; H, 6.9; Cl, 17.0; N, 3.2. $C_{17}H_{29}Cl_2NPd$ requires C, 48.05; H, 6.9; Cl, 16.7; N, 3.3%); Λ_M = 86.5 S cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} methanol solution at 20 °C; ν(Pd–Cl) 269s, 255s, and 250 (sh) cm^{-1}. Satisfactory analytical and physical data were also obtained for the analogous allyl complex (R^4 = H).

Purification of Solvents.—1,2-Dichloroethane was purified by washing with aqueous NaOH solution, drying over P_2O_5, and distillation (b.p. 83.5—83.7 °C). The other solvents were purified by standard literature methods.[12]

Kinetics.—The progress of the reaction was followed spectrophotometrically with an almost ten-fold excess of the anion (A) over the substrates (1) in order to provide pseudo-first-order conditions and force the reaction to completion (range 500—460 nm; substrate of the order of 5×10^{-5} mol dm^{-3}). The total concentration of ionic species was kept constant at 3×10^{-2} mol dm^{-3} by appropriate additions of NBu_4ClO_4. The reactions were carried out in a silica cell in the thermostatted cell compartment of a double-beam Varian Cary 219 spectrophotometer. The cell temperature was controlled to within ±0.05 °C by means of a Haake F3-C circulating cryothermostat. The pre-thermostatted, freshly prepared reactant solutions were rapidly mixed in the reaction cell to start kinetic runs. The reactions appear to be first order in substrate concentration, as shown by the dependence of absorbance readings of the reaction mixture on time (A_t), after establishment of the immediate pre-equilibrium step.

Determination of rate and activation parameters. For most experiments an infinite time reading (A_∞) could be obtained directly. However, an iterative non-linear least-squares program was employed to determine the values of $k_{obs.}$, A_0, and A_∞ which best fit the A_t *vs. t* data within the first-order rate expression $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs.}t)$, the function minimized being $\Sigma(A_{calc.} - A_{obs.})^2$. The algorithm is based on an optimized version [13] of Marquardt's minimization procedure [14] and converges in a few cycles from an estimated starting vector of parameters. For the sake of internal consistency, all kinetic data were processed by this non-linear technique. When direct comparison was feasible, the optimized values of A_0 and A_∞ agreed with the observed values to well within experimental error. Within each experiment, the values of A_t calculated from the above expression and the optimized values of A_0, A_∞, and $k_{obs.}$ always agreed with the observed values of A_t to a standard deviation of less than 0.002 absorbance unit and on the average to a standard deviation of less than 0.001 absorbance unit. The residuals were randomly scattered and never greater than 0.002 absorbance unit in absolute value.[15] The initial guesses required to trigger the iterative process were obtained as described elsewhere.[16] The best-fit $k_{obs.}$ values are listed in Tables 1 and 2.

The rate and equilibrium parameters in expression (v) were determined by non-linear least-squares fitting of $k_{obs.}$ values to [(A)] by the use of the modified Marquardt method, whereas the parameters in expression (vii) were obtained by linear regression. The curves (*a*) and (*b*) in the Figure are plots of the theoretically predicted dependences based on the best-fit parameters for each of the two models considered. Uncertainties quoted in the Tables are standard errors of estimate. Activation parameters were determined by weighted non-linear regression of rate constants with temperature according to a reparametrized model which proved particularly suitable for reducing the correlation between parameters by improving the conditioning of the response surface and allowing fast convergence of the iterative process.[16] The dependent variable was weighted as $w_i = 1/\sigma_i^2$. Initial guesses were obtained from weighted linear regression of $\ln(k/T)$ with $1/T$ using the weighting scheme $w_i = k_i^2/\sigma_i^2$ to maintain the original distribution of errors.

The standard thermodynamic parameters for the equilibrium constant K were similarly obtained by non-linear regression of K with T data based on a reparametrized form of the equation $K = \exp(-\Delta G^\circ/RT)$.

Statistical Reduction and Handling of Data.—All statistical and graphical data analyses described above were performed by one of us (P. U.) with a comprehensive software package implemented on a Tektronix 4052 Graphic System (65 kbytes RAM) equipped with a Tektronix 4662 Digital Plotter and an Anadex DP-9500 fast printer. The package was in part derived from the Tektronix Plot 50 Statistical Analysis Software and locally tailored to suit the needs of the system under study. Detailed information is available from this author upon request.

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