Pyrolysis of Diaryl(phosphine)platinum(II) Complexes: Reductive Elimination followed by Subsequent Decomposition of the Platinum-containing Residue †

By **Paul S. Braterman,* Ronald J. Cross,*** and **G. Brent Young,** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

The condensed-phase thermolyses of complexes [PtR$_2$L$_2$] and [PtR$_2$(P–P)] [R = Ph or C$_6$H$_4$Me-4; L = PPh$_3$ or P(C$_6$H$_4$Me-4)$_3$; P–P = Ph$_2$PC$_2$H$_4$PPh$_2$(dppe) or Ph$_2$PCH$_2$PPh$_2$ (dppm)] have been examined by t.g.a., d.t.a., d.s.c., and product analysis. The primary decomposition step is concerted reductive elimination forming R$_2$. Experiments on mixtures established both that this elimination is intramolecular, and that no scrambling of ligands occurs prior to pyrolysis. Secondary decompositions of [PtL$_2$] and [Pt(P–P)] give reproducible but non-stoicheiometric amounts of biaryl and arene, probably *via* insertion of Pt^0 into aryl–phosphorus and –hydrogen bonds followed by eliminations from Pt. Red-brown glassy residues remain. The mechanisms of these steps and the nature of the residues are discussed.

THERE has recently been a great upsurge of interest in the decomposition modes of organotransition-metal complexes.[1] Of particular importance, β elimination,[2] reductive elimination,[3] binuclear elimination,[4] and α elimination[5] have been identified as common reaction paths, and knowledge of these processes has been exploited in the design of stable organotransition-metal complexes, and in the interpretation of synthetic and catalytic reactions involving such complexes.

β Elimination is undoubtedly the best understood of these four reactions. Numerous examples afford a full understanding of its operation, and it can be controlled at will in many cases. Much less is known about reductive elimination and the other reactions. For example, well established cases of concerted reductive elimination of two one-electron carbon ligands from a metal centre are quite rare, and confined largely to compounds of Au^{III} and Pt^{IV}.[3] Such processes involve lowering the oxidation number, the co-ordination number, and the formal electron count, all by 2. We have argued[1] that such a reaction should be favoured by compounds with unusually high levels of orbital occupation and high co-ordination numbers.

By analogy with other elimination processes, such as loss of co-ordinated unidentate ligands or olefins, we further predicted[1] that an increase in electron occupancy at the reactive metal centre should facilitate elimination processes, including reductive elimination. Examples of oxidative addition achieving this are numerous (see ref. 1 and refs. therein), but examples of the simple addition of two-electron donors, which should produce the same result, are uncommon. We believe that the facilitation by olefins of the reductive elimination of butane from [NiEt$_2$(bipy)] (bipy = 2,2′-bipyridyl)[6] is one such example. The activation energy of the elimination is greatly reduced by olefin co-ordination at nickel. The effect of 1,2-bis(diphenylphosphino)ethane (dppe) on [PtH(GePh$_3$)(PEt$_3$)$_2$], producing [Pt(dppe)$_2$], PEt$_3$, and GePh$_3$H,[7] is probably another example of attack of a two-electron donor promoting reductive elimination, but the accompaniment of ligand exchange clouds the issue somewhat.

We have examined the pyrolyses of several diarylbis(phosphine)platinum(II) complexes in the hope of observing reductive elimination in these systems. Platinum derivatives were chosen in preference to their palladium or nickel analogues as they are more easily purified and decompose at conveniently high temperatures. Aryl compounds were selected to suppress any competing β elimination {[PtBu$_2$(PPh$_3$)$_2$] decomposes readily by this route[8]}. Although phosphine complexes of the type [PtR$^1_2$(PR$^2_3$)$_2$] (R^1 = aryl, R^2 = alkyl) are generally of *cis* configuration[9] (another prerequisite for concerted reductive elimination), some complexes of the chelating ligands dppe and Ph$_2$PCH$_2$PPh$_2$ (dppm), which ensure retention of this geometry, were also examined. Results of this study are presented here. We have also examined the effects of tertiary phosphine nucleophiles on the thermolyses of [PtR$^1_2$L$_2$] and [PtR$^1_2$(P–P)] (P–P = bidentate phosphine) and this work is described in the following paper. Preliminary accounts have been presented.[10]

During the early stages of this work a report of the thermolyses of [PtR$^1_2$(PPh$_3$)$_2$] (R^1 = Ph, C$_6$H$_4$F-*m* or -*p*), eliminating R$^1_2$ and benzene, was published.[11] More recently, reductive elimination of R^{1}R^2 from *trans*-[MR^{1}R^2(PEt$_3$)$_2$] (M = Pd or Ni) in solution has

---

† No reprints available.

[1] P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, 1973, **2**, 271.

[2] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533; J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1968, 190.

[3] M. P. Brown, R. J. Puddephatt, and C. E. Upton, *J. Organometallic Chem.*, 1973, **49**, C61; A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1974, **96**, 6140.

[4] G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Fillipo, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 1426; J. Schwartz and J. B. Cannon, *ibid.*, 1974, **96**, 2276.

[5] N. J. Cooper and M. L. H. Green, *J.C.S. Chem. Comm.*, 1974, 208, 761; T. Ikariya and A. Yamamoto, *ibid.*, p. 720.

[6] T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1971, **93**, 3350, 3360.

[7] E. H. Brooks, R. J. Cross, and F. Glockling, *Inorg. Chim. Acta*, 1968, **2**, 17.

[8] G. M. Whitesides, J. F. Gaash, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 1972, **94**, 5258.

[9] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.

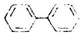
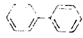
[10] P. S. Braterman, R. J. Cross, and G. B. Young, (*a*) 7th Sheffield–Leeds Symposium on Organometallic Chem., 1974; (*b*) *J.C.S. Chem. Comm.*, 1975, 627.

[11] F. Glockling, T. McBride, and R. J. I. Pollock, *J.C.S. Chem. Comm.*, 1973, 650.

been described,[12] but decomposition of *trans*-[$NiR^1(PR^2_3)_2X$] (R^1,R^2 = aryl) produces all combinations of biaryl, *i.e.* R^1_2, R^2_2, and R^1R^2.[13]

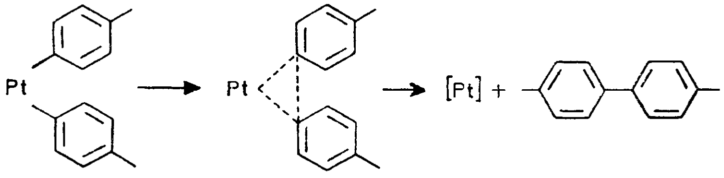
RESULTS AND DISCUSSION

The pure complexes were pyrolysed at 1 atm pressure under N_2 or argon,* and at a temperature *ca.* 10 K above the onset of decomposition (indicated by a d.s.c. or d.t.a. exotherm). The volatile decomposition products were subsequently transferred *in vacuo* at a similar temperature to a trap at 77 K, to be analysed quantitatively by g.l.c., and decomposition undoubtedly continued during the transfer. In all cases a melting endotherm immediately preceded the decomposition exotherm in the d.t.a. traces, and volatile aromatic products were eliminated leaving an involatile red-brown glassy residue. In view of the non-stoicheiometric amounts of some products, each reaction was carried out at least twice to verify the reproducibility of the experiments. The error in product determination is ±2% for biaryls and ±4% for arenes. The reaction conditions and products are listed in the Table. Trace amounts of free phosphine were detected from the complexes of unidentate ligands. (The chelate complexes could also have lost free ligand, but this would neither have been wholly transferred nor detected under our conditions.) No other volatile materials (with the possible exception of H_2, which was not looked for) were produced.

System	Temperature of onset of decomposition (T_d/K)	Thermolysis temperature (T_t/K)	Thermolysis time (t/h)	Amount of product (mol [mol Pt]$^{-1}$)					
									PR_3 P–P
[$PtPh_2$(dppm)]	503	508	2.0	0.29		1.19			*a*
[$PtPh_2$(dppe)]	516	523	2.0	0.20		1.13			*a*
cis-[$PtPh_2(PPh_3)_2$]	419	(*i*) 433 (*ii*) 523	1.0 1.0	0.35		1.12			0.14
[$Pt(C_6H_4Me\text{-}4)_2$(dppm)]	516	518	2.0	0.13	0.15	0.09	0.89	0.08	*a*
cis-[$Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2$]	380	(*i*) 403 (*ii*) 528	1.0 7.0	0.30	0	0.29	0.97	*b*	0.15
cis-[$PtPh_2\{P(C_6H_4Me\text{-}4)_3\}_2$]	418	518	5.0	0	0.59	1.01	0.29	⩽0.01	0.06
1 : 1 [PtR_2(dppm)] [c]	502	508	1.8	0.29 (0.21)	0.09 (0.08)	0.60 (0.64)	0.45 (0.45)	0.03 (0.04)	*a*
1 : 1 *cis*-[$PtPh_2(PR_3)_2$] [c]	418	(*i*) 433 (*ii*) 523	1.0 1.0	0.15	0.13	1.02	0.03	0.08	*d*

[a] Not detectable by technique employed. [b] Trace amount detected ($<10^{-3}$ mol). [c] R = Ph or C_6H_4Me-4. [d] Both phosphines detected but not quantified.

The thermolyses of the phenyl complexes *cis*-[$PtPh_2(PPh_3)_2$], [$PtPh_2$(dppe)], and [$PtPh_2$(dppm)] showed that more than one equivalent of biphenyl was produced. Some benzene was also formed and it was immediately apparent that elimination of aryl groups originally located on the phosphine ligands was also involved. To establish the origin of these materials, [$Pt(C_6H_4Me\text{-}4)_2$(dppm)], *cis*-[$Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2$], and *cis*-[$PtPh_2\{P(C_6H_4Me\text{-}4)_3\}_2$] were examined. Pyrolyses of the latter two complexes confirmed that the aryl groups originally bonded to platinum were eliminated quantitatively as biaryl, and the extra biaryl and arene were exclusively derived from the ligands. 4-Methylbiphenyl was virtually absent, indicating that, although eliminations of aryl from platinum and phosphorus take place under the same conditions, the processes are quite separate. The complex [$Pt(C_6H_4Me\text{-}4)_2$(dppm)] did produce arene from both Pt and P, and a significant amount (0.08 mol) of 4-methylbiphenyl. The behaviour of this complex seems atypical, however, and will be discussed later.



SCHEME 1

These results establish that the primary mode of decomposition of these [$PtR^1_2L_2$] complexes is concerted reductive elimination of biaryl (Scheme 1). The failure to observe R^1H strongly indicates that free aryl radicals are not involved, and also shows that *ortho*-metallation, a well established process in this part of the periodic table,[14] does not occur at least prior to elimination from platinum. Furthermore, the fact that no isomerisation accompanies biaryl formation (4,4′-bitolyl was the only isomer produced) rules out the operation of a β-elimination route *via* a hydrido–benzyne intermediate.†

---

* 1 atm = 101 325 Pa; 1 D ≈ 3.33×10^{-30} C m.

† Benzyne complex formation is implicated in the thermolyses of [$TiPh_2(cp)_2$] (cp = η-cyclopentadienyl).[15]

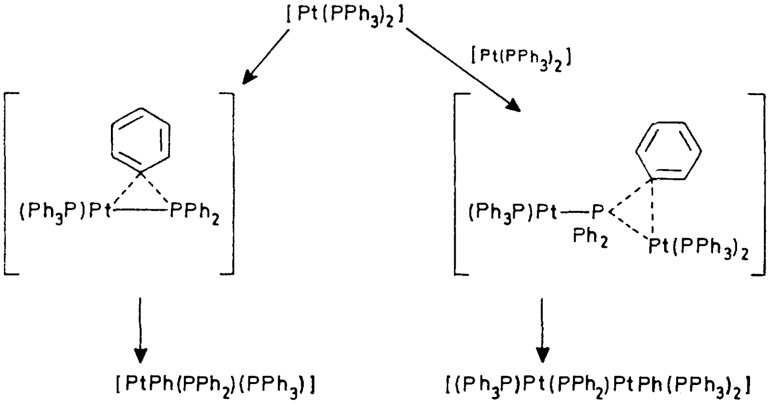
[12] G. W. Parshall, *J. Amer. Chem. Soc.*, 1974, **96**, 2360.

[13] A. Nakamura and S. Otsuka, *Tetrahedron Letters*, 1974, 463.

[14] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

[15] I. Dvorak, R. J. O'Brien, and W. Santo, *Chem. Comm.*, 1970, 411; C. P. Bockel, J. H. Teuben, and H. J. De Liefde Meijer, *J. Organometallic Chem.*, 1974, **81**, 371.

The operation of concerted reductive elimination is implicit in the reported thermolyses of $[Pt(C_6H_4F)_2(PPh_3)_2]$,[11] and tends to confirm that such elimination of biaryl is the general primary mode of decomposition in platinum complexes of this type. Also, the elimination of R^1R^2 from $[MR^1R^2(PEt_3)_2]$ (M = Pd or Ni) [12] might indicate that this mechanism has even wider application in 16-electron complexes of Group 8 elements, although the reported acceleration of the decomposition of these complexes by impurities complicates the issue here. The complexes $[NiR^1(PR^2{}_3)_2X]$ (R^1,R^2 = aryl) give all combinations of biaryl.[13] Thus the lower thermal stability of nickel and palladium organometallics might be due in part at least to reaction paths which compete with reductive elimination.



SCHEME 2

As final confirmation that the primary reductive elimination of biaryl from our complexes is intramolecular, 1 : 1 mixtures of $[Pt(C_6H_4Me\text{-}4)_2(dppm)]$ and $[PtPh_2(dppm)]$ (prepared by freeze-drying mixed solutions) were pyrolysed in the usual manner. The results (Table) agree closely with those expected from independent thermolyses of the single complexes (values in parentheses). No increase in the amount of 4-methylbiphenyl, an expected product of binuclear eliminations, was apparent. This experiment also shows that no intermolecular exchange of aryl groups takes place, either in benzene solution or in the melt prior to decomposition.

After reductive elimination of biaryl, the subsequent (secondary) decomposition of the (presumed) $[Pt(PPh_3)_2]$, $[Pt\{P(C_6H_4Me\text{-}4)_3\}_2]$, [Pt(dppm)], or [Pt(dppe)] fragments gives both biaryl and arene in non-stoicheiometric amounts. Our results conflict with a previous report [11] that, under similar conditions, $[Pt(PPh_3)_2]$ gives one equivalent of benzene only. The secondary processes take place under the same conditions as the primary elimination. Nevertheless the secondary eliminations are slower. While the primary processes appear to be generally complete within minutes (d.t.a.), the primary residues continue to evolve arene and biaryl uninterruptedly for several hours. For example $[Pt(C_6H_4Me\text{-}4)_2(PPh_3)_2]$ still evolved C_6H_6 and Ph_2 after 10 h at 528 K *in vacuo*. Thus the amounts of arene and ligand-derived biaryl in the Table are to an extent dependent on the time (and, relatedly, the temperature) of the thermolyses.

It seems probable that the secondary products are formed *via* transfer of hydrogen and/or aryl from ligand to platinum, followed by reductive elimination of arene or biaryl from platinum. This can account for both primary and secondary eliminations proceeding under identical conditions. The transfer of hydrogen from L to Pt can readily be envisaged as occurring *via* *ortho*-metallation.[14] The complexes $[PtL_2]$ or [Pt(P–P)], 14-electron two-co-ordinate species, are likely to take part in such processes.[1] In each case, i.r. examination of the thermolysis residues revealed the presence of new absorptions at *ca.* 1 110—1 115 cm^{-1}. The appearance of bands in this region has previously been considered indicative of *ortho*-metallation of arylphosphines.[16]

The transfer and elimination of aryl from the phosphines takes place once again without isomerisation (4,4′-bitolyl was the only isomer from $[PtPh_2\{P(C_6H_4Me\text{-}4)_3\}_2]$). Scheme 2 indicates possible transfer routes. Here also the low electron availability and co-ordination number at platinum should aid such processes. Not all the transferred aryl is eliminated. Treatment of toluene solutions of the residue by concentrated aqueous HCl followed by g.l.c. analysis revealed the presence of arene. (Standard experiments demonstrated that platinum aryls quantitatively generate arene under these conditions.) No phenylplatinum species were present in the residue from $[PtPh_2\{P(C_6H_4Me\text{-}4)_3\}_2]$ and, notably, in each case no σ-bound biaryl species were detected. Both the *ortho*-metallation and aryl-transfer processes are essentially insertions of Pt^0 into aryl–hydrogen or –phosphorus bonds.

The secondary processes are likely to be binuclear. An experiment on a 1 : 1 intimate mixture of $[PtPh_2\{P(C_6H_4Me\text{-}4)_3\}_2]$ and $[PtPh_2(PPh_3)_2]$ produced the statistically expected amount of 4-methylbiphenyl,

---

[16] J. J. Levinson and S. S. Robinson, *J. Chem. Soc.* (*A*), 1970, 639; M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 2098; 1973, 1667.

assuming prior elimination of Ph_2 from both species (at similar and rapid rates, compared to the secondary processes) followed by scrambling of the remaining aryl groups in the secondary processes. This does not unequivocally prove an intermolecular mechanism for the aryl-transfer step, however, because, although a ^{31}P n.m.r. investigation showed that no phosphine exchange took place prior to thermolysis, it is possible that such exchange does take place after the primary reductive elimination but before the secondary steps.

A strong interaction between a phosphorus-bonded phenyl group and the relatively electron-starved platinum atom of $[PtL_2]$ or [Pt(P–P)] seems likely to operate either synchronously with the primary reductive elimination of biaryl or immediately afterwards. A recent crystal-structure analysis of $[RuH(PPh_3)_3]^+$ shows one of the phosphines to be π-arene bonded,[17] and similar structures, such as $[(Ph_3P)_2Pt\{(\eta\text{-Ph})Ph_2P\}\text{-}Pt(PPh_3)]$, might be formed as intermediates in our cases. This η-bonded phenyl group would be well placed for H or aryl transfer to platinum.

Despite the operation of (apparently) two secondary processes, both take place under the same conditions as the primary process for each complex. This makes their slowness, their lack of stoicheiometry, and their reproducible product ratios the more difficult to explain. We suggest that both hydrogen and aryl transfer to Pt might take place rapidly, and perhaps reversibly. However, rapid irreversible elimination of biaryl or arene can only take place under stringent conditions. Either both fragments must be located *cis* on the same metal atom, or else they must be on neighbouring metal atoms so disposed that binuclear elimination can take place with formation of Pt–Pt bonds.[18] Irreversible elimination would of course open the way to further insertion reactions, although Pt–Pt bond formation might be chain terminating.

Another possibility which must be considered, however, is that the intermediates $[PtL_2]$ or [Pt(P–P)] may not be as unstable as has been believed (see refs. 11 and 18 and refs. therein). The slow generation of secondary products might then simply reflect a slow decomposition. In support of this can be cited mechanistic evidence for the participation of $[Pt(PPh_3)_2]$ in reactions,[19] and the isolation of several $[Pd^0L_2]$ species (L = bulky tertiary phosphines).[20] On the other hand we failed to isolate any crystalline material from the residues after decomposition, even after (apparently) only a low percentage of secondary reaction. Indeed our red-brown glassy residues resisted all attempts at crystallisation or purification after either long or short thermolyses. This behaviour would be consistent with random polymeric species containing PPh_2–C_6H_4 and PPh_2 bridging units.

The complex $[Pt(C_6H_4Me\text{-}4)_2(dppm)]$ produced both toluene and benzene, as well as some mixed biaryl, 4-methylbiphenyl. (The diphenylplatinum complexes with chelate ligands may also behave in this way, but lack of a suitable label on the aryls obscures analysis.) Since no isomerisation of the tolyl group takes place, it is at least possible that the same reaction paths operate as in unidentate compounds (reductive elimination of bitolyl is still by far the most prominent process), but competitively instead of the secondary processes being entirely dominated by the primary one.

We cannot explain this anomaly at present but a number of possibilities come to mind. First, the small bite of the dppm ligand at platinum (only 73°)[21] might expose the Pt atom to aryl attack before elimination of bitolyl. Secondly, the higher pyrolysis temperatures necessarily employed for the chelate complexes might make available additional reaction paths. Most relevant could be the scrambling of aryls between P and Pt. Such a transfer has been observed for $[PtMe_2(PPh_3)_2]$:[22] pyrolysis produces $PMePh_2$ as well as PPh_3. After this type of operation, the usual primary and secondary sequences would account for all the observed materials.

EXPERIMENTAL

^1H N.m.r. parameters were recorded on JEOL C-60HL or Varian HA100 instruments. ^{31}P N.m.r. data were accumulated by a Varian XL100 spectrometer, using pulse Fourier-transform techniques due to the generally low solubility of the complexes. Differential scanning calorimetry (d.s.c.) was made on a Perkin-Elmer DSC-1B instrument at 16° min^{-1} under a nitrogen atmosphere. Simultaneous thermal-gravimetric- and differential-thermal-analytical (t.g.a. and d.t.a.) data were obtained at a heating rate of 4° min^{-1} on Stanton-Redcroft equipment, also under an atmosphere of nitrogen. Chromatographic analyses of decomposition products were carried out on a Pye series 104 gas chromatograph. Aryl-derived products were separated and quantified on a 5-ft glass column of 8% Apiezon L–Gas-Chrom Q (100—120 mesh) using n-decane as internal standard (temperature programme: isothermal at 60 °C for 60 s; maximum 200 °C, linearly at 15° min^{-1}; isothermal at 200 °C for 10 min). Monotertiary phosphines were monitored using a 5-ft column of 2% OV-1–Gas-Chrom Q (100—120 mesh), again with internal n-decane as standard (temperature programme: isothermal at 60 °C for 60 s; maximum 250 °C, linearly at 15° min^{-1}). Detection was by the flame-ionisation technique (f.i.d.).

All procedures were carried out in oven-dried glassware under an atmosphere of pure nitrogen or argon. Inert gases were dried by passing through a column (4 ft × 1 in diameter) of activated Linde 5A molecular sieves. For thermal decomposition, nitrogen was additionally diverted through a spiral trap at 77 K.

---

[17] J. C. McConway, A. C. Skapski, L. Phillips, R. J. Young, and G. Wilkinson, *J.C.S. Chem. Comm.*, 1974, 327.

[18] N. J. Taylor, P. C. Chieh, and A. J. Carty, *J.C.S. Chem. Comm.*, 1975, 448.

[19] J. P. Birk, J. Halpern, and A. P. Pickard, *J. Amer. Chem. Soc.*, 1968, **90**, 4491; A. V. Kramer, J. A. Labinger, J. S. Bradley, and J. A. Osborn, *ibid.*, 1974, **96**, 7145; J. Halpern and T. A. Weil, *J.C.S. Chem. Comm.*, 1973, 631.

[20] A. Immirzi and A. Musco, *J.C.S. Chem. Comm.*, 1974, 400; M. Matsumoto, H. Yashioka, K. Nakatsu, T. Yoshida, and S. Otsuka, *J. Amer. Chem. Soc.*, 1974, **96**, 3322; W. Kuran and A. Musco, *Inorg. Chim. Acta*, 1974, **12**, 187.

[21] P. S. Braterman, R. J. Cross, Lj. Manojlovic-Muir, K. W. Muir, and G. B. Young, *J. Organometallic Chem.*, 1975, **84**, C40.

[22] F. Glockling and T. McBride, personal communication.

Complexes were prepared by the standard transmetallation route,[9] and were purified by three recrystallisations. Satisfactory C and H microanalyses were obtained for all complexes. Whilst the complexes were sufficiently air-stable to be stored under air, all were protected from light as the [$PtR_2(PPh_3)_2$] systems displayed a susceptibility to turn yellow when exposed. The *cis* configuration of the monotertiary complexes was confirmed from their values of $^1J(^{195}Pt-^{31}P)$. Also the dipole moment of *cis*-[$PtPh_2(PPh_3)_2$] in benzene (7.2 D) compared well with the literature value (7.0 D).[9]

Intimate 1 : 1 solid mixtures were prepared by freeze-drying of the appropriate mixture in benzene solution. The homogeneity of the sample was verified by examination of the thermal profile by d.s.c. The mixture invariably displayed a single sharp fusion endotherm prior to a decomposition exotherm over the range expected from consideration of the individual complexes.

Thermolyses.—Instrumental methods. Differential thermal techniques revealed a general trend for these complexes: *i.e.* a preliminary melting endotherm which was rapidly overwhelmed by a sharp decomposition exotherm. These irreversible procedures were accompanied (t.g.a.) by an accelerating weight loss, which slowly diminished after 45—60 min to a continuing gradual effusion. {At the higher heating rate used in d.s.c. studies, the initial endotherm for the complexes *cis*-[$PtR_2(PPh_3)_2$] (R = Ph or C_6H_4Me-4) is swamped by the decomposition exotherm. The onset of the exotherm, however, is markedly less rapid, and with R = C_6H_4Me-4 displays a small transient endothermic inflection.} T.g.a. showed no demarcation between primary and secondary processes. This is expected since product volatilisation is slow. Thermodynamic data were not accessible by d.t.a. or d.s.c. since the processes of fusion and decomposition, which have opposed thermal characteristics, are evidently overlapping.

Product analyses. After thermolyses, volatile materials were removed from the residue *in vacuo* at temperatures similar to those used during the pyrolysis (Table). They were analysed by quantitative g.l.c. as standard solutions in diethyl ether. The instrumental molar sensitivity was the same (to within 2%) for arenes, biaryls, and standard, but lower for phosphines by a factor of 1.34. There was generally good agreement between the weight losses observed directly (from the residual weight) and those calculated from g.l.c. observations. Elemental analyses of the variously red-brown to dark-brown residues, although indicative of no (apparent) regular stoicheiometry, also corresponded with predictions from g.l.c. measurements of molar losses.

Attempts to purify the residues by recrystallisation resulted in the same amorphous glass-like substances as were formed initially. Endeavours to resolve components by t.l.c. on alumina failed. N.m.r., i.r., and mass-spectroscopic techniques equally failed to provide any information.

We thank Dr. D. McSween of Paisley College of Technology for access to thermal analytical equipment, Mr. J. McEwan for invaluable technical assistance, Johnson, Matthey and Co. for the loan of platinum halides, and the S.R.C. for the award of a studentship (to G. B. Y.).

[5/1433 *Received*, 21*st July*, 1975]