Reductive Elimination of Biaryl from Diarylbis(phosphine)platinum(II) Complexes in Solution: Kinetics and Mechanism

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The thermal decompositions of complexes *cis*-[PtR_2L_2] [R = Ph or C_6H_4Me-4; L_2 = $(PPh_3)_2$, $\{P(C_6H_4Me\text{-}4)_3\}_2$, $(PMePh_2)_2$, $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, or $Me_2PCH_2CH_2PMe_2$] in toluene solution have been investigated. Their stability to thermolysis varies markedly with L_2, and only complexes of monotertiary phosphines are labile at 60 °C. Reaction occurs *via* primary concerted unimolecular reductive elimination of biaryl, and conforms to a first-order kinetic rate law. Concurrent but independent secondary decomposition of [PtL_2] generates both arene and biaryl as minor products. The elimination of 4,4′-bitolyl from *cis*-[$Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2$] exhibits a pronounced negative entropy of activation, suggestive of a conformationally restricted transition state. The inclusion of free PPh_3 suppresses secondary processes and accelerates primary decay. Although itself inert under these conditions, [$PtR_2(Ph_2PCH_2PPh_2)$] also eliminates biaryl in a concerted and kinetically first-order manner when allowed to react in the presence of 10 equivs. of $Ph_2PCH_2PPh_2$. These observations provide further evidence for the facilitation of reductive elimination by added nucleophiles.

ORGANOTRANSITION-METAL complexes can decompose in many different ways.[1-4] These are of interest in themselves, and also relevant to our understanding and control of many catalytic and synthetic processes. The most fully documented processes involve β- (or more rarely, α-) hydride migration.[1-4] Less well understood is reductive elimination, despite its potential for carbon–carbon bond synthesis. Binuclear (or polynuclear) elimination is known for derivatives of Cu^{I} [5,6] and Ag^{I},[6,7] which tend to form aggregates, while reports of concerted reductive elimination from a single centre are largely confined to derivatives of Pt^{IV} [8] and Au^{III}.[9,10] Some of us have pointed out that reductive elimination (which is the concerted loss of two one-electron donors) bears some formal analogy to the loss of one two-electron donor, and inferred that the addition of a neutral ligand might facilitate the process.[1] This effect is indeed found for some acyclic [11] and cyclic [12] dialkylnickel(II) derivatives. We have described the thermal reductive elimination of biaryl from a series of neat complexes of the type *cis*-[PtR_2L_2] (L = a monotertiary phosphine or L_2 = a ditertiary phosphine, R = aryl) alone or in the presence of free ligand.[13] We now report on the thermal decomposition of such species in solution.

EXPERIMENTAL

Spectra were obtained on JEOL C-60HL and HA(100) (^1H n.m.r.), Varian XL100 (^{31}P n.m.r. by Fourier-transform pulse accumulation), Perkin-Elmer 225 (i.r., as KBr discs), and A.E.I. MS12 instruments (mass spectra [14] of some species, at 70 eV).‡ Chromatographic analysis of volatiles was performed using a Pye series 104 gas chromatograph. The glass column (5 ft × 0.25 in O.D.) was packed with 8% Apiezon Lon Gaschrom Q (100—200 mesh); its temperature was held at 80 °C for 60 s, and then increased at 15 °C min^{-1} to 190 °C (maintained for 12 min, or, if biphenyl was the least volatile component present, 6 min).

All the diarylplatinum complexes were prepared in the standard manner by treatment of the corresponding *cis*-dichloroplatinum species with the appropriate aryl-lithium reagent,[15] and were recrystallised three times and stored in the dark. The *cis* configurations were confirmed from $^1J(^{195}Pt-^{31}P)$ values (Table 1) and from the electric dipole moment of *cis*-[$PtPh_2(PPh_3)_2$] in benzene (obs. 7.2 D; lit.,[15] 7.0 D).

TABLE 1

Values of $^1J(^{195}Pt-^{31}P) \pm 2$ Hz for [PtR_2L_2]

	R	
Complex	Ph	C_6H_4Me-4
[PtR_2(dppm)]	1 392 *	1 390
[PtR_2(dppe)]	1 669 *	
[PtR_2(dmpe)]	1 642	1 643
cis-[$PtR_2(PMePh_2)_2$]	1 762	1 759
cis-[$PtR_2(PPh_3)_2$]	1 748	1 742

* The values in ref. 39*a* are incorrect.

Operations, including thermal decompositions, were carried out under pure dry N_2 or argon in oven-dried glassware. Light was excluded as much as possible. Volumetric apparatus was stored in vacuum desiccators which were subsequently flooded with nitrogen.

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‡ Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J; 1 D ≈ 3.33 × 10^{-30} C m; 1 Torr = (101 325/760) Pa.

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Thermal Decompositions.—The chosen solvent was toluene, which can donate hydrogen to any free aryl radicals formed.[16] Toluene (B.D.H., AnalaR) was dried over sodium wire and distilled over activated 5A molecular sieves using a 40-cm stainless-steel spinning-band column to remove trace amounts of benzene and xylenes. Typically, of an initial volume of 80 cm^3, the first 30 cm^3 were rejected while the next 40 cm^3 were pure to g.l.c. and were retained, vacuum degassed through two freeze–thaw cycles, and stored under N_2 over activated 5A sieves. Tertiary phosphines (B.D.H. or Strem Chemicals) were recrystallised from propan-2-ol and stored under N_2.

The solubility of $[PtPh_2(PPh_3)_2]$ in toluene was determined to be 2.1 mg cm^{-3} at 25 °C. The resulting concentration (*ca.* 2×10^{-3} mol dm^{-3}) was accordingly adopted as standard for these studies. Solutions were prepared in volumetric flasks which had been purged (8 h) with nitrogen and were protected from light.

At timed intervals during kinetic runs, aliquot portions (0.5 cm^3) were withdrawn by syringe and injected into septum-capped glass phials containing 12 mol dm^{-3} aqueous HCl (1.0 cm^3). These samples were stored at -5 °C for 16 d (minimum) prior to quantitative analysis by g.l.c. {These conditions had been established as optimal for the quantitative protolytic destruction of any surviving $[PtR_2L_2]$ (generating arene and $[PtCl_2L_2]$) without further primary decomposition.} Other calibration experiments indicated that yields of decomposition products could be determined in this manner with a precision of $\pm 2\%$ for biaryls and $\pm 4\%$ for benzene.

Since the above process converts surviving metal-bound aryl into arene, a separate experiment is required to test for arene formation from thermolysis. Accordingly, portions of residual solution were submitted to trap-to-trap distillation (273 to 77 K at 10^{-3} Torr) followed by g.l.c. with n-decane as added internal standard. Calibration experiments showed this method to be at least 98% efficient in collecting any benzene formed. For non-kinetic studies, a toluene solution of the organoplatinum species and the appropriate internal g.l.c. standard was maintained at 333 K in a Pyrex tube under N_2 for *ca.* 24 h. One aliquot portion was then vacuum distilled without further treatment, and a second after acid quenching.

RESULTS AND DISCUSSION

Triarylphosphine Complexes.—(*i*) *Product analysis and mechanism.* These complexes were the most suitable for detailed study, since, unlike the others, they decomposed conveniently quickly in toluene below its normal boiling point.[*] Decomposition was accompanied by a progressive change in solution colour from colourless, through amber, to ruby red.

The decomposition path may be inferred from the products. Decomposition of *cis*-$[PtPh_2(PPh_3)_2]$ gives biphenyl as the main product, in addition to a smaller amount of benzene (18.9 mol % after 25 h at 333 K).[†] All or nearly all this benzene must originate from phosphorus-bound phenyl rings, since the yields of benzene from thermolysis of $[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$ and $[PtPh_2\{P(C_6H_4Me\text{-}4)_3\}_2]$ are 19.8 and <2 mol % respectively.

After 6.7 h at 333 K, in addition to near-quantitative formation of 4,4'-bitolyl (95.3 mol %) and a minor yield of benzene (12.9 mol %), thermolysis of $[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$ also resulted in a small quantity of biphenyl (7.7 mol %). At no time during examinations of this complex did the yield of 4-methylbiphenyl exceed 1.0 mol %; indeed it was only detectable after decomposition was 85% complete. No other biaryl isomers were observed.

These results rule out any major contribution from a free-radical process for it is known[17a] that phenyl radicals in cyclohexane (generated by thermolysis of phenylazotriphenylmethane, pat) give rise to benzene (82 mol % detected, based on pat) and not to biphenyl. Since the specific hydrogen-atom donor ability of aliphatic CH is about the same in toluene as in cyclohexane,[17b] we would expect at least 20% of the phenyl radicals liberated in toluene to be converted into benzene. This is in fact an underestimate, and thermolysis of pat in toluene actually gives 50 mol % benzene.[18] It follows that, if the predominant primary decomposition mode of $[PtPh_2\{P(C_6H_4Me\text{-}4)_3\}_2]$ were platinum–carbon bond homolysis, the yield of benzene in this case would be at least 40 mol % and probably *ca.* 100 mol %. Moreover, the absence of bibenzyl and of diarylmethanes in all cases shows[19] the lack of formation of benzyl radicals.

Three further possibilities may also be excluded at this stage. Primary orthometallation of phosphine-bound aryl would convert metal-bound aryl into arene,[20] as would conversion of one metal-bound aryl into benzyne and hydride followed by reductive elimination of its partner, while reversible conversion of metal aryl to metal benzyne hydride would lead to isomerisation of metal-bound 4-tolyl,[‡] contrary in each case to what is found.

Thus the only plausible mechanism for the production of biaryl from $[PtR_2L_2]$ is reductive elimination. A further experiment shows that this reductive elimination is mononuclear in character; 90% complete thermolysis of a mixture of equivalent amounts of $[PtPh_2(PPh_3)_2]$

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[*] This implies that recrystallisation of such substances from warm solvents is unwise.

[†] mol % = (mol of product/mol of Pt) × 100%.

[‡] Benzyne–hydridometal intermediates contribute to the thermal decomposition of $[Ti(\eta\text{-}C_5H_5)_2Ph_2]$ (I. Dvorak, R. J. O'Brien, and W. Santo, *Chem. Comm.*, 1970, 411; C. P. Boekel, J. H. Teuben, and H. J. De Liefde Meijer, *J. Organometallic Chem.*, 1974, **81**, 371).

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and $[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$ gave <2.0 mol % of 4-methylbiphenyl. (This result shows that little or no intermolecular aryl exchange takes place prior to, or during, the coupling step, and gives additional evidence against aryl free-radical participation.) Thus in solution, as in neat melts,[13a] concerted unimolecular reductive elimination is the only thermolytic path of any importance.

From observation of the decomposition of $[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$ it is evident that both arene and biaryl derived from the phosphine ligand are ultimately released in minor, although significant, amounts. Although the conditions are milder, these secondary processes occur (as in the neat substances [13a]) under the same conditions as primary biaryl elimination but are essentially independent of it, as shown by the vanishing yield of 4-methylbiphenyl from $[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$.

There is no evidence against our earlier [13a] explanations. Indeed, the present results support our contention that free radicals are not involved to any significant degree even in the secondary processes. It appears that the fragment $Pt^0(PPh_3)_2$ is not effectively stabilised by solvation in toluene, and even at 333 K, as at higher temperatures,[13a] undergoes decomposition *via* oxidative insertions of the low-valent metal into P–C and C–H bonds, with subsequent reductive eliminations.

Closely related addition–elimination reactions involving PPh_3 clearly operate in nickel [21,22] and palladium [21] systems, and presumably account for the products of thermolysis of $[Pt(PPh_3)_4]$.[23] The most likely source of hydrogen atoms incorporated in ligand-derived arene is considered to be orthometallation rather than the alternative of transfer hydrogenolysis of co-ordinated PPh_3; [24] xylene displayed no reactivity of this type. The ultimate solid decomposition residues, which, in red-brown colour and glassy consistency, were indistinguishable from those obtained after thermolysis of the neat complexes, were not extensively studied. Infrared analysis did, however, reveal a new absorption at 1 115 cm^{-1}, suggestive of the presence of orthometallated arylphosphine.[13,25]

(*ii*) *Kinetics, and effect of added phosphines.* The thermal decomposition of $[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$ was observed (by monitoring the appearance of 4,4'-bitolyl) to be first order for at least two half-lives (Figure 1). Empirical first-order rate constants (k_T/s^{-1}) at 323, 333, and 343 K are presented in Table 2. These parameters conform (Figure 2) to the linear Arrhenius relation (1), and

$$\ln k = 18.51 - (9\,180/T) \qquad (1)$$

correspond to an overall activation energy for decomposition $E^‡$ of 76.3 ± 3.9 kJ mol^{-1} and a frequency factor A of 1.10×10^8 s^{-1}.

Similar observation of biphenyl evolution during thermal decomposition of $[PtPh_2(PPh_3)_2]$ in toluene at 60 °C confirm that this elimination also proceeds in accordance with first-order kinetics to a comparable extent of decomposition. The empirical rate constant associated with this process was measured to be $k_{333} = (7.60 \pm 0.78) \times 10^{-5}$ s^{-1}.* These kinetic results are collectively consistent with the proposed unimolecular mode of decomposition (see above).

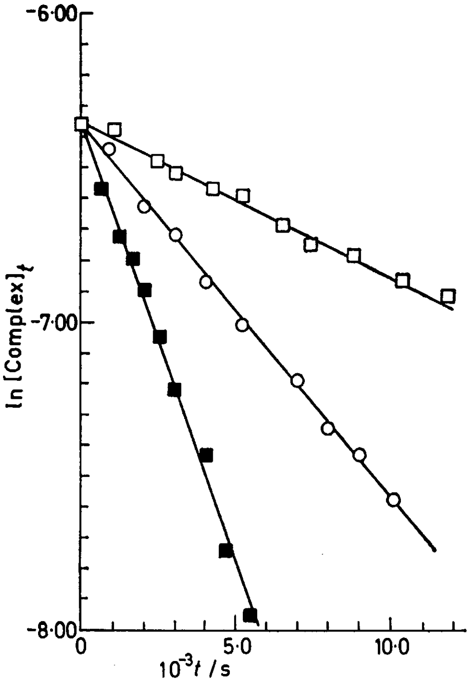

FIGURE 1 First-order plots for thermal decomposition of *cis*-$[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$ in toluene at 50 (□), 60 (○), and 70 °C (■)

TABLE 2

Kinetic parameters for thermal decomposition of *cis*-$[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$ in toluene *

θ_c/°C	$10^5k_T/s^{-1}$	$t_{\frac{1}{2}}^T$/h
50	4.95 ± 0.25	3.89
60	12.34 ± 0.61	1.56
70	26.04 ± 0.82	0.74

* Results were reproducible to ±4%; gradients of plots and errors were determined by least-squares computation.

For reactions occurring in solution two further kinetic relations (2) and (3) [26,27] lead to values for the enthalpy ($\Delta H^‡$) and entropy ($\Delta S^‡$) of activation: (R = 8.314 3 J K^{-1} mol^{-1}). Overall, thermal decay of $[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$ was found to exhibit an activation enthalpy

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*Assuming secondary biphenyl formation from $[PtPh_2(PPh_3)_2]$ parallels that from $[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$, the consequent systematic error in kinetic monitoring would lead to a primary rate constant *ca.* 5% too high, which is of the order of experimental uncertainty.

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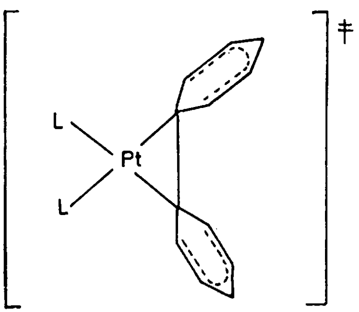
of 74 ± 4 kJ mol^{-1} and an activation entropy of −99 ± 16 J K^{-1} mol^{-1}. {Reductive elimination of ethane from [$PtMe_3I(PMePh_2)_2$] reportedly gave values for $\Delta H^\ddagger$ and

$$\Delta H^\ddagger = E^\ddagger - RT \text{ kJ mol}^{-1} \qquad (2)$$

$$\Delta S^\ddagger = 19.155(\log A - 13.23) \text{ J K}^{-1} \text{ mol}^{-1} \qquad (3)$$

$\Delta S^\ddagger$ of 129 ± 5 kJ mol^{-1} and 87 J K^{-1} mol^{-1} respectively.[8a]} The bond-dissociation energy D(Pt–Ph) in *trans*-[$PtPh_2(PEt_3)_2$] has been calculated [28a] as 272 kJ mol^{-1}. Assuming this as an approximate lower limit for *cis*-[$PtR_2(PPh_3)_2$] (the *trans* influence of PPh_3 is less than than of aryl [28b]), spontaneous dissociation of a single aryl substituent does not appear to be a plausible contributor to the activation process occurring here.

The notable negative value for $\Delta S^\ddagger$ indicates considerable loss of conformational freedom on proceeding to the transition state, presumably through appreciable new bond formation, as in those concerted sigmatropic rearrangements (*e.g.* Cope and Claisen) whose transition states demand considerable restriction of molecular flexibility.[29] A plausible activated state for the reductive elimination of biaryl from *cis*-[PtR_2L_2], in accord with this observation, is depicted in (I). Such an intermediate could perhaps be attained *via* preliminary interaction of the p_π orbitals of suitably orientated aryl substituents. This would constrain the mutual orientation of the aryl groups, thus contributing to the large negative entropy of activation. The electron density which contributes to the embryonic ligand–ligand σ bond might be derived largely from ligand π orbitals in other cases also; * and in fact, in many cases of carbon–carbon coupling *via* transition-metal–carbon scission, one or more of the carbon atoms involved has formal sp^2 or sp hybridisation. (Examples include aryl,[5b,30-32] vinyl,[7,30,33] alkynyl,[5b] and acyl [8b,32,34] substituents.)



(I)

The small but reproducible increase in lability observed for the 4-tolyl derivative ($t_{\frac{1}{2}}^{333}$ 1.56 h) relative to its phenyl analogue ($t_{\frac{1}{2}}^{333}$ 2.53 h) is of course consistent with electron release from aryl in the transition state; however, comprehensive studies of a wide range of ring-substituted arylplatinum derivatives would be needed to test this suggestion and to distinguish inductive and mesomeric from stereorestrictive effects.

Tertiary phosphines can play important but diverse roles in the decomposition of their organotransition-metal derivatives. For example, β elimination from *cis*-[$PtBu^n{}_2(PPh_3)_2$] is retarded on addition of PPh_3 since phosphine dissociation to vacate a co-ordination site is ordinarily rate-limiting.[35] Alkene elimination from the platinacyclopentane [$Pt\{(CH_2)_4\}(PPh_3)_2$] is, in contrast, facilitated by excess of PPh_3.[36]

The kinetic consequences of the presence of free PPh_3 during decomposition of [$PtR_2(PPh_3)_2$] (R = Ph or C_6H_4Me-4) have been briefly investigated. On addition of an 8—10-fold excess of PPh_3, thermal destruction proceeded at **333** K *via* primary concerted reductive elimination according to a (pseudo-) first-order rate law. Only trace amounts of secondary products were detectable (after 2—3 half-lives) and the residual solutions were the bright yellow characteristic [37] of $Pt^0(PPh_3)_n$ (n = 3 or 4). Decay of both species was consistently more rapid [by 26 (R = Ph) and 27% (C_6H_4Me-4)] than under ligand-free conditions, in accord with previous observations.[13b] The origin of this effect has not, however, been clarified as yet. Preliminary studies suggest that it does not display an easily interpretable concentration dependence, and a more exhaustive investigation is planned. The results do, however, demonstrate that phosphine dissociation is not a normal requirement for reductive elimination from these diorganoplatinum(II) complexes. Certain polyalkyl(phosphine)gold(III) species have, in contrast, been shown to undergo thermal reductive elimination which is retarded on the addition of free ligand, and electron-deficient three-co-ordinate intermediates have been proposed.[9] However, aggregation may also be important in these systems, particularly in poorly co-ordinating solvents. Thus the chemical differences between derivatives of Au^{III} and Pt^{II} can lead to mechanistic differences even in closely related reactions. Moreover, alkyl- and aryl-transition-metal complexes often differ in their behaviour. Alkylgold(III) and arylplatinum(II) species both exhibit primary carbon–carbon coupling, but the process has

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* Interestingly, a crucial, if not quite parallel, role has been proposed for a molecular orbital derived from the (hyperconjugative) π residues on alkyl ligands during *cis*-reductive elimination from alkylgold(III); see ref. 9*b*.

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[33] J. Schwartz, D. W. Hart, and J. L. Holden, *J. Amer. Chem. Soc.*, 1972, **94**, 9269.

[34] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2969; also *cf.* J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1976, **98**, 6529; E. Weissburger and P. Laszlo, *Accounts Chem. Res.*, 1976, **9**, 209 and refs. therein.

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[36] J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1976, **98**, 6521.

[37] See, for example, L. Malatesta and F. Cariello, *J. Chem. Soc.*, 1958, 2323.

yet to be demonstrated in dialkylplatinum(II) derivatives.*

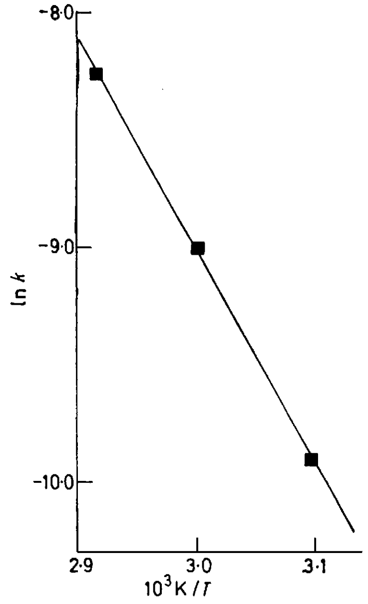


Figure 2 Arrhenius plot of the first-order rate constant k for decomposition of $[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$

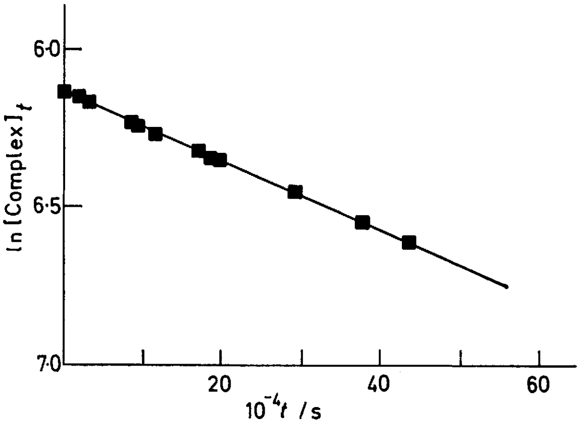


Figure 3 First-order plot for thermal decomposition of $[Pt(C_6H_4Me\text{-}4)_2(dppm)]$ in toluene in the presence of 10 equiv. of dppm

The secondary decomposition processes, although readily identifiable, were too slow for kinetic studies. It is, however, clear that free PPh_3 appears to stabilise the platinum(0) species as expected.

Complexes of Other Phosphine Ligands.—The other diarylplatinum(II) species examined all decomposed more slowly, under identical conditions, than those incorporating PR_3 (R = aryl), but the primary mechanism still seemed to be concerted reductive elimination.

The chelate complex $[PtPh_2(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] was stable over 12 d at 333 K, either alone or in the presence of six mol equivs. of dppe. Similarly, neither of the species $[PtR_2(dmpe)]$ [dmpe = 1,2-bis(dimethylphosphino)ethane; R = Ph or C_6H_4Me-4] afforded any indication of thermal decomposition at 333 K in the same time. Whereas neither of the analogues $[PtR_2(dppm)]$ [dppm = bis(diphenylphosphino)methane; R = Ph or C_6H_4Me-4] showed detectable signs of disintegration when heated alone, both were observed slowly to eliminate biaryl at 333 K when a 10 mol equiv. excess of dppm was introduced. The (pseudo-) first-order rate constant for decomposition of $[Pt(C_6H_4Me\text{-}4)_2(dppm)]$ under these circumstances (Figure 3) was measured to be $(1.07 \pm 0.03) \times 10^{-6}$ s^{-1} ($t_{\frac{1}{2}}$ 180 ± 5). A similar, notable, labilisation of these complexes on addition of free phosphine had emerged during examination of thermolyses of the neat substances.[13b] There was no sign of a secondary reaction in solution, in contrast to our results[13b] in the absence of solvent, although primary decay had proceeded to an extent of 35% in the 5 d during which it was monitored. (1 mol % benzene or biphenyl would have been readily detected; $PMePh_2$ or PPh_3[13b] would not have survived the HCl quench.) Further analysis of the lemon-yellow solution was not pursued. 4,4'-Bitolyl was also, interestingly, liberated sluggishly at 333 K by a solution of $[Pt(C_6H_4Me\text{-}4)_2(dppm)]$ to which 10 mol equiv. of $PMePh_2$ had been added. The identity of the decomposing species cannot, however, be assigned with certainty because of the possibility of ligand exchange.

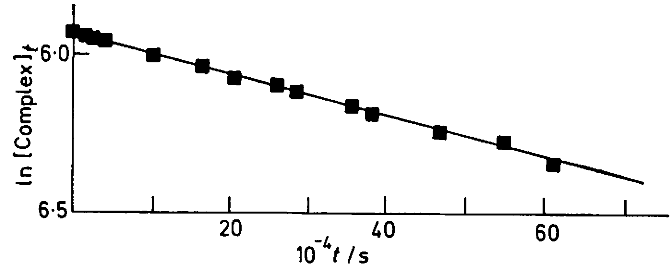
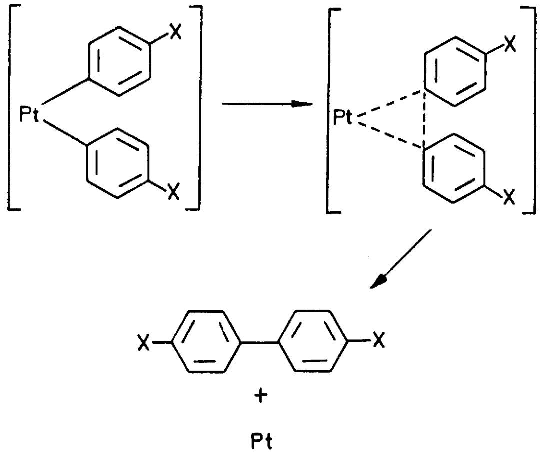


Figure 4 First-order plot for thermal decomposition of *cis*-$[PtPh_2(PMePh_2)_2]$ in toluene



Scheme Concerted reductive elimination of biaryl from *cis*-PtR_2

High thermal stability does not necessarily require a

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* It is now apparent that the previously reported[36] generation of cyclobutane during thermal decomposition of $[Pt\{(CH_2)_4\}(PBu^n_3)_2]$ originates from a platinum(IV) intermediate (G. M. Whitesides and G. B. Young, unpublished work).

chelating phosphine, since the complexes *cis*-[$PtR_2(PMePh_2)_2$] (R = Ph or C_6H_4Me-4) underwent concerted biaryl elimination only very slowly at 333 K in toluene. The first-order rate constant for the decay of [$PtPh_2(PMePh_2)_2$] (Figure 4) was determined to be $(6.66 \pm 0.12) \times 10^{-7}$ s^{-1} ($t_{\frac{1}{2}}$ 290 ± 6 h), slower by two orders of magnitude than that of [$PtPh_2(PPh_3)_2$] under the same conditions. Only a small quantity (*ca.* 2 mol %) of secondary benzene was released during the 37% decomposition which occurred during the period of observation (7 d).

It appears, therefore, that complexes of the general type *cis*-[PtR_2L_2] (R = aryl) display a general mechanistic preference for concerted reductive elimination of (metal-derived) biaryl as their primary mode of thermal decomposition in solution, as in the neat melts.[13,38] Formation of phosphine-derived biaryl and arene is a secondary process which occurs, in each case, concomitantly with but independent of primary metal–carbon scission. There emerges, however, a notable diversity of eliminative lability as L is varied. The $^1J(^{195}Pt-^{31}P)$ values (Table 1) obtained from ^{31}P n.m.r. analyses do not betray any great dissimilarities of electronic nature among the Pt–P bonds in the complexes studied which could reasonably account for an increase, of at least 10^2, in the rate of decay of [$PtR_2(PPh_3)_2$] compared with its $PMePh_2$- or dppe-containing analogues. {The anomalously low coupling constants associated with dppm complexes have been noted elsewhere;[39] [PtR_2(dppm)] is, in any case, more thermally stable than [$PtR_2(PMePh_2)_2$].} However, it may be significant that the greatest lability is associated with the most sterically demanding ligand, PPh_3 (cone angle[40] 145°). In complexes of less cluttered ($PMePh_2$) and less flexible (bidentate) ligands * greater freedom of movement of the aryl ligands may render their requisite interaction more difficult. Unfortunately, our attempts to prepare the more hindered † [$PtR_2\{P(C_6H_{11})_3\}_2$] by treating *trans*-[$PtCl_2\{P(C_6H_{11})_3\}_2$] with LiR (R = aryl) were unsuccessful.

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* The P–Pt–P angle in [$PtPh_2$(dppm)] is only 73° (although the C–Pt–P angle remains close to 90°). Interestingly, the aryl rings are approximately perpendicular to the co-ordination plane and the C–C distance is less than the van der Waals diameter of carbon, *cf.* structure (I).

† The cone angle for $P(C_6H_{11})_3$ is 179°.[40]

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