Behaviour of α-Functional Organotransition Metal Compounds: Nuclear Magnetic Resonance Investigation of a Novel Friedel–Crafts Metallacyclisation of Halogenomethyl(arylphosphine)platinum(II) Complexes

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Reaction of complexes *trans*-$[Pt(CH_2X')XL_2]$ with 2 equivalents of $AgBF_4$ in the presence of triarylphosphine (L′) affords cationic metallacyclic species $[\overline{Pt\{PPh_2(2\text{-}C_6H_4C}H_2)\}L(L')]BF_4$ [X = Cl, Br, or I; X′ = Cl or I; L = PPh_3; L′ = PPh_3 or $P(C_6H_4Me\text{-}4)_3$]. When L′ = $P(C_6H_4Me\text{-}4)_3$ the isomeric metallacycle $[\overline{Pt\{P(C_6H_4Me\text{-}4)_2(4\text{-}MeC_6H_3C}H_2\text{-}2)\}L_2]BF_4$ is also formed in significant amount. In the absence of additional phosphine the cyclic product $[\overline{Pt\{PPh_2(2\text{-}C_6H_4C}H_2)\}L(S)]BF_4$ is observed instead (S = solvent molecule). This novel metallacyclisation route features a remarkably facile intramolecular electrophilic substitution by the metal-bound methylene on an aryl substituent of a co-ordinated phosphine. The extent to which this involves the incoming phosphine is controlled by the rate of isomerisation of intermediates. Multinuclear n.m.r. characteristics of the products and intermediates are reported and mechanistic implications discussed.

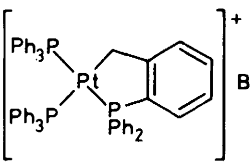
α-Functional organotransition-metal compounds may be key intermediates in a variety of metal-mediated organic transformations; 1-hydroxyalkyl metal compounds, for example, are implicated in the oxidative hydrolysis of alkenes (Wacker process),[1] and, also, topically, in the catalytic reduction of carbon monoxide.[2] Halogenomethylmetal derivatives are of interest as electronegatively substituted metal alkyls and as precursors to other α-functional organometal compounds, but their chemistry has remained largely unexplored after a few early reports.[3]

The discovery that dihalogenomethanes could add oxidatively to neutral, low-valent transition-metal complexes affording isolable halogenomethyl species[4] led us to investigate this approach as a general method for other metal substrates, including those of Pt^0. Independently of our studies other workers have recently reported upon the synthesis and some reactivity of halogenomethylmetal compounds,[5] including halogenomethylplatinum(II) complexes derived from $[Pt(PPh_3)_3]$ and $[Pt(C_2H_4)(PPh_3)_2]$.[5a–c] Here, we report a novel aspect of their chemical behaviour.

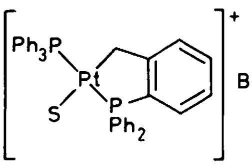
Results and Discussion

We have synthesised and characterised a number of compounds $[Pt(CH_2X')X(PPh_3)_2]$ [X′ = X = I (1a); X′ = Cl, X = Br (1b); or X′ = Cl, X = I (1c)] in both *cis* and *trans* configurations, by reaction of $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ with the appropriate dihalogenomethane in benzene at ambient temperature. The compounds were identified by their elemental analyses and i.r. and n.m.r. characteristics. Additionally, halogen-redistribution reactions during production of (1b) and (1c) produced smaller yields of other derivatives *trans*-(1d) (X′ = Br, X = Cl), *trans*-(1e) (X′ = X = Br), *cis*- and *trans*-(1f) (X′ = X = Cl). n.m.r. parameters for these complexes are summarised in Table 1.

As a measure of the relative labilities of metal- and carbon-bound halides, we treated the *trans* isomers (1a)—(1c) in chloroform with acetone solutions of $AgBF_4$. In the first instance, the reactions were carried out in the presence of 1 equivalent of triphenylphosphine. When 2 equivalents of silver salt were employed a single product resulted, in essentially quantitative yield. It crystallised from dichloromethane as air-stable, colourless prisms formulated as the cationic metallacycle (2). The structure shown is supported by microanalytical evidence, and by extensive magnetic resonance measurements on the nuclei present in the compound (Table 2). The compound is a 1 : 1 electrolyte in acetonitrile.



(2)



(3)

N.M.R. Characterisations.—^{31}P N.m.r. data are especially useful for identifying the metallacycles. The spectrum of compound (2) reveals an ABX system (Figure). Two of the nuclei give rise to an AB quartet with doublet fine structure indicating coupling with a third nucleus P_X. (All ^{31}P signals display satellites due to coupling with ^{195}Pt.) The magnitudes of the coupling constants $^2J(P_A–P_B)$, $^1J(P_A–Pt)$, and $^1J(P_B–Pt)$ suggest that P_A and P_B are mutually *trans*, while the values of $^2J(P_X–P_A)$, $^2J(P_X–P_B)$, and $^1J(P_X–Pt)$ are consistent with the nucleus P_X being *cis* to two other phosphorus atoms and *trans* to a ligand of higher *trans* influence, for example, a hydrocarbyl.[6] Also of note is the appreciable downfield shift (Δ_R = 15.8 p.p.m.) of $\delta(P_A)$ relative to $\delta(P_B)$. The latter is in the range normally found for co-ordinated PPh_3. This positive contribution to the chemical shift of P_A is strongly indicative of its incorporation in a five-membered ring. (The four-membered metallacycle which would result from direct *ortho*-metallation would supply a negative ring contribution and P_A would resonate upfield of P_B.[7])

In the ^{13}C n.m.r. spectrum the phenyl resonances formed a series of complex multiplets in the range 126—138 p.p.m. There was also a weak doublet with apparent ^{195}Pt satellites further downfield at 155.1 p.p.m. The low intensity of the signal is consistent with that due to a carbon lacking a hydrogen substituent (which consequently experiences no nuclear Overhauser enhancement as a result of the proton-decoupling

Table 1. Phosphorus-31 and ^1H n.m.r. parameters [a] for $[Pt(CH_2X')X(PPh_3)_2]$ (1) in $CDCl_3$

				^{31}P			^1H		
Compound	X	X′	Configuration	δ(P) [b]	^1J(P–Pt)	^2J(P–P)	$δ(CH_2)$ [c]	^2J(H–Pt)	^3J(H–P)
(1a)	I	I	*trans*	23.0	3 070		2.3(t)	34	9
			cis	*trans* to X 16.7	4 215	17	3.2(d)	36	9
				trans to C 14.3	1 816	17			
(1b)	Br	Cl	*trans*	26.5	3 136		3.0(t)	52	9
(1c)	I	Cl	*trans*	24.2	3 096		3.1(t)	50	9
			cis	*trans* to X 18.1	4 258	16	4.0(d)	51	8
				trans to C 14.7	1 748	16			
(1d)	Cl	Br	*trans*	27.1	3 134		*d*	*d*	*d*
(1e)	Br	Br	*trans*	26.2	3 112		2.9(t)	44	9
(1f)	Cl	Cl	*trans*	27.3	3 161		*d*	*d*	*d*
			cis	*trans* to X 19.8	4 499	16	*d*	*d*	*d*
				trans to C 21.0	1 684	16			

[a] Coupling constants *J* in Hz. [b] In p.p.m. relative to external 60% H_3PO_4, downfield shifts positive. [c] In p.p.m. relative to internal tetramethylsilane. [d] Complex is a by-product in yield insufficient for ^1H n.m.r. characteristics to be resolved.

Table 2. N.m.r. parameters for cationic platinaindan complexes [a]

	Complex	(2)	(3)	(4a) [b]	(4b) [b]	(4c) [b]
^{31}P	$δ(P_A)$ [c]	43.5	45.9	43.3	43.0	41.3
	$^1J(P_A$–Pt)	3 020	3 189	3 027	2 992	3 021
	$δ(P_B)$ [c]	27.7	31.6	26.5	25.5	27.3
	$^1J(P_B$–Pt)	2 790	2 962	2 808	2 795	2 819
	$^2J(P_A$–$P_B)$	364	380	364	367	363
	$δ(P_X)$ [c]	18.8	—	18.7	18.6	19.0
	$^1J(P_X$–Pt)	1 990	—	2 003	2 003	1 987
	$^2J(P_X$–P)	21	—	21	21	21
^{13}C	$δ(C^3)$ [d]	37.5	9.3	37.5	37.3	37.1
	$^1J(C^3$–Pt)	485	742	490	483	484
	$^2J(C^3$–$P_X)$	75	—	78	74	75
	$^2J(C^3$–$P_B)$	5	*e*	5	5	5
	$δ(C^{3a})$ [d]	155.1	157.8	155.2	155.5	158.2
	$J(C^{3a}$–Pt)	43	59	*e*	*e*	*e*
	$J(C^{3a}$–P)	29	37	28	28	32
	$δ(C^{7a})$ [d]	136.7	*f*	*f*	*f*	*f*
	$J(C^{7a}$–Pt)	*e*	*f*	*f*	*f*	*f*
	$^1J(C^{7a}$–P)	62 [g]	*f*	*f*	*f*	*f*
^1H	$δ(CH_2)$ [d]	3.21	3.40	3.20	3.17	3.11
	^2J(H–Pt)	65	94	66	64	64
	^3J(H–P)	7	6	7	7	6
^{19}F	$δ(BF_4^-)$ [h]	−152.0	−150.0	−152.0	−152.0	−152.0

[a] Recorded in $CDCl_3$–$(CD_3)_2CO$, except for (2), in $CDCl_3$. Coupling constants *J* in Hz; ^{13}C and ^{31}P data were obtained with ^1H decoupling. [b] Isomers (4) also showed characteristic signals for the ring methyl substituent(s): (4a) δ(H) = 2.30, δ(C) = 21.27; (4b) δ(H) = 2.27, δ(C) = 21.27; (4c), cyclometallated ring, δ(H) = 2.39, δ(C) = 21.63; free rings, δ(H′) = 2.33, δ(C′) = 21.14 p.p.m. [c] In p.p.m. relative to external 60% H_3PO_4; downfield shifts positive. [d] In p.p.m. relative to internal tetramethylsilane. [e] Not resolved. [f] Obscured. [g] $^3J(C^{7a}$–P) = 9 Hz. [h] In p.p.m. relative to external trichlorofluoromethane; no susceptibility correction.

irradiation). The most likely assignment is C^{3a} (see Figure); similar chemical shifts and couplings have been observed for related compounds.[8] A similarly weak doublet of doublets appears further upfield at 136.7 p.p.m. This is ascribed to C^{7a}, in view of the relatively larger coupling to P_A. The metallacyclic methylene carbon C^3 generates a characteristic doubled doublet pattern, with Pt satellites, centred on 37.5 p.p.m. There is apparently no spin coupling with the ring phosphorus P_A. We suggest that coupling to this nucleus comprises two components, one *via* the metal atom and one *via* the carbon skeleton of the ring, which have very similar magnitudes but are opposite in sign. Analogous arguments have been presented to explain apparently low or zero coupling between phosphorus nuclei in five-membered metallacycles.[9]

In the ^1H n.m.r. spectrum the metallacyclic methylene hydrogens appear as an apparent triplet with flanking satellites [as expected for an $ABCMX_2$ system where *J*(A–X) and *J*(B–X) are similar and *J*(C–X) is *ca.* 0 [8,10]] indicative of coupling to two phosphorus nuclei as well as to platinum. Absence of interaction with P_A can be explained by the same rationale used to account for lack of coupling between P_A and C^3. Coupling to the *cis* and *trans* nuclei P_B and P_X appears very similar in magnitude. Measurement of the ^{19}F n.m.r. spectrum of compound (2) revealed one absorption, as expected, for the tetrafluoroborate counter ion.

The formation of metallacycle (2) clearly involves attack by the carbon centre of the (initial) halogenomethyl substituent on the *ortho* position of a phosphine phenyl group. This is in marked contrast to the previous reports of attack on a phosphorus atom,[5a,c] which we did not observe under our conditions, even though the silver salt and phosphine were normally added simultaneously. We were interested to establish at which stage this attack occurs, *i.e.* whether incoming or established ligand is involved, and, if possible, to observe intermediate species. Accordingly, we spectroscopically monitored the reaction of *trans*-(1) in chloroform–acetone with 2 equivalents of $AgBF_4$ in the absence of added triphenylphosphine. The sole product was formulated as the platinacycle [3; S = $(CD_3)_2CO$] on the basis of multinuclear n.m.r. measurements on its solutions. The ^{31}P n.m.r. spectrum comprises only an AB pattern, whose *J*(P–Pt) and *J*(P–P) values (Table 2) are entirely consistent with mutually *trans* phosphines. There is, furthermore, a downfield shift of $δ(P_A)$ relative to $δ(P_B)$ ($Δ_R$ = 14.3 p.p.m.), characteristic of incorporation in a five-membered heterocycle.[7]

The ^{13}C absorption for the methylene nucleus C^3 occurs at high field, with corresponding platinum satellites. The ^1J(Pt–C) value is considerably larger than the corresponding coupling in compound (2). These observations reflect a more tightly bound carbon, consistent with its position *trans* to a co-ordinated solvent molecule, S, of relatively low *trans* influence. This impression is borne out by the low-field absorption assigned to C^{3a}, where the value for $^2J(Pt–C^{3a})$ is also higher than that in compound (2).

The ^1H n.m.r. parameters serve further to underline the consequences of co-ordinating solvent rather than a phos-

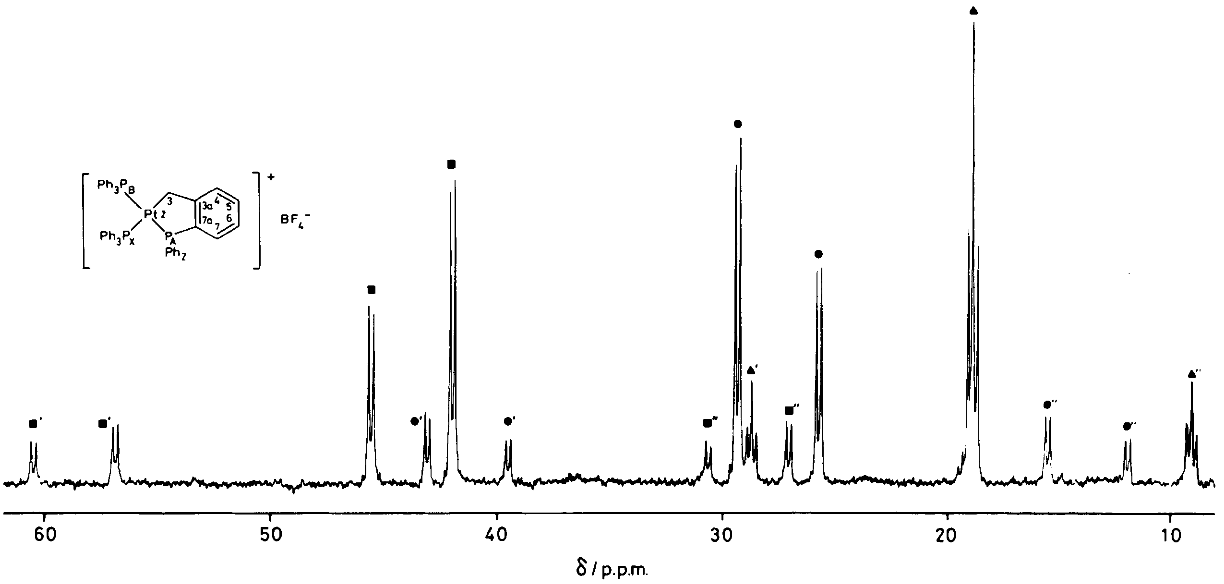


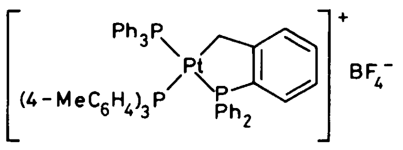
Figure. ^{31}P N.m.r. spectrum (101 MHz) of compound (2) in p.p.m. downfield relative to (external) 60% H_3PO_4 and atom-labelling scheme adopted for the platinaindans (2)—(4). Symbols with primes and double primes identify respective downfield and upfield ^{195}Pt satellites for the designated ^{31}P resonance(s): P_A (■), P_B (●), and P_X (▲)

phine; the coupling of methylene hydrogens to platinum in compound (3) is relatively increased. Of additional interest is the appearance of this signal as a doublet, indicating coupling only to one phosphorus, presumably P_B (see above).

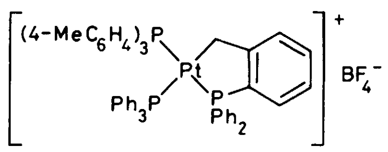
The ^{19}F spectra of the solutions reveal two absorptions, one (at −150.0 p.p.m.) assignable to BF_4^- in compound (3), and the other at −149.1 p.p.m. is attributed to free HBF_4, the result of proton displacement from the phenyl ring. This product could not be detected by ^1H n.m.r., but the presence of 1 equivalent of free acid was established by titration against standard aqueous hydroxide. The appearance of two ^{19}F signals suggests that the platinacyclic cation exists as tight ion pairs with its counter anion, and that exchange with external BF_4^- (from HBF_4) is relatively slow.

In contrast to compound (2), (3) is air-sensitive in solution. Furthermore, attempts at isolation led to decomposition. When 1 mol equivalent of triphenylphosphine was added to solutions of compound (3), however, (2) formed immediately. When on the other hand, (3) was treated with equivalent tri-4-tolylphosphine, a 1 : 1 mixture of two isomeric metallacycles was obtained, formulated as (4a) and (4b) respectively on the basis of their n.m.r. characteristics (Table 2), and in particular on comparison of the A and B elements of the ^{31}P spectrum with those of (2).* A different array of products resulted when compound (1a) was treated *simultaneously* with $AgBF_4$ and $P(C_6H_4Me\text{-}4)_3$, rather than sequentially. In this case, isomers (4a) and (4c) were identified in *ca.* 2 : 1 ratio; (4b) was notably absent (an amount 5% of the total isomer content would have been detected).

Mechanistic Implications.—A notable feature of this novel route to platinacycles is its facility under very mild conditions compared with formation of analogous metallacycles by carbometallation of *ortho*-tolylphosphines.[8b,11] The mechanism clearly involves two types of process, halogen abstraction from compound (1) and electrophilic displacement of hydrogen from an aromatic ring, although it is not clear that the two are mutually independent. The course of halogen abstraction is remarkably insensitive to the nature of the halogen(s) present. The cyclic product was always formed in an amount proportional to the silver salt added † and irrespective of variations in X and X′. Thus, *trans*-$[Pt(CH_2I)IL_2]$, *trans*-$[Pt(CH_2Cl)BrL_2]$, and *trans*-$[Pt(CH_2Cl)IL_2]$ all yield (3). The observation that a metallacycle is the predominant product regardless of the Ag : Pt ratio suggests that abstraction of the second halogen is more favourable from a species from which halide has already migrated. There is evidence that it is the metal–halogen bond which tends to be broken first. This follows from the experiments using tri-4-tolylphosphine as the



(4a)



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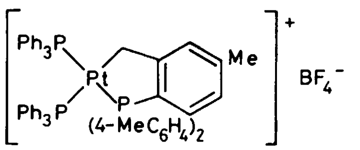

(4c)

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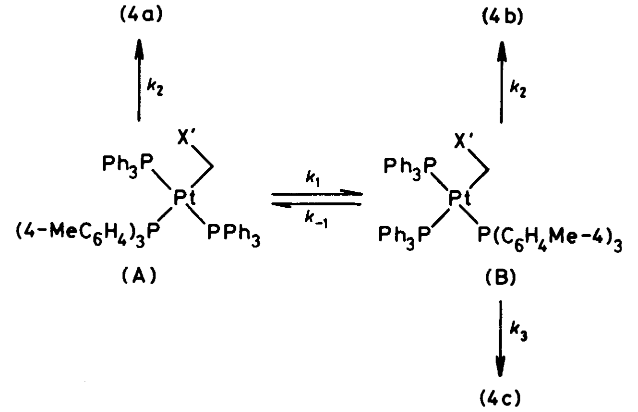
* The general form of the n.m.r. spectra for all the isomers of (4) was the same as that described in detail for compound (2).

† The order of addition, $AgBF_4$ to (1), would ensure that silver is *always* the yield-limiting quantity during these experiments.



Scheme 1. Processes controlling production of isomers (4a)—(4c)

added ligand. When this agent is introduced simultaneously with the silver salt a substantial proportion of the metallacyclic product arises from electrophilic attack on a methylphenyl substituent of the incoming phosphine. Such a step requires a substitution of X by $P(C_6H_4Me\text{-}4)_3$ and, if substitution occurs stereospecifically with retention,[12] a *trans–cis* isomerisation.[13] The absence of isomer (4b) among the products suggests, *inter alia*, that the platinacycle (4a) is configurationally inert once formed; the positions of the phosphines in (4a) and (4c) reflect those in the immediate isomeric precursors to electrophilic substitution. We can infer further from the non-appearance of (4b) that (3) is not itself an intermediate *en route* to (4) [and presumably, also, (2)] *in the presence of added phosphine*, since treatment of preformed (3) with $P(C_6H_4Me\text{-}4)_3$ affords the statistical distribution of (4a) and (4b) [in spite of the fact that (3) was the only isomeric form detectable by n.m.r. spectroscopy]. The indications are, therefore, that X has been displaced by L′ and a process which scrambles the phosphorus sites is underway before electrophilic substitution, and implicitly C–X scission occurs.

It seems reasonable to assume, in the first instance, that attack on the arylphosphine occurs from halogenoalkyl in a *cis* site. An approximately 1 : 1 : 1 distribution of isomers (4a), (4b), and (4c) would be expected from the reaction of (1) with $AgBF_4$ in the presence of $P(C_6H_4Me\text{-}4)_3$ if several conditions were met, namely (see Scheme 1) (*a*) if the equilibrium constants governing site-scrambling of phosphines were close to unity ($k_1 \approx k_{-1}$), resulting in a statistical distribution in which the concentration of (B) is double that of (A), (*b*) if the rate of *cis–trans* isomerisation were appreciably greater than that of electrophilic substitution ($k_1 > k_2,k_3$), and (*c*) if attack on phenyl and tolyl substituents were equally favourable ($k_2 \approx k_3$). Clearly, these requirements are not fulfilled. In particular, the absence of isomer (4b) indicates that, faced with the choice between attack on phenyl- and tolyl-phosphine, the metal-bound electrophile favours the latter exclusively. The inductive effect of an alkyl substituent is an established activator of aromatic rings towards electrophilic substitution (although the *ortho* and *para* ring sites normally most activated by the methyl substituent are sterically inaccessible in this case).[14] A difference in activation energy of only 6.4 kJ mol^{-1} between the two routes would be enough to ensure a rate ratio of *ca.* 13 : 1 in favour of isomer (4c) over (4b) at 25 °C[15] [assuming $\Delta\Delta G^{\ddagger} = RT \ln (k_1/k_2)$]; (4c) would not have been detected below this level.

Our spectroscopic investigations revealed no gross differences in Pt–P bonding between the two phosphines which might lead us to believe that the 2 : 1 preponderance of isomer (4a) over (4c) was controlled by disparities among the equilibrium constants in Scheme 1.* A more likely explanation is that the rate of isomerisation is somewhat slower than that of electrophilic attack on PPh_3; a rate ratio $k_2 : k_1 \approx 2 : 1$ would agree with our observations, given the previous proposal that $k_3 : k_2 \geqslant 13 : 1$.

An important consideration, of course, is the possible role of the platinum in activating the halogenocarbyl substituent towards the development of carbenium ion character. Silver tetrafluoroborate is an established reagent for inducing Friedel–Crafts alkylations in benzene and methylbenzenes under mild conditions where stoicheiometric reactions with the alkyl halides concerned would not normally be observed.[17] It was proposed that the silver species forms an intermediate complex with the aromatic ring which then reacts concertedly with the incoming halogenoalkane. Such an eventuality cannot unequivocally be discounted here.† Furthermore, conventionally catalysed, intramolecular Friedel–Crafts cycloalkylations in aromatic systems have been shown to be appreciably faster than, for example, corresponding intermolecular reactions.[18] The relative activation of one halogen by removal of the other, however, suggests at least some mediation by platinum.

A more active role for platinum is depicted in Scheme 2. The metal may fulfil one or both of two functions. It might provide stability to a carbenium/carbene centre by $d\pi$–$p\pi$ overlap; methyleneplatinum species as reactive intermediates have been discussed elsewhere.[19] It might also act as a vehicle for C–X scission *via* α-halide migration to platinum prior to expulsion as silver halide. Such 1,2-halide migrations from α-halogenoalkylmetal compounds have ample precedent[20] and their operation in organoplatinum reactions has been cited previously.[4a,5c] A trigonal-bipyramidal intermediate (or transition state) such as (5), stabilised by the π-acid carbenium ligand and from which X$^-$ may migrate, is an attractive proposition. Equatorial π-acid ligands are generally regarded as important contributors to the ease of attainment of similar five-co-ordinate intermediates in conventional ligand-substitution reactions.[12,13] Pseudo-rotation of (5) might also provide a route to the observed phosphine site exchange,[13] which may in principle be occurring up to and including the step which affords the metallacycle. Although we cannot specify an isomerisation mechanism, we note that solutions of compound (4) did not contain detectable amounts of (2) or of, for example, $[Pt\{PPh_2(2\text{-}C_6H_4CH_2)\}\{P(C_6H_4Me\text{-}4)_3\}_2]BF_4$, which might have arisen through a consecutive displacement or a bimolecular isomerisation route (see ref. 13).

Whether ring closure itself occurs in a species from which X′ has already departed is speculation which we cannot, for the moment, resolve. The marked discrimination between tolyl and phenyl substrates suggests, though, that the electrophilic precursor complex does have an appreciable lifetime, longer, for instance, than purely alkyl carbenium ions, which are poorly selective between toluene and benzene in competitive, intermolecular Friedel–Crafts reactions. 'Stabilised' electrophiles, such as the RCO^+ (R = acyl) and NO_2^+ in contrast, discriminate more effectively in favour of attack on toluene.[14] The intramolecular cyclisation is, nevertheless, a highly favourable step, as attested by our attempts

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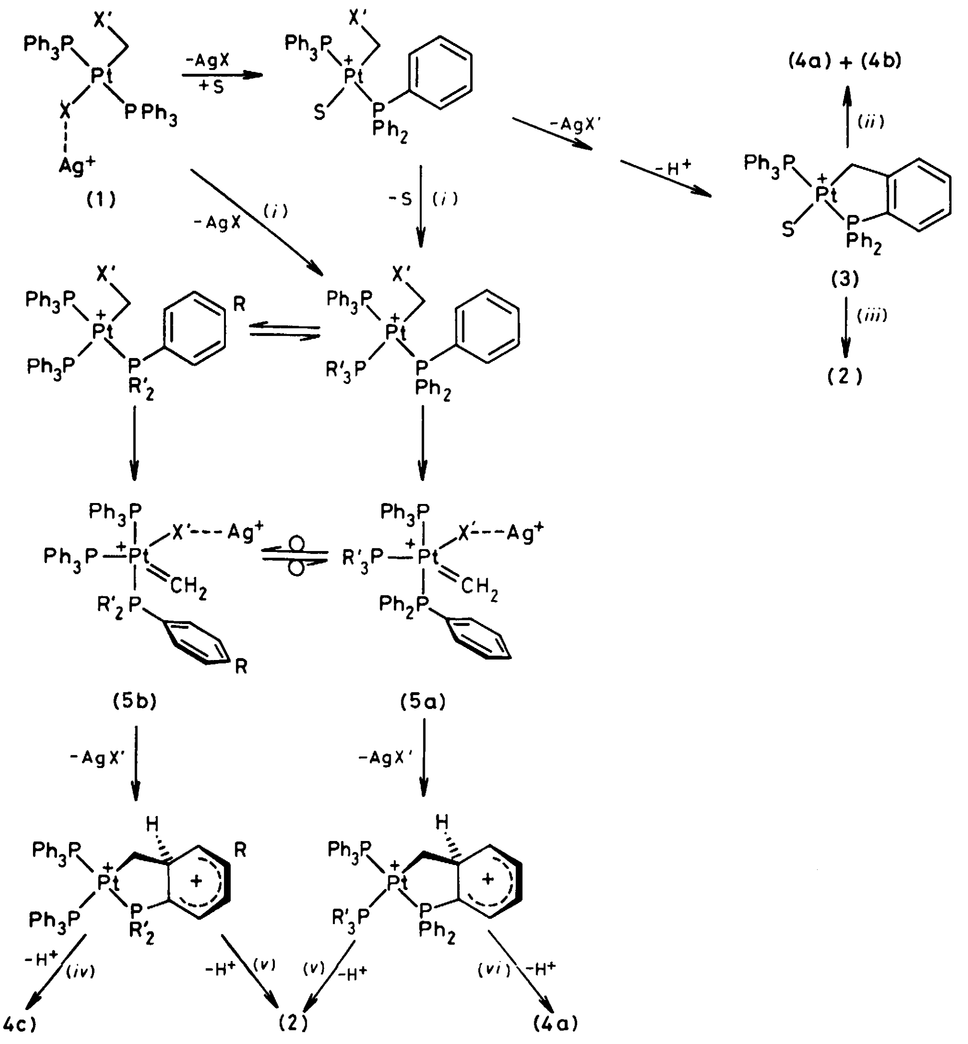
* The phosphines were selected for their steric and electronic similarities as ligands. Previous work[16] has shown that they differ at most only slightly in their influence on the thermodynamics and kinetics of complexation.

† Although (3) is not a precursor to (4) when $AgBF_4$ and $P(C_6H_4\text{-}Me\text{-}4)_3$ are added simultaneously, this does not necessarily imply that the 'solvent path' (see ref. 12) makes no contribution to displacement of X. Both 'solvent' and 'direct' substitution routes are included in Scheme 2.



Scheme 2. (*i*) PR'_3 (R′ = aryl); (*ii*) $P(C_6H_4Me\text{-}4)_3$; (*iii*) PPh_3; (*iv*) R = Me, R′ = C_6H_4Me-4; (*v*) R = H, R′ = Ph; (*vi*) R′ = C_6H_4Me-4

to trap the immediate precursor *via inter*molecular reaction. When compound (1a) was treated with $AgBF_4$ and PPh_3 in the presence of (2 equivalents of) ferrocene, an extremely nucleophilic substrate,[21] (3) was the only observable product. Ferrocene undergoes Friedel–Crafts acylation at a rate 3.3×10^6 times that of benzene and 1.1×10^3 times that of mesitylene.[21b] The substitution-rate control exerted on a ring site by an *ortho*-diarylphosphino-group bound to a transition metal cannot easily be assessed, but the ring is unlikely to be as susceptible as mesitylene on purely electronic grounds. Here, however, the intramolecularity of attack is the undoubted advantage, which may be augmented by steric encroachment of the other ligands around the electrophilic centre, restricting ready access by an extra-molecular substrate as bulky as ferrocene.

Many carbene–metal complexes, on the other hand, are known to react readily with alkenes to yield metallacyclobutanes which may or may not react further.[22] Isolable platinacyclobutanes, moreover, are well established.[23] The reaction of compound (1a) with $AgBF_4$ was, accordingly, carried out in the presence of an excess of 2-methylpropene. The ^{31}P n.m.r. spectrum revealed the presence only of (3), and no metallacycle, C_5-alkene or -cyclopropane (which might arise from metallacycle decomposition [23,24]) were detectable by ^1H n.m.r. spectroscopy.

We did not detect phosphonium ylide complexes at any stage. Given that the production of compound (2) is independent of whether additional phosphine is introduced simultaneously with, or subsequent to, addition of $AgBF_4$, there seems little reason to invoke ylide intermediates. Nevertheless, we explored the possibility of their participation in these rearrangements. When *trans*-(1a) was allowed to react with equivalent triphenylphosphine in chloroform the cationic ylide complex *cis*-$[Pt(CH_2PPh_3)I(PPh_3)_2]I$ was produced quantitatively (n.m.r. characteristics identical to those reported previously [5a,25]). When this species was treated with 2 equivalents of $AgBF_4$, however, no metallacycle could be detected. A new ylide derivative, formulated as $[Pt(CH_2PPh_3)(PPh_3)_2S][BF_4]_2$ [S = $(CD_3)_2CO$] on the basis of its ^{31}P n.m.r. spectrum, was formed quantitatively and did not rearrange further at ambient temperature over 48 h. The absence of phosphonium species further underlines the rapidity of the steps leading to metallacyclisation, since incipient carbenium centres [5a,c] and electrophilic metal carbenes [22a,26] readily attack tertiary phosphines.

An interesting final aspect of compounds (2) and (4) [and (3)] is their inertness in the presence of equivalent HBF_4. The Pt–C bond in (2) *is* cleaved, however, by treatment with excess of dry hydrogen chloride in benzene. The reaction was characterised by loss of the ^1H n.m.r. signal at 3.21 p.p.m. The product cation $[PtCl\{PPh_2(2\text{-}C_6H_4Me)\}(PPh_3)_2]^+$ was identified only by its ^1H and ^{31}P n.m.r. spectra.

We are currently investigating the analogous triethylphosphine derivatives, as well as those of other metals and 1-halogenoalkyl groups, to probe the intermolecular potential of this reaction and to cast more light on its mechanism.

Experimental

General.—N.m.r. measurements were carried out on Bruker WM 250 (^1H, ^{31}P, and ^{13}C; Fourier-transform mode) and Perkin-Elmer R32 (^1H and ^{19}F; continuous-wave mode) instruments. Infrared data were obtained on a Perkin-Elmer 683 spectrophotometer. Microanalyses were by Imperial College Microanalytical Laboratory. All chemical manipulations were carried out in dried, degassed solvents under an atmosphere of argon, unless otherwise specified.

Triphenylphosphine was obtained from Aldrich Chemical Co. and was recrystallised prior to use. Tri-4-tolylphosphine was synthesised by a standard literature route.[27] Silver tetrafluoroborate was obtained from Lancaster Synthesis. It was stored in the dark in a vacuum desiccator, but was otherwise used as received. Di-iodomethane, bromochloromethane, and chloroiodomethane were supplied by Lancaster Synthesis and stored over Linde 4A molecular sieves, but were also used as received. Halogenomethylhalogenobis(triphenylphosphine)platinum(II) complexes, (1), were prepared from [Pt(η^2-C_2H_4)(PPh_3)$_2$] [28] in a manner very similar to that described elsewhere.[5a,c] Satisfactory elemental analyses and spectroscopic parameters (Table 1) were obtained for the halogenomethyl complexes isolated. In this paper, the *cis* and *trans* designations, used to describe metallacyclic cations, refer to the (final) mutual orientations of the two triphenylphosphine ligands originally present in *trans*-[Pt(CH_2X')X(PPh_3)$_2$] (1).

Preparation of (o-*Diphenylphosphinobenzyl*-C$^\alpha$P)*bis*(*triphenylphosphine*)*platinum*(II) *Tetrafluoroborate*, (2).—The same procedure was followed irrespective of the precursor (1). That for (1a) is typical. To a stirred solution of *trans*-[Pt(CH_2I)I(PPh_3)$_2$] (1a) (0.5 g, 0.51 mmol) in chloroform (5 cm^3) under an argon atmosphere was gradually added a solution of $AgBF_4$ (0.201 g, 1.03 mmol) and PPh_3 (0.139 g, 0.530 mmol) in acetone (8 cm^3). If addition is too rapid, precipitation of (unidentified) brown impurities occurs and the yield is impaired. The mixture was stirred for 10 min after addition, the pale yellow supernatant filtered off from silver halide, and the solvent removed by evaporation, leaving an ivory solid. Recrystallisation from dichloromethane gave colourless crystals of compound (2) (0.47 g, 86% after purification) (Found: C, 60.75; H, 4.25; P, 8.50. Calc. for $C_{55}H_{46}BF_4P_3Pt$: C, 61.05; H, 4.30; P, 8.55%). Preparations of (2) for n.m.r. monitoring differed only in the use of $CDCl_3$ and $(CD_3)_2CO$ as solvents and in the amount of parent complex used (typically 0.1 g, 0.1 mmol).

Preparation and N.M.R. Characterisation of trans-(o-*Diphenylphosphinobenzyl*-C$^\alpha$P)(*hexadeuterioacetone*)(*triphenylphosphine*)*platinum*(II) *Tetrafluoroborate*, (3).—To a stirred solution of *trans*-[Pt(CH_2I)I(PPh_3)$_2$] (1a) (0.109 g, 0.11 mmol) in $CDCl_3$ (1.5 cm^3) under an argon atmosphere was very carefully added a solution of $AgBF_4$ (0.051 g, 0.26 mmol) in $(CD_3)_2CO$ (2.0 cm^3). The orange supernatant was filtered from the silver iodide precipitate into argon-flushed n.m.r. tubes and the spectroscopic parameters of compound (3) determined (see Table 2). Upon addition of an excess (1—2 equivalents) of PPh_3 in $CDCl_3$, the solution paled notably in colour and the n.m.r. characteristics of (2) were observed (Table 2).

Preparation and N.M.R. Characterisation of cis- *and* trans-(o-*Diphenylphosphinobenzyl*-C$^\alpha$P)(*triphenylphosphine*)(*tri*-4-*tolylphosphine*)*platinum*(II) *Tetrafluoroborate*, (4a) *and* (4b).—To a stirred solution of *trans*-[Pt(CH_2I)I(PPh_3)$_2$] (1a) (0.061 g, 0.062 mmol) in $CDCl_3$ (1.0 cm^3), at ambient temperature under argon, was very slowly introduced a solution of $AgBF_4$ (0.030 g, 0.154 mmol) in $(CD_3)_2CO$ (1.0 cm^3). The mixture was stirred for 30 min after addition and further slow addition was made of P(C_6H_4Me-4)$_3$ (0.020 g, 0.065 mmol) in $CDCl_3$ (0.8 cm^3). The pale yellow supernatant was filtered from the silver iodide precipitate into argon-filled tubes for n.m.r. analysis (see Table 2). A 1 : 1 mixture of the *cis* and *trans* isomers was produced.

Preparation and N.M.R. Characterisation of trans-(4a) *and cis*-(2-*Di*-p-*tolylphosphino*-5-*methylbenzyl*-C$^\alpha$P)*bis*(*triphenylphosphine*)*platinum*(II) *Tetrafluoroborate*, (4c).—To a stirred solution of *trans*-[Pt(CH_2I)I(PPh_3)$_2$] (1a) (0.061 g, 0.062 mmol) in chloroform (1.2 cm^3) under argon at ambient temperature was gradually added a solution of $AgBF_4$ (0.026 g, 0.134 mmol) and P(C_6H_4Me-4)$_3$ (0.019 g, 0.062 mmol) in $(CD_3)_2CO$ (1.5 cm^3). The pale yellow supernatant was filtered from the silver iodide into argon-flushed tubes for n.m.r. characterisation. The spectroscopic characteristics of compound (4a) were identified from the foregoing experiment and the parameters for (4c) were assigned (Table 2). From integration of the ^{31}P spectrum, the ratio of (4a) to (4c) was 2 : 1. The integration did not vary when the pulse delay was increased from 3 to 10 s and appears, therefore, to be reliable.

Detection and Quantification of Evolved HBF_4.—The procedure for preparation of compound (2) *via* (3) was repeated using *trans*-(1a) (0.510 g, 0.516 mmol) in chloroform (5.0 cm^3) and $AgBF_4$ (0.202 g, 1.038 mmol) and PPh_3 (0.138 g, 0.526 mmol) in acetone (5.0 cm^3). After addition of the reagents under argon at ambient temperature the mixture was stirred for 30 min and the pale yellow supernatant filtered off from the silver iodide precipitate. Distilled water (5.0 cm^3) containing bromothymol blue as indicator was then added to the organic mixture, and the whole well shaken. The solution was titrated against standard aqueous sodium hydroxide until the aqueous phase retained a permanent blue colour, even on further shaking with the organic layer. The total acid resulting from the reaction was thus estimated as 0.588 mmol (114% based on Pt).

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