Pyrolyses of Diaryl(phosphine)platinum(II) Complexes: Effect of Added Phosphines †

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The presence of additional tertiary phosphine, L or P–P, promotes the thermal reductive elimination of biaryl, R_2, from *cis*-$[PtR_2L_2]$ or $[PtR_2(P-P)]$ (R = Ph or C_6H_4Me-4; L = PPh_3; P–P = $Ph_2PC_2H_4PPh_2$ or $Ph_2PCH_2PPh_2$). Secondary decomposition modes, which operate in the pyrolysis of the platinum complexes themselves, are largely suppressed, and the primary metal-containing products are $[PtL_3]$ or $[Pt(P-P)_2]$. The platinum(0) complexes themselves undergo thermolysis at elevated temperatures, and the products from the chelating phosphine derivatives indicate a reaction route involving insertion of Pt^0 into alkyl–phosphorus bonds. There is evidence that in some cases added phosphine exchanges with that already in the complex before thermolysis begins.

In order to test our hypothesis that reductive eliminations from a metal centre should be enhanced by added nucleophiles,[1] we have examined the effect of tertiary phosphines on the thermolyses of $[PtR_2L_2]$ and $[PtR_2(P-P)]$ [R = Ph or C_6H_4Me-4; L = PPh_3 or $P(C_6H_4Me\text{-}4)_3$; P–P = $Ph_2PC_2H_4PPh_2$ (dppe) or $Ph_2PCH_2PPh_2$ (dppm)]. These systems are quite suitable, as reductive elimination of R_2 has already been established as the primary decomposition route of the pure complexes.[1] Tertiary organic phosphines were chosen for their nucleophilic potency towards platinum(II) substrates,[2] and also, since several tris and tetrakis phosphine complexes of Pt^0 are known, in the hope of stabilising the metal product subsequent to reductive elimination. Moreover, by using the same phosphine as that already present, we avoid the complications of ligand exchange.

RESULTS AND DISCUSSION

Intimate mixtures of $[PtR_2L_2]$ and free L were thermolysed, as previously described for the pure

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† No reprints available.

[1] P. S. Braterman, R. J. Cross, and G. B. Young, *J.C.S. Dalton*, previous paper.

[2] R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, 1968, **90**, 319.

platinum complexes.[1] Each system was examined by t.g.a., d.t.a., and d.s.c., and product analysis was effected by quantitative g.l.c.

TABLE 1

Complex	Temperature of onset of decomposition ±2 K		δT_L
	a	*b*	
$[PtPh_2(dppm)]$	503	398	−105
$[Pt(C_6H_4Me\text{-}4)_2(dppm)]$	516	410	−106
$[PtPh_2(dppe)]$	516	481	−35
cis-$[PtPh_2(PPh_3)_2]$	419	380	−39
cis-$[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$ [c]	380	365	−15

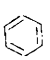
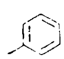
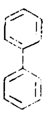
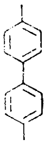
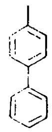
[a] Nucleophile absent. [b] Nucleophile (L or P–P) present. [c] D.s.c. determined only.

Two notable effects of the presence of free phosphine on the thermolytic behaviour of the complexes are apparent. First, decomposition is facilitated in every case. This is shown by d.t.a. and/or d.s.c. measurement of the temperatures at onset of decomposition (Table 1). The effect is greatest for the complexes of dppm in the presence of an equimolar amount of free dppm. These systems decompose *ca.* 105 °C below the normal onset of decomposition of pure $[PtR_2(dppm)]$. Even where the effect is less pronounced, however, such as in the case of the dppe complex, comparison of d.s.c. data (Figure 1) reveals that decomposition in the presence of free dppe is accomplished at a temperature at which the pure complex is quite stable. The reasons for individual variations in the magnitude of this effect are not obvious, and probably arise from a complicated interaction of individually unassessable parameters, but the qualitative implications are clear.

That the effect is truly attributable to the nucleophilic action, and is not merely a solvent effect, is, of course, a matter of importance. Prolonged thermolysis of a saturated solution of $[Pt(C_6H_4Me\text{-}4)_2(dppm)]$ in perhydrotriphenylene (a fused cyclohexane system to which low nucleophilicity is ascribed) at 413 K (when decomposition occurs readily in the presence of free dppm) consistently produced no detectable indication of decomposition. We conclude, therefore, that the electron-donor capability of the added phosphine has a major role in the facilitation of thermal decomposition.

Secondly, and in juxtaposition, analyses of the thermolysis products confirm that the decomposition process is indeed that of primary reductive elimination of biaryl from platinum. This reaction is quantitative in every case (Table 2), including the one case $\{[Pt(C_6H_4Me\text{-}4)_2(dppm)]\}$ [1] in which, when added ligand is absent, other processes compete significantly with R_2 elimination. Moreover, it is evident that generation of secondary aryl-derived products is generally suppressed (relative to analogous treatment in the absence of phosphine),[1] and in the action of dppe on $[PtPh_2(dppe)]$ is prevented altogether.

TABLE 2

System	Temperature of onset of decomposition (T_d/K)	Thermolysis temperature (T_t/K)	Thermolysis time (t/h)	Amount of product [mol (mol Pt)$^{-1}$] [a]								
									L	Other		Residues
$[PtPh_2(dppm)]$ + dppm	398	403	2.0	0.09		0.98			0.18	PPh_3 $PMePh_2$	0.04 0.14	contain $[Pt^0(dppm)_2]$
$[Pt(C_6H_4Me\text{-}4)_2(dppm)]$ + dppm	410	413	2.0	0.02	0	0	0.98	0	0.20	PPh_3 $PMePh_2$	0.03 0.21	contain $[Pt^0(dppm)_2]$
$[PtPh_2(dppe)]$ + dppe	481	488	2.0	0		1.01						$[Pt^0(dppe)_2]$
cis-$[PtPh_2(PPh_3)_2]$ + PPh_3	380	385	4.0	0.03		0.99			0.08	0		largely $[Pt^0(PPh_3)_3]$
cis-$[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$ + $2PPh_3$	365	393	4.0	0.06	0	0.05	1.02	0	0.58	0		largely $[Pt^0(PPh_3)_3]$
$[Pt(dppe)_2]$	573	603	2.0	0.29		0.12			0.11	$PPh_2(C_2H_3)$ PPh_3 C_2H_4	0.30 0.26 0.03	*b*

[a] Errors in product determination are ±2% for biaryls and ±4% for arenes, except in the thermolysis of $[Pt(dppe)_2]$ for which errors of ±10% are estimated. [b] Not investigated.

The metal-containing product from the reaction of dppe and $[PtPh_2(dppe)]$ is $[Pt^0(dppe)_2]$. This was characterised by elemental analysis and mass spectrometry, and its i.r. spectrum and d.s.c. thermal profile were identical to those of an authentic sample. The

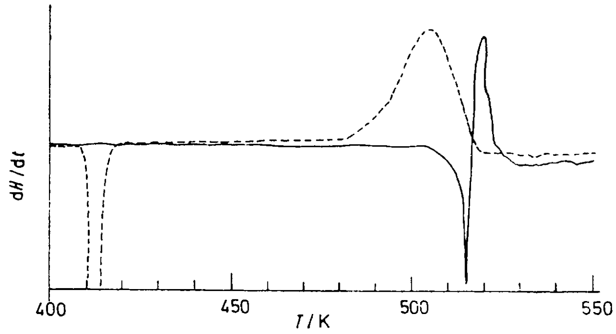


FIGURE 1 D.s.c. thermal profiles of $[PtPh_2(dppe)]$ (——) and $[PtPh_2(dppe)]$ + dppe (— — —)

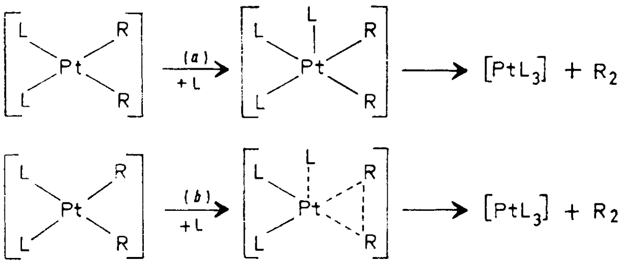
reactions of dppm and $[PtR_2(dppm)]$ appeared more complex, however, as the metal-containing fragment

$$[PtPh_2(dppe)] + dppe \xrightarrow{490\ K} [Pt(dppe)_2] + Ph_2 \quad (1)$$

decomposed further even at the relatively mild conditions of its formation. The mass spectra of the residues unequivocally showed the presence of $[Pt(dppm)_2]$, however, and no toluene or 4-methylbiphenyl was detected from the thermolysis of dppm and $[Pt(C_6H_4Me\text{-}4)_2(dppm)]$, indicating an uncomplicated quantitative primary reductive elimination of R_2. Thus the reactions seem quite analogous to the dppe system discussed above, and the small amounts of benzene (and other products, see below) can be accounted for by the subsequent decomposition of $[Pt(dppm)_2]$. Interestingly, our attempts to synthesise pure $[Pt(dppm)_2]$ by conventional means [3,4] also met with failure, and it seems that this material decomposes very readily in solution, despite reports of its existence [5] and of the analogous $[Pd(dppm)_2]$ [6] and $[Ni(dppm)_2]$.[7]

The main metal-containing product from the reactions of one or two equivalents of PPh_3 with $[PtR_2(PPh_3)_2]$ was identified as $[Pt(PPh_3)_3]$. The latter is known to form $[Pt(PPh_3)_2]$ readily, and this resulting material easily decomposes (see ref. 1 and refs. therein), accounting satisfactorily for the benzene and ligand-derived biphenyl from these systems. Here, too, no toluene or 4-methylbiphenyl was formed from $2PPh_3$ and $[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$, indicating again that the primary step is quantitative reduction elimination of R_2.

The precise mechanism of nucleophilic labilisation of these platinum complexes requires discussion. That the ultimate metal product is the requisite zerovalent platinum species (which may or may not decompose further) seems clear. Inevitably the route to this point, with concomitant assistance of elimination, involves interaction of the (added) phosphorus donor orbital with the metal atom. The exact nature of this interaction along the reaction co-ordinate may, however, only be guessed. Two extreme views are possible (Scheme 1). The platinum atom may expand its co-ordination by full ligation of phosphine, yielding a true metastable intermediate prior to biaryl elimination, thus maximising the transient electron occupation at the metal [Scheme 1(*a*)]. Five-co-ordinate derivatives of platinum(II) [8,9] are well known as either stable or metastable entities. Alternatively the reaction may pursue a course related to classical nucleophilic substitution at carbon, in which an initially weak donor–acceptor interaction is progressively strengthened while concurrent scission of metal–carbon bonds proceeds [Scheme 1(*b*)]. This format ensures the minimum increase in the metal electron population along the reaction co-ordinate.



SCHEME 1

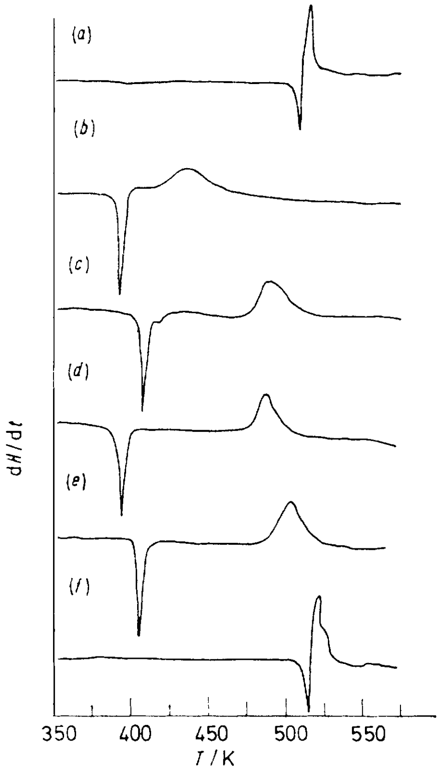


FIGURE 2 D.s.c. thermal profiles for $[PtPh_2(P\text{–}P)] + P\text{–}P$: (*a*) $[PtPh_2(dppm)]$; (*b*) $[PtPh_2(dppm)] + dppm$; (*c*) $[PtPh_2(dppm)] + dppe$; (*d*) $[PtPh_2(dppe)] + dppm$; (*e*) $[PtPh_2(dppe)] + dppe$; (*f*) $[PtPh_2(dppe)]$

It is of interest that, whereas $[PtPh_2(dppm)]$ shows a marked instability in the presence of free dppm [indicated by the relative positions of decomposition exotherms in the d.s.c. thermal profiles (Figure 2)], the same complex in the presence of dppe decomposed at a temperature comparable with those shown by $[PtPh_2(dppe)]$ in the

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[8] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., John Wiley, New York, 1967, ch. 5 and refs. therein; C. G. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 1960, 4379; J. P. Fackler, jun., W. C. Seidel, and J. A. Fetchin, *J. Amer. Chem. Soc.*, 1968, **90**, 2707; K. R. Dixon and A. D. Rattray, *Canad. J. Chem.*, 1973, **51**, 618; A. D. Westland, *J. Chem. Soc.*, 1965, 3060.

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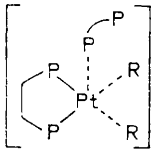
presence either of free dppe or dppm. These three temperatures of onset of decomposition lie within a range of 10 °C. A strong implication is that the observed exotherms of (*c*)—(*e*) in Figure 2 reflect the decomposition of closely similar species such as (I) (no significance is to be attached to the dotted bonds). This suggests that dppe displaces dppm from $[PtPh_2(dppm)]$ at a rate much greater than the (presumably rate-limiting) reductive elimination of biaryl. Relief of the steric strain of the four-membered ring in $[PtPh_2(dppm)]$ [10] should favour such a reaction. Thus the d.s.c. profiles (*c*) and (*d*) of Figure 2 indicate the operation of identical intermediates, and (*e*) will differ only in the chain length of the unidentate diphosphine of (I).



(I)

The similarity of temperatures of onset of decomposition in (*c*)—(*e*) means also that five- rather than the potential six-co-ordination is likely for the intermediate. Further support might be derived from the similarity of the effect of one or two equivalents of PPh_3 in promoting reductive elimination from $[PtR_2(PPh_3)_2]$.

It appears then, that for these arylplatinum complexes at least, the hypothesis that the interaction with nucleophiles should encourage reductive elimination is correct. Other examples which may conform to this theory include the elimination of H_2 from $[Os(CO)H_2(NO)(PPh_3)_2][PF_6]$ promoted by PPh_3 or CO (L) to yield $[Os(CO)(NO)(PPh_3)_2L][PF_6]$,[11] and those cited in the previous paper.[1] There is evidence, however, that other factors may predominate in some cases. The inhibition by tertiary phosphines of the decompositions of $[PtBu_2(PR_3)_2]$ and $[Pt\{(CH_2)_4\}(PR_3)_2]$ (R = alkyl) is easily explained, since the primary reaction paths here are β eliminations.[12] Excess of PR_3 fails to promote reductive elimination, but suppresses ligand dissociation, necessary to make available an extra co-ordination site for β elimination.

There are two more serious counter examples. In the presence of the spin trap Bu^tNO, the alkene-induced thermolysis of species $[PtR_2L_2]$ [L = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen); R = Me or Et] gives rise to free radicals.[13] This is in marked contrast to the alkene-induced decomposition of $[NiEt_2(bipy)]$,[14] and it may well be that Bu^tNO is itself involved in reactions with the initial complex.[15] The most direct contrast to our results comes from the reductive elimination of bialkyl from trialkyl(phosphine)gold(III) complexes $[AuR^1{}_2R^2L]$. This process is concerted, stereospecific, and takes place in preference to α or β elimination; added phosphine, however, inhibits it, and it has been suggested that the reductive elimination takes place from a phosphine-free transient.[16] Present knowledge does not provide any explanation for this difference between the platinum(II) and gold(III) series.

A feature of the thermolysis of $[PtR_2L_2]$ or $[PtR_2(P\text{–}P)]$ above is the significant amount of arene and biaryl produced from the secondary decompositions of $[PtL_2]$ or $[Pt(P\text{–}P)]$, respectively.[1] This is largely suppressed in the presence of excess of L or P–P. A simple explanation is that the platinum atoms in the products of these processes $\{[PtL_3]$ or $[Pt(P\text{–}P)_2]\}$ have higher co-ordination numbers and electron availabilities at the metal, and consequently are unlikely to form the strong arene to platinum interactions which, we believe, are likely preliminaries to the secondary processes.[1] Nevertheless, small amounts of benzene and biphenyl are formed when $[PtL_3]$ or $[Pt(P\text{–}P)_2]$ decompose. In the case of $[Pt(PPh_3)_3]$ this can be accounted for by dissociation to $[Pt(PPh_3)_2]$, and its subsequent decomposition. It seems possible that, at the higher temperatures involved, ligand dissociation from $[Pt(P\text{–}P)_2]$ might also precede similar sequences.

Of greater interest are the other products from the thermolyses of $[Pt(P\text{–}P)_2]$. The complex $[Pt(dppm)_2]$ decomposes under the conditions of its formation in our reactions to yield $PMePh_2$ and a smaller amount of PPh_3; $[Pt(dppe)_2]$ survives to higher temperatures, and decomposes to $PPh_2(CH{=}CH_2)$ and (less) PPh_3 (Table 2). This latter complex also yielded a small amount of ethylene, but no ethane or methane (no test for H_2 was made), and trace amounts of four unidentified less-volatile species, the g.l.c. retention times of which suggested tertiary phosphines.

Oxidative insertion of low-valent metals into aryl–phosphorus and –hydrogen bonds is well documented.[1,17] Oxidative insertion into an alkyl–phosphorus bond has not, as far as we know, been proposed before, although there is a precedent for the formation of diphenylvinylphosphine from a dppe complex.[18] Such oxidative insertion would account for our observed products. The resulting diphenylphosphinoethylmetal would decompose by β elimination to give diphenylvinylphosphine, as observed. Such a route is not available for the diphenylphosphinomethyl group of dppm, which would degrade to methyldiphenylphosphine by hydrogen-atom abstraction from a Pt–H (or conceivably a C–H) bond.

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[13] N. G. Hargreaves, R. J. Puddephatt, L. H. Sutcliffe, and P. J. Thompson, *J.C.S. Chem. Comm.*, 1973, 861.

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[17] See, for example, C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J.C.S. Chem. Comm.*, 1972, 87.

[18] G. Van Koten and J. G. Noltes, *J.C.S. Chem. Comm.*, 1972, 452.

EXPERIMENTAL

All instrumental techniques used have been described previously.[1] Platinum(0) phosphine species were prepared according to established procedures by reduction of the requisite dichloroplatinum(II) system in ethanol solution in the presence of a suitable excess of phosphine, using either tetrahydroborate[4] or ethanolic hydroxide[3] as reductants.

Intimate mixing of complex and phosphine was normally achieved by freeze-drying of appropriate mixtures in benzene solution. The tendency of $[PtR_2(PPh_3)_2]$ to undergo slight decomposition in solution, even at ambient temperature under an inert atmosphere, necessitated mixing by grinding in an agate mortar for those complexes.

Thermolyses.—Instrumental methods. As reported for the thermal behaviour of the pure complexes,[1] a general pattern was evident. The resultant of the processes of ligand melting and concomitant solvation of complex was a single sharp endotherm. This was followed (though not, generally, immediately) by an irreversible exothermic process which was accompanied by the onset of loss in weight. This decomposition exotherm was invariably less sharp than that observed for the complex alone (Figure 1).

Product analysis. Techniques and procedures for recovery and determination of volatile thermolysis products were as previously described.[1] The known platinum(0) species $[Pt(dppe)_2]$ and $[Pt(PPh_3)_3]$ were characterised by their elemental analyses, and by comparison of i.r. and mass spectroscopic and d.s.c. parameters with those of an authentic sample or with reported data.[19] The less stable species $[Pt(dppm)_2]$ was identified as a residual component by mass spectrometry.

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