Evidence for Asymmetrical Cleavage of Halide-bridged Platinum(II) Complexes by Nucleophiles

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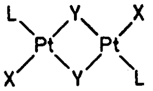
The addition of PMe_2Ph to $[Pt_2Cl_4(PMe_2Ph)_2]$ at low temperatures produces the ions $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl_3(PMe_2Ph)]^-$ as major products, as well as some of the expected $[PtCl_2(PMe_2Ph)_2]$. It is argued that the ionic species result from two molecules of the attacking nucleophile adding to a single platinum atom of the dimer, instead of the more common symmetrical attack. Less ionic product is produced from the addition of PBu_3 to $[Pt_2Cl_4(PMe_2Ph)_2]$ and PMe_2Ph to $[Pt_2Cl_4(PBu_3)_2]$, and none at all was detected from the addition of PBu_3 to $[Pt_2Cl_4(PBu_3)_2]$, so the nature of the phosphines involved has a profound effect on the course of the reactions. The ionic materials are able to undergo rapid phosphine exchange even at −60 °C if excess ligand (PR_3 or Cl^-) is present. These exchange reactions can complicate the range of products observed unless precautions are taken to prevent local accumulations of the phosphine in the course of mixing the reactants.

MANY binuclear ligand-bridged complexes of the d^8 ions, common towards the end of the transition series, are known. They are particularly numerous for square-planar co-ordinated Pd^{II} and Pt^{II}. The strength of the bridge bonds has been found to increase in the series $Cl < Br < I$[1,2] and $Cl < PEt_2O < SR < PR_2$[3] for platinum derivatives. The weaker bridges (usually all but SR, PR_2,[3,4] and OH[4,5] for Pt^{II}) can be broken by unidentate ligands, equation (1), making a useful and widely applied synthetic route.



$+ 2\,L' \longrightarrow 2\,[PtXYLL']$ (1)

A few kinetic studies on the bridge-cleavage reactions of Pt^{II} complexes revealed rate law (2),[1,6] similar to those

$$\text{rate} = (k_1 + k_2[L'])[\text{dimer}] \qquad (2)$$

obtained for ligand substitutions of square-planar complexes, and compatible with the simultaneous operation of the two reaction pathways of Scheme 1 (S = solvent). The same rate law was found with bidentate entering ligands, L–L,[6] although the reaction products were not symmetrical (3). The implication was that singly

$$[Pt_2X_6]^{2-} + L\text{–}L \longrightarrow cis\text{-}[PtX_2(L\text{–}L)] + [PtX_4]^{2-} \qquad (3)$$

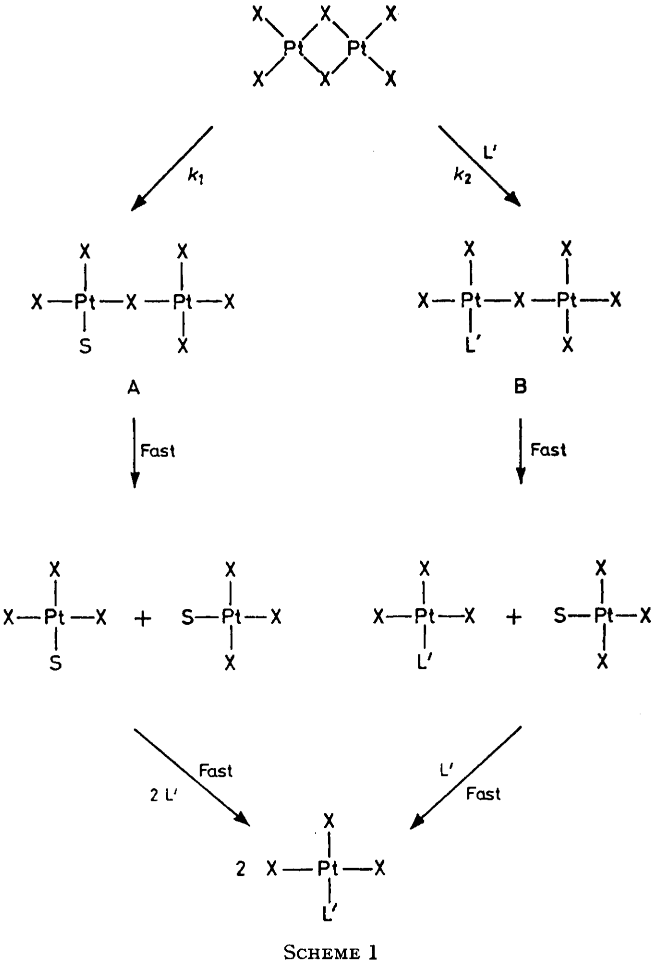
bridged intermediates such as A and B of Scheme 1 had an appreciable lifetime, and could persist until chelate formation with a bidentate ligand. Binuclear species with single halide bridges have been postulated as intermediates in other reaction systems.[7]

Bridge cleavage by monodentate ligands of $[Pt_2(\mu\text{-}X)_2Y_2L_2]$ or $[Pt_2(\mu\text{-}X)_2X_2L_2]$ (where L are neutral ligands) can produce two isomers. The bond broken is generally found to be that opposite the terminal ligand of higher *trans* effect.[1] This is illustrated by equations (4) and (5), where the *trans*-effect order is olefin > Cl^- > am (am = amine).[8]

$$[Pt_2Cl_4(am)_2] + 2\,C_2H_4 \longrightarrow 2\,cis\text{-}[PtCl_2(am)(\eta\text{-}C_2H_4)] \qquad (4)$$

$$[Pt_2Cl_4(\eta\text{-}C_2H_4)_2] + 2\,\text{am} \longrightarrow 2\,trans\text{-}[PtCl_2(am)(\eta\text{-}C_2H_4)] \qquad (5)$$

Frequently, the initial (kinetic) product isomerises to the thermodynamically stable form.[8,9] Such isomerisations are readily catalysed by traces of free ligand,[10] so great care may be necessary to obtain the kinetic isomer, and in deducing the reaction course from the products detected. Despite this, isomer ratios have been taken as an indication of the relative *trans* effect of X^- and L [see equation (1)].[11] In the majority of applications of the bridge-cleavage reaction,



SCHEME 1

however, little attention has been paid to the isomeric nature of the products.

It is from a consideration of the geometry of reaction products that the first indications are obtained that these reactions may not be as well ordered as implied above. $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ exists in solution as both *cis* and *trans* isomers,[12] yet bridge cleavage by CO in $CDCl_3$ at −60 °C produces almost exclusively the product with CO *trans* to $PMePh_2$. Although equilibria between *cis* and *trans* forms of such halide-bridge dimers are rapidly achieved,[12,13] the singularity of the cleavage product is difficult to explain. Pearson and Muir [1] have suggested that the opening of the second bridge (probably by solvent) may not be independent of the first cleavage.

A second problem area is the production in some cases of non-symmetrical products. Their production from bidentate ligands is common [6,14] and not remarkable [equation (3)], but the many examples of their formation from unidentate ligands [15,16] is less easy to account for [equations (6) and (7)]. A possible explanation is the

$$[Pt_2X_6]^{2-} + 2\,L \longrightarrow [PtX_2L_2] + [PtX_4]^{2-} \quad (6)$$

$$[Pt_2X_4L_2] + 2\,L' \longrightarrow [PtX_2L_2] + [PtX_2L'_2] \quad (7)$$

disproportionation of the initial products [equilibrium (8)].[8,9,17] Such processes are well documented, and their equilibria are very dependent on the natures of

$$2\,[PtX_2LL'] \rightleftharpoons [PtX_2L_2] + [PtX_2L'_2] \quad (8)$$

the metal, ligands, and solvents.[1,18] These processes, too, are catalysed by traces of free ligand,[19] although ' spontaneous ' examples abound (they may in fact be solvent catalysed or autocatalysed, like isomerisations),[10] especially amongst palladium compounds. In the absence of mechanistic investigations, the possibility of ligand transfer between metal atoms during cleavage cannot be discounted. Indeed, this has been proposed [20] for some nickel complexes, although the disproportionation reaction could well apply.

Finally, a few bridge-cleavage reactions have been reported to proceed, then later to reverse, eliminating the cleaving ligand.[21] These reactions were slow and temperature dependent.

We present here the results of low-temperature ^{31}P n.m.r. studies of some cleavage reactions of platinum dimers, $[Pt_2X_4(PR_3)_2]$. They suggest that many processes compete in solution, and the products of bridge-cleavage reactions cannot reliably be anticipated.*

RESULTS AND DISCUSSION

The effects of additions of tri-n-butylphosphine to $[Pt_2Cl_4(PBu_3)_2]$ and $[Pt_2Cl_4(PMe_2Ph)_2]$ respectively, and of dimethylphenylphosphine to $[Pt_2Cl_4(PMe_2Ph)_2]$ and $[Pt_2Cl_4(PBu_3)_2]$ respectively have been examined in detail by ^{31}P n.m.r. spectrometry. The nature of the reaction products was found to be very dependent on both the reactants and conditions.

The simplest reaction was the addition of one mol equivalent of PBu_3 to *trans*-$[Pt_2Cl_4(PBu_3)_2]$ in $CDCl_3$. The only materials present after reaction at either −60 °C or ambient temperatures were *trans*-$[PtCl_2(PBu_3)_2]$ and unreacted $[Pt_2Cl_4(PBu_3)_2]$. Clearly a straightforward bridge-cleavage reaction operates [equation (9)], and conforms to Scheme 1 and equations (1) and (5).

$$2\,PBu_3 + trans\text{-}[Pt_2Cl_4(PBu_3)_2] \longrightarrow 2\,trans\text{-}[PtCl_2(PBu_3)_2] \quad (9)$$

The addition of PMe_2Ph to *trans*-$[Pt_2Cl_4(PMe_2Ph)_2]$ in $CDCl_3$ was more complicated. In all cases, the ^{31}P n.m.r. spectra revealed that 50% of the dimer was unreacted, so the stoicheiometry of the reaction was the expected two phosphine molecules to one dimer. At −60 °C, however, only about 10—15% of the reaction products was $[PtCl_2(PMe_2Ph)_2]$, found as both *trans* and *cis* isomers with the *trans* form predominating. The remaining 85—90% consisted of the ions $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl_3(PMe_2Ph)]^-$ (1 : 1 ratio). The ions were identified by preparing them independently according to published procedures [equations (10) and (11)].[19,22]

$$cis\text{-}[PtCl_2(PMe_2Ph)_2] + PMe_2Ph \longrightarrow [PtCl(PMe_2Ph)_3]Cl \quad (10)$$

$$[Pt_2Cl_4(PMe_2Ph)_2] + 2\,[NEt_4]Cl \longrightarrow 2\,[NEt_4][PtCl_3(PMe_2Ph)] \quad (11)$$

The products from this dimer-cleavage reaction remained unchanged in solution at −60 °C for several hours, but when the solution was allowed to warm up to room temperature the ionic materials disappeared and the final products were *cis*- and *trans*-$[PtCl_2(PMe_2Ph)_2]$, 1 : 1 ratio, reaction (12) {still with unreacted $[Pt_2Cl_4(PMe_2Ph)_2]$}. This reaction probably proceeds *via* halide-ion attack on the cation and phosphine attack on the anion. The interaction of Cl^- with $[PtCl(PMe_2Ph)_3]^+$ leads exclusively to *cis*-$[PtCl_2(PMe_2Ph)_2]$ (see below), and its seems reasonable from *trans*-effect considerations for PMe_2Ph to produce *trans*-$[PtCl_2(PMe_2Ph)_2]$ from $[PtCl_3(PMe_2Ph)]^-$. The reaction between $[Pt_2Cl_4(PMe_2Ph)_2]$ and 2 PMe_2Ph at room temperature produced only *cis*- and *trans*-$[PtCl_2(PMe_2Ph)_2]$.

$$[PtCl(PMe_2Ph)_3]^+ + [PtCl_3(PMe_2Ph)]^- \longrightarrow trans\text{-}[PtCl_2(PMe_2Ph)_2] + cis\text{-}[PtCl_2(PMe_2Ph)_2] \quad (12)$$

The most complicated reactions were the additions of PBu_3 to $[Pt_2Cl_4(PMe_2Ph)_2]$ and of PMe_2Ph to $[Pt_2Cl_4(PBu_3)_2]$. In three experiments 0.5, 1.0, and 1.9 mol equivalents of PMe_2Ph were added by syringe to $CDCl_3$ solutions of $[Pt_2Cl_4(PBu_3)_2]$ at −60 °C, and the ^{31}P n.m.r. spectra of the mixtures were recorded at this temperature. As well as signals from the major product, *trans*-$[PtCl_2(PBu_3)(PMe_2Ph)]$, and resonances from unreacted dimer, *cis*-$[PtCl_2(PBu_3)(PMe_2Ph)]$ (*cis* : *trans* ratio 2 : 3), *trans*-$[PtCl_2(PBu_3)_2]$, $[PtCl(PMe_2Ph)_3]^+$, and $[PtCl_3(PBu_3)]^-$ were identified. A trace of *trans*-$[PtCl(PBu_3)_2(PMe_2Ph)]^+$ was also present, along with several un-

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* Preliminary communication, R. J. Cross and I. G. Phillips, *Inorg. Chim. Acta*, 1981, **54**, L1.

identified minor products. These had n.m.r. signals grouped in doublets (J *ca.* 20 Hz), and were probably other mixed phosphine cations. The measured anion : cation ratio was close to 1 : 1, and the relative amounts of ionic materials increased with increasing added phosphine to a maximum amount of about 35% when 1.9 mol of PMe_2Ph was used. The amount of *trans*-$[PtCl_2(PBu_3)_2]$ also increased with increasing PMe_2Ph.

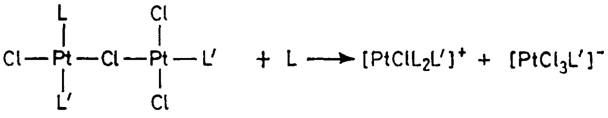
No changes were observed in these spectra over several hours at −60 °C but when the solutions warmed to room temperature signals from the ionic species disappeared and resonances from *cis*-$[PtCl_2(PMe_2Ph)_2]$ grew in strength. The final ratio of *cis*-$[PtCl_2(PMe_2Ph)_2]$ to *trans*-$[PtCl_2(PBu_3)_2]$ was about 1 : 1. The *cis* : *trans* ratio of the mixed phosphine complex $[PtCl_2(PBu_3)(PMe_2Ph)]$ did not alter. These same final products were obtained when $[Pt_2Cl_4(PBu_3)_2]$ was allowed to react with one equivalent of PMe_2Ph at room temperature.

The analogous experiments adding 0.6, 1.0, and 2.0 equivalents of PBu_3 to $[Pt_2Cl_4(PMe_2Ph)_2]$ in $CDCl_3$ at −60 °C produced similar results, but the minor products differed. The major product was again *trans*-$[PtCl_2(PBu_3)(PMe_2Ph)]$, and unreacted dimer was present except in the case where 2.0 equivalents of phosphine were added. No *cis*-$[PtCl_2(PBu_3)(PMe_2Ph)]$ nor *trans*-$[PtCl_2(PBu_3)_2]$ was evident but a wider variety of ionic species were present, with *trans*-$[PtCl(PMe_2Ph)(PBu_3)_2]^+$ and $[PtCl_3(PMe_2Ph)]^-$ predominating and $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl(PBu_3)_3]^+$ being identified amongst the remainder. As in the previous reactions, the importance of the ionic products grew with increasing added phosphine, rising to *ca.* 35% at 2.0 equivalents. Although many of the signals assigned to minor cationic species could not be identified, coupling constants of *ca.* 20 Hz typical of $J(PP)$ in *cis*-diphosphineplatinum compounds were apparent, and the overall intensities of the ^{31}P signals assigned to the cations were three times that of the signals from the anion $[PtCl_3(PMe_2Ph)]^-$.

Again, no change occurred in any of these spectra over several hours at −60 °C, but, as before, when the solutions warmed to ambient temperatures the salts disappeared and $[PtCl_2(PBu_3)_2]$ (*cis* : *trans* ratio 10 : 1) and *cis*-$[PtCl_2(PMe_2Ph)_2]$ became apparent instead. In these three reactions, isomerisation of the mixed phosphine complex did proceed at ambient temperatures, resulting eventually in its total conversion to *cis*-$[PtCl_2(PBu_3)(PMe_2Ph)]$. Once again, similar final products were obtained from the room-temperature reaction between $[Pt_2Cl_4(PMe_2Ph)_2]$ and PBu_3, although no *cis*-$[PtCl_2(PBu_3)_2]$ or *cis*-$[PtCl_2(PMe_2Ph)_2]$ was apparent.

The most surprising of the products obtained from the low-temperature reactions are the ionic species. Two distinct routes could produce such compounds. First, the interaction of phosphine (PR_3) with the principal bridge-cleavage products {*trans*-$[PtCl_2(PMe_2Ph)_2]$ or *trans*-$[PtCl_2(PBu_3)(PMe_2Ph)]$ respectively} could produce cations by Cl^- elimination, which in turn could cleave unreacted dimer to produce the observed anions. These reactions are analogous to equations (10) and (11), and we have confirmed by independent experiments at −60 °C that when PMe_2Ph or PBu_3 is added to *trans*-$[PtCl_2(PBu_3)(PMe_2Ph)]$, or when PBu_3 is added to *cis*-$[PtCl_2(PMe_2Ph)_2]$, the cationic products formed include those detected from the mixed phosphine dimer cleavages.

The second plausible route to the ionic species involves attack of the second incoming nucleophile at the same platinum atom of the dimer as the first one. This would occur at the singly bridged intermediate corresponding to B of Scheme 1, equation (13), and produce both cation and anion in one step. Such singly bridged intermediates are known to have appreciable lifetimes.[6,7] Even if the bridge opening is a result of solvent attack, rather than phosphine, there seems no reason why this, too, might not produce an anion/cation combination.



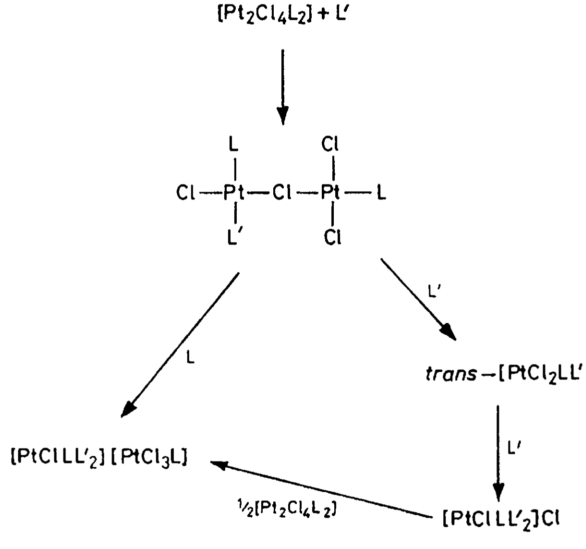
$$\text{Cl}-\underset{\text{L}'}{\overset{\text{L}}{\text{Pt}}}-\text{Cl}-\underset{\text{Cl}}{\overset{\text{Cl}}{\text{Pt}}}-\text{L}' + \text{L} \longrightarrow [\text{PtClL}_2\text{L}']^+ + [\text{PtCl}_3\text{L}']^- \quad (13)$$

The arrangement of the phosphine ligands of the cations is not random: $[PtCl(PMe_2Ph)_3]^+$, *trans*-$[PtCl(PBu_3)_2(PMe_2Ph)]^+$, and $[PtCl(PBu_3)_3]^+$ feature predominantly from the addition reactions of both PBu_3 and PMe_2Ph. This could occur from a process of phosphine exchange leading to products which are thermodynamic rather than kinetic. Rapid room-temperature exchange of phosphines between $[PtCl(PMe_2Ph)_3]Cl$ and *cis*-$[PtCl_2(PMe_2Ph)_2]$ has been reported from ^1H n.m.r. studies [19] and we have confirmed this using ^{31}P n.m.r. spectrometry. When 0.6 mol equivalents of PMe_2Ph were added to *cis*-$[PtCl_2(PMe_2Ph)_2]$, signals from both the cation and the *cis* complex were distinct at −60 °C, but at +30 °C the signals broadened, indicative of fast ligand exchange. The operation of such phosphine exchange processes in our bridge-cleavage reactions would seem to indicate the secondary-attack mechanism, equations (10) and (11), to be the route to the ionic species.

Two facts run counter to this explanation, however. First, the rate of bridge cleavage is reported to be faster by a factor of some 10^3 than ligand-replacement reactions at square-planar complexes.[1] We have confirmed this for complexes of the type studied here: the pseudo-first-order rate constant for the cleavage of $[Pt_2Cl_2(PBu_3)_2]$ by PMe_2Ph in chloroform solution was found from stopped-flow kinetic methods to be 4.3 $dm^3\ mol^{-1}\ s^{-1}$ at 20 °C, and although the reactions of tertiary phosphines with monomeric platinum(II) compounds proved to be too slow to follow by this method, published data [19] give a rate constant of $1.3 \times 10^{-3}\ dm^3\ mol^{-1}\ s^{-1}$ for phosphine exchange at *cis*-$[PtI_2(PMe_2Ph)_2]$ at 38 °C in methanol. Secondly, excess halide-bridged dimer was present in most of the reactions studied, and any phosphine released from cations by halide attack [19] would be rapidly consumed by the dimer. Since the ionic materials survived unchanged at −60 °C in the presence of the dimers, it must be concluded that no phosphines are released from the final products (and hence no ligand exchange takes place) at this temperature.

One possibility remained to be checked; that secondary attack of phosphine on the primary bridge-cleavage products could take place in the few seconds before mixing of the reactants was complete and in those regions of the reaction vessel where a locally high concentration of phosphine was temporarily present. The halide released would later react with dimer to produce the observed anion. The experiments which produced ionic species were therefore repeated several times using a tangentially arranged two-jet glass mixing apparatus and capillary to achieve rapid mixing of the dimer and phosphine solutions. The mixtures were injected directly into n.m.r. tubes, and the whole assembly was maintained at either −60 °C (with $CDCl_3$ solvent) or −78 °C (with a $CDCl_3$–CH_2Cl_2 solvent mixture).

The proportion of ionic material produced from the reaction between $[Pt_2Cl_4(PMe_2Ph)_2]$ and PMe_2Ph at low temperatures showed no variation with the method by which the reactants were mixed. About 85% of the products consisted of $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl_3(PMe_2Ph)]^-$ after adding pure liquid PMe_2Ph to solutions of dimer, adding the PMe_2Ph as a solution, or by rapid tangential mixing. We take this as evidence that the operative mechanism in this case is asymmetrical attack of two phosphines at one platinum of the dimer [equation (13) and Scheme 2].



Scheme 2

The proportion of ionic species produced at low temperatures from the reactions between $[Pt_2Cl_4(PMe_2Ph)_2]$ and PBu_3, and between $[Pt_2Cl_4(PBu_3)_2]$ and PMe_2Ph, on the other hand, were markedly reduced when tangential mixing of solutions was employed. Thus while it is probable that some of the ionic species observed originate *via* mechanism (13), under normal mixing conditions most appear to arise from secondary interactions in local phosphine-rich environments. Unexpected reaction products arising from inhomogeneous reaction conditions have been observed in other cases.[23]

Phosphorus-31 n.m.r. parameters [a]

Complex	δ [b]/ p.p.m.	^1J (Pt–P)/ Hz	^2J (P–P)/ Hz	Ref.
$[Pt_2Cl_4(PBu_3)_2]$	+4.0	3 720		24
$[Pt_2Cl_4(PMe_2Ph)_2]$	−16.3	3 861		*c*
$[PtCl(PBu_3)_3]^+$ [d]	+10.9 d	2 266	19.2	
	−1.1 t	3 459	19.2	16
$[PtCl(PMe_2Ph)_3]^+$	−3.4 d	2 302	21.4	*c*
	−16.4 t	3 520	21.4	
$[PtCl_3(PBu_3)]^-$	−5.2	3 790		*e*
$[PtCl_3(PMe_2Ph)]^-$	−20.6	3 656		*c*
trans-$[PtCl_2(PBu_3)_2]$	+4.3	2 349		24
cis-$[PtCl_2(PBu_3)_2]$	+1.0	3 521		24
trans-$[PtCl_2(PMe_2Ph)_2]$	−7.6	2 407		*f*
cis-$[PtCl_2(PMe_2Ph)_2]$	−14.2	3 540		*f*
trans-$[PtCl_2(PBu_3)(PMe_2Ph)]$	+4.8	2 340	470	16
	−6.7	2 330	470	
cis-$[PtCl_2(PBu_3)(PMe_2Ph)]$	+0.4 d	3 371	18.6	16
	−14.0 d	3 710	18.6	
trans-$[PtCl(PBu_3)_2(PMe_2Ph)]^+$	+8.5 d	2 206	21.1	16
	−11.2 t	3 507	21.1	

[a] In $CDCl_3$ at −60 °C. [b] Relative to external H_3PO_4, positive is downfield; d = doublet, t = triplet. [c] This work. [d] Literature values, recorded at room temperature. [e] G. G. Mather, A. Pidcock, and G. J. N. Rapsey, *J. Chem. Soc., Dalton Trans.*, 1973, 2095. [f] S. O. Grimm, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133.

It is clear that the nature of the products changes with the phosphines employed. Less ionic material results from use of PBu_3 (either as ‘ resident ’ or incoming nucleophile) than PMe_2Ph. Indeed, no ionic species were detected at all from the addition of less than 2.0 mol equivalents of PBu_3 to $[Pt_2Cl_4(PBu_3)_2]$. It seems highly unlikely, however, that the operation of reaction (13) should be restricted to one phosphine, and no doubt other examples will be found.

Whilst there exists a possibility that phosphine-exchange and isomerisation reactions could take place at the singly bridged reaction intermediates (this represents another possible route to some of the complex product mixtures observed), it is clear that there is no simple exchange between incoming and resident phosphines, as the anions observed are exclusively those containing the phosphine of the dimer involved. It is unlikely also that phosphine exchange at the anionic platinum complexes occurs, or the migration of phosphines from metal to metal as suggested by Coronas *et al.*[20]

Finally, it can be noted that although most reactions were performed with excess dimer, in no case was any evidence obtained for the presence in solution of singly bridged intermediates. It thus seems likely that even at −78 °C such species rearrange or react further in the time required to complete the spectroscopic analysis (*ca.* 10 min).

EXPERIMENTAL

Phosphorus-31 n.m.r. spectra were recorded on a Varian XL100 spectrometer operating in the Fourier transform mode. The complexes $[Pt_2Cl_4(PMe_2Ph)_2]$ and $[Pt_2Cl_4(PBu_3)_2]$ were prepared by standard methods.[24] N.m.r. parameters of the reaction products are listed in the Table. Fast-mixing experiments were performed by injecting from 5-cm^3 aliquots of 3×10^{-2} mol dm^{-3} solutions of dimer and phosphine directly into 5-mm outside diameter n.m.r. tubes (0.25 cm^3 at a time) *via* a tangentially arranged two-jet glass mixing apparatus and capillary. The entire apparatus was packed in powdered dry ice. In other experiments, the solutions of the dimer were cooled to −60 °C in a 5-mm n.m.r. tube, to which was added phosphine as pure liquid, as a pre-cooled (−60 °C) solution in $CDCl_3$; the mixture was vigorously agitated immediately after the addition.

Stopped-flow experiments were run on an all-glass apparatus with a tangentially arranged two-jet mixer with a dead-time of 10 ms. Solutions ($CHCl_3$) were 1.96×10^{-3} mol dm^{-3} in PMe_2Ph and 0.87×10^{-4} mol dm^{-3} in $[Pt_2Cl_4(PBu_3)_2]$, and the reaction was monitored using the absorbance change at 330 nm.

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