Thermal Decomposition of Some Acyl(dialkyl)-, Dialkyl(allyl)-, Dialkyl-(benzyl)-, and Trialkyl-halogenobis(dimethylphenylphosphine)platinum-(IV) Complexes

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The complexes $[PtR_2(R')X(PMe_2Ph)_2]$ (X = halogen: R = Me, R' = benzyl or allyl; R = CD_3, R' = acetyl; R = Et, R' = Me) have been prepared. On pyrolysis, the benzyl and acetyl complexes undergo reductive elimination with C–C bond formation, the former giving ethane and ethylbenzene and the latter giving CD_3COMe as the organic products. Acetone elimination from the complex $[PtMe_2(COMe)Cl(PMe_2Ph)_2]$ has been studied by differential-scanning calorimetry and a mean value of the Pt–C σ-bond energy has been estimated. The complex $[PtBr(Me)_2(CH_2CH{=}CH_2)(PMe_2Ph)_2]$ apparently decomposes by a free-radical mechanism, and $[PtI(Me)Et_2(PMe_2Ph)_2]$ decomposes by a mechanism involving β-elimination of ethylene as the first step. The relative ease of elimination of a series of alkyl, acyl, and allyl groups from Pt^{IV} complexes has been deduced.

RECENT thermochemical studies have indicated that the alkyl–transition-metal bond is generally as strong as corresponding bonds to main-group elements, so that the relatively low thermal stability of many transition-metal alkyl complexes must be associated with the availability of decomposition mechanisms having low activation energies.[1-3] One such decomposition route which has attracted particular interest is β-elimination. Thus, for instance, decomposition of di-n-butylbis(triphenylphosphine)platinum(II) gives equal amounts of n-butane and but-1-ene as organic products,[4] by the mechanism (1). Dissociation of a phosphine ligand gives

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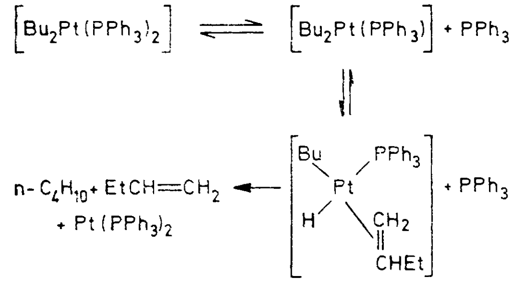
[1] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.

[2] P. S. Braterman and R. J. Cross, *J.C.S. Dalton*, 1972, 657; *Chem. Soc. Rev.*, 1973, 271.

[3] S. J. Ashcroft and C. T. Mortimer, *J. Chem. Soc.* (*A*), 1967, 930.

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

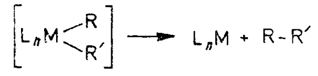
a free co-ordination site, then but-1-ene is eliminated and the resulting n-butyl(hydrido)platinum(II) complex undergoes intramolecular elimination of n-butane. It



(1)

has been shown that many transition-metal alkyl complexes of types previously inaccessible can be isolated if the alkyl group is chosen so that β-elimination is suppressed.[1]

A second mechanism of decomposition, which is well established for alkyl derivatives of Rh^{III},[5] Pt^{IV},[6-9] Au^{III},[10-13] and Ni^{II},[14,15] may be represented by the



$$\left[L_nM\begin{matrix}R\\R'\end{matrix}\right] \longrightarrow L_nM + R{-}R' \quad (2)$$

general equation (2). The decomposition is a reductive-elimination reaction in which two transition-metal–carbon bonds are broken and a carbon–carbon bond is formed. Reductive eliminations from platinum(IV) alkyl complexes are particularly suited to mechanistic studies since the resulting platinum(II) complexes are stable and easily characterised. The reactions are already known to be selective in many cases, as illustrated by the equations (3)—(5) (L = PMe_2Ph), from which the order of ease of elimination from Pt^{IV} complexes, MeCO > Me > CF_3, can be obtained.

$$[PtI(Me)_3L_2] \longrightarrow C_2H_6 + trans\text{-}[PtI(Me)L_2] \text{ (refs. 6, 8, and 9)} \quad (3)$$

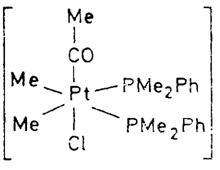
$$[PtCl(COMe)(Me)_2L_2] \longrightarrow Me_2CO + trans\text{-}[PtCl(Me)L_2] \text{ (ref. 6)} \quad (4)$$

$$[PtI(Me)_2(CF_3)L_2] \longrightarrow C_2H_6 + trans\text{-}[PtI(CF_3)L_2] \text{ (ref. 7)} \quad (5)$$

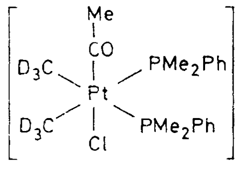
In order to extend this series we have prepared and pyrolysed a number of platinum(IV) complexes containing different alkyl groups, while in a parallel investigation we have studied in detail the mechanism of elimination of ethane from the complexes $[PtX(Me)_3L_2]$ (X = halide, L = tertiary phosphine or arsine).[9,16] We believe that this reaction proceeds by concerted elimination of ethane from a (possibly solvated) five-co-ordinate intermediate, which is formed by dissociation of a phosphine (or arsine) ligand from the initial platinum(IV) complex. It may well be that the elimination reactions described below proceed by a similar mechanism.

RESULTS AND DISCUSSION

Pyrolysis of $[PtCl(Me)_2(COMe)(PMe_2Ph)_2]$, (I).—Ruddick and Shaw showed that pyrolysis of this complex gave acetone and *trans*-$[PtCl(Me)(PMe_2Ph)_2]$ as the only products.[6] We confirmed this and also found that pyrolysis of the complex $[PtCl(CD_3)_2(COMe)(PMe_2Ph)_2]$,



(I)



(II)

(II), prepared by reaction of acetyl chloride with *cis*-$[(CD_3)_2Pt(PMe_2Ph)_2]$, gave $MeCOCD_3$ with greater than 96% isotopic purity on pyrolysis. The compound $MeCOCD_3$ has been prepared previously only with difficulty and in an impure form,[17] so that this preparation may well be useful for preparing specifically labelled acetone and related compounds in small quantities suitable for spectroscopic studies.

Elimination of acetone from complex (I) takes place from the solid at *ca.* 100 °C, and we studied the reaction by differential-scanning calorimetry (d.s.c.). The elimination is exothermic, beginning at 102 °C, reaching a maximum rate at 121 °C, and being complete at 126 °C. This is followed at higher temperature by an endothermic process corresponding to fusion of the product *trans*-$[PtCl(Me)(PMe_2Ph)_2]$ at 146—152 °C. The following enthalpies were determined:

$$(I)(c) \longrightarrow trans\text{-}[PtCl(Me)(PMe_2Ph)_2](c) + Me_2CO(g)$$
$$\Delta H = -33{\cdot}6 \pm 3{\cdot}2 \text{ kJ mol}^{-1}$$

$$trans\text{-}[PtCl(Me)(PMe_2Ph)_2](c) \longrightarrow trans\text{-}[PtCl(Me)(PMe_2Ph)_2](l)$$
$$\Delta H = +35{\cdot}6 \pm 1{\cdot}3 \text{ kJ mol}^{-1}$$

The enthalpy and temperature of fusion of the product

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

[6] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2969.

[7] H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, 1970, **9**, 2556.

[8] H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1973, **12**, 362.

[9] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J. Organometallic Chem.*, 1973, **49**, C61.

[10] A. Tamaki and J. K. Kochi, *J. Organometallic Chem.*, 1972, **40**, C81.

[11] C. F. Shaw, J. W. Lundeen, and R. S. Tobias, *J. Organometallic Chem.*, 1973, **51**, 365.

[12] A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 6487.

[13] J. A. J. Jarvis, A. Johnson, and R. J. Puddephatt, *J.C.S. Chem. Comm.*, 1973, 373.

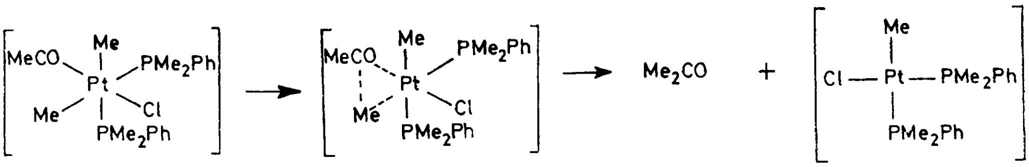
[14] K. Tamao, K. Sumitani, and M. Kumada, *J. Amer. Chem. Soc.*, 1972, **94**, 4374.

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

[16] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, unpublished work.

[17] G. Dellepiane and J. Overend, *Spectrochim. Acta*, 1966, **22**, 593.

were identical within experimental error with those for a sample of pure *trans*-[PtCl(Me)(PMe$_2$Ph)$_2$].


(6)

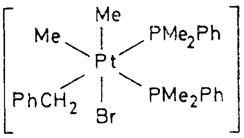
If the elimination is a concerted process from the six-co-ordinate platinum(IV) complex, one might expect the product to be *cis*-[PtCl(Me)(PMe$_2$Ph)$_2$] [equation (6)]. In order to investigate the possibility that *cis*-[PtCl(Me)(PMe$_2$Ph)$_2$] might be an intermediate in the elimination reaction, we studied it too by d.s.c. Its behaviour is rather complex. First a complex peak appeared between 99 and 127 °C, in which an endothermic change due to fusion of *cis*-[PtCl(Me)(PMe$_2$Ph)$_2$] is superimposed on an exothermic change due to isomerisation to *trans*-[PtCl(Me)(PMe$_2$Ph)$_2$] and resolidification of this product. Then there is an endothermic change at 141—152 °C due to fusion of *trans*-[PtCl(Me)(PMe$_2$Ph)$_2$]. The heat of fusion obtained was always less than that determined for pure *trans*-[PtCl(Me)(PMe$_2$Ph)$_2$], so that it appears that resolidification is never complete. In this sense the behaviour is different from that of the product of pyrolysis of complex (I) and we do not consider that *cis*-[PtCl(Me)(PMe$_2$Ph)$_2$] is formed as an intermediate. Direct formation of *trans*-[PtCl(Me)(PMe$_2$Ph)$_2$] is easily understood if the elimination is preceded by reversible loss of a phosphine ligand, since on recombination the thermodynamically more stable *trans*-isomer would be formed preferentially. The following enthalpy measurement was made:

$$cis\text{-}[\mathrm{PtCl(Me)(PMe_2Ph)_2}](\mathrm{c}) \longrightarrow trans\text{-}[\mathrm{PtCl(Me)(PMe_2Ph)_2}](\mathrm{l})$$
$$\Delta H = +17{\cdot}9 \pm 2{\cdot}5\ \mathrm{kJ\ mol^{-1}}$$

Thus the enthalpy of isomerisation of crystalline *cis*- to crystalline *trans*-isomer, $\Delta H = -17{\cdot}7 \pm 3{\cdot}8$ kJ mol^{-1}, could be calculated.

Elimination of acetone from complex (I) involves cleavage of two Pt–C bonds and formation of a C–C bond. If the C–C bond energy in acetone is assumed to be 350 kJ mol^{-1},[18,19] then the sum of the two bond energies E(Pt–Me) + E(Pt–COMe) = 350 − 33·6 = 316 kJ mol^{-1} giving a mean Pt–C σ-bond energy of 158 kJ mol^{-1}. The calculation takes no account of Pt$^{\mathrm{IV}}$–Pt$^{\mathrm{II}}$ promotion energy gained on elimination, nor of any other bond-energy differences between the starting material and products. Nevertheless, the bond energy obtained agrees closely with the value of E(Pt–Me) of 160 kJ mol^{-1} determined for the complex [(cp)PtMe$_3$] (cp = η-cyclopentadienyl) from a kinetic study of its thermal decomposition.[20]

Preparation and Pyrolysis of [PtBr(Me)$_2$(CH$_2$Ph)(PMe$_2$Ph)$_2$], (III).—Benzyl bromide reacts with *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] to give an adduct [PtBr(Me)$_2$(CH$_2$Ph)(PMe$_2$Ph)$_2$], (III), whose stereochemistry can be deduced from its n.m.r. spectrum. Thus Ruddick and Shaw have shown that the coupling constants $^{2}J(^{195}\mathrm{PtMe})$ in a series of platinum(IV) complexes are dependent on the nature of the *trans*-ligand, being 67—73 (*trans*-halogen), 56—59 (*trans*-phosphine), and 43·5—44 Hz (*trans*-carbon).[21]


(III)

The n.m.r. spectrum of complex (III) contained resonances due to two methyl–platinum groups, one at τ 9·35, an apparent triplet due to coupling to two phosphorus atoms [^{3}J(PH) 7·1 Hz] with satellites due to coupling with ^{195}Pt, ^{2}J(PtMe) 71 Hz, and the other at τ 9·57, again apparently a triplet with ^{3}J(PH) 7·2 Hz with ^{195}Pt satellites, ^{2}J(PtMe) 54 Hz. The coupling constants indicate that the methyl groups are *trans* to bromide and phosphine respectively, and so suggest the stereochemistry (III).

Evidently coupling constants for interaction between the two phosphorus atoms and the methyl protons are accidentally equal, thus giving the observed 1 : 2 : 1 triplets for the methyl–platinum resonances rather than the expected doublet of doublets. The CH$_2$ protons of the benzyl group gave two peaks at τ 7·46 and 7·37, each an apparent triplet due to coupling with phosphorus, ^{3}J(PH) 11 Hz with ^{195}Pt satellites, ^{2}J(PtCH$_2$) 65·4 Hz. Two peaks are expected for the methylene protons of the benzyl group for stereochemistry (III) since there is no plane of symmetry containing the Pt–benzyl bond. The methyl–phosphorus protons gave a complex resonance at τ 8·42. It seems that benzyl bromide adds *cis* to the complex *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$], in a similar way to allyl bromide (see later); most other molecules X–Y undergo *trans*-addition to *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$].[21]

Complex (III) decomposed above its melting point (135—138 °C) with elimination of a mixture of ethane and ethylbenzene, which were identified by their characteristic n.m.r. and mass spectra. No 1,2-diphenylethane could be detected by mass spectrometry amongst

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[18] T. L. Cottrell, 'The Strengths of Chemical Bonds,' 2nd edn., Butterworths, London, 1958.

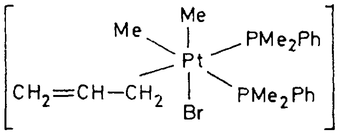
[19] C. T. Mortimer, 'Reaction Heats and Bond Strengths,' Pergamon, 1962.

[20] K. W. Egger, *J. Organometallic Chem.*, 1970, **24**, 501.

[21] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801.

the decomposition products, so that the elimination is probably intramolecular. The ethane and ethylbenzene formed from weighed samples of complex (III) were separated by vacuum fractionation; the ethane was then estimated by measuring its volume and the ethylbenzene from its u.v. absorbance after dissolving in dioxan. Duplicate determinations gave 58 ± 1% ethane and 42 ± 2% ethylbenzene, whereas from statistical considerations only one would expect the products to be 33% ethane and 67% ethylbenzene. It seems then that methyl groups are eliminated more readily than benzyl groups from this platinum(IV) complex. A study of the elimination reaction by n.m.r. spectroscopy showed that complex (III) decomposed slowly at 65 °C in benzene solution, whereas *fac*-$[PtX(Me)_3(PMe_2Ph)_2]$ (X = halogen) are stable under these conditions. This increase in overall rate, despite the lower tendency to elimination of the benzyl compared with the methyl groups, could be due to effects of the bulkier benzyl group.[22]

Preparation and Pyrolysis of $[PtBr(Me)_2(CH_2CH{=}CH_2)(PMe_2Ph)_2]$, (IV).—Allyl bromide is known to undergo *cis* oxidative addition to dimethylplatinum(II) complexes with tertiary arsine ligands,[23,24] and addition to *cis*-$[PtMe_2(PMe_2Ph)_2]$ takes place in the same way. Thus the n.m.r. spectrum of the adduct contains two resonances due to methyl–platinum groups, each apparently a triplet with ^{195}Pt satellites, at τ 9·43 [^3J(PH) 7·2, ^2J(PtMe) 73·2 Hz (*trans* to Br)] and 9·08 [^3J(PH) 6·6, ^2J(PtMe) 53 Hz (*trans* to P)], consistent only with the stereochemistry (IV). Complex peaks due to the allyl protons appeared at τ 5·13 and 4·20 and due to methyl–phosphorus protons at τ 8·44. An attempt to prepare the first (η-allyl)platinum(IV) complex by treating (IV) with silver hexafluorophosphate, gave none of the desired $[PtMe_2(\eta\text{-}C_3H_5)(PMe_2Ph)_2]PF_6$, but only $[PtMe(PMe_2Ph)_3]PF_6$. If the (η-allyl)platinum(IV) cation is formed it evidently undergoes reductive elimination.



(IV)

Pyrolysis of complex (IV) gave a mixture of gases which were identified, by comparison of their g.l.c. retention times and mass spectra with those of authentic samples, as methane, ethane, propene, but-1-ene, and hexa-1,5-diene. The platinum containing product was almost pure *trans*-$[PtBr(Me)(PMe_2Ph)_2]$, showing that the allyl group was lost preferentially. However a concerted intramolecular elimination reaction should yield only ethane and but-1-ene, and the remaining organic products are probably formed by a free-radical mechanism. Thus elimination of an allyl radical from complex (IV) followed by proton abstraction or dimerisation would yield propene or hexa-1,5-diene respectively, while methane may be formed by hydrogen abstraction by methyl radicals.

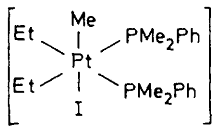
In an attempt to gain further insight into the mechanism of reaction, we analysed quantitatively by g.l.c. the gaseous products formed under various experimental conditions. The results are shown in the Table. Unfortunately the quantities of each gas produced varied markedly even when the experimental conditions were kept constant, and the results in the Table are average values. The high quantities of propene formed suggest that the reaction may be initiated by loss of an allyl radical from complex (IV). It is possible of course that at least some of the ethane and but-1-ene may be formed in a competing concerted elimination, while some hexa-1,5-diene might be formed from a dimeric intermediate containing a bridging allyl group.[25] One might speculate that a free-radical mechanism for decomposition of complex (IV) might be preferred due to resonance stabilisation of the incipient allyl radical, but, if this were the case, the benzylplatinum(IV) complex might also be expected to decompose by a radical mechanism. We are unable to offer a convincing explanation of this difference in behaviour between the allyl and benzyl complexes.

Composition of organic products formed on pyrolysis of complex (IV)

	Pyrolysis time/	Conversion [a]/	Product (%)				
t/°C	min	%	CH_4	C_2H_6	C_3H_6 [b]	C_4H_8 [c]	C_6H_{10} [d]
160 [e]	2	6	0·5	31	34	32	3
160 [e]	12	83	2	41	32	16	9
160 [f]	60	83	1	41	25	15	18

[a] Based on quantities of organic products formed. [b] Propene. [c] But-1-ene. [d] Hexa-1,5-diene. [e] Average of results for six runs. [f] Average of results for two runs.

Formation and Decomposition of $[PtI(Me)Et_2(PMe_2Ph)_2]$, (V).—An attempt to prepare a Pt^{IV} complex containing both methyl– and ethyl–platinum bonds by oxidative addition of ethyl iodide to *cis*-$[PtMe_2(PMe_2Ph)_2]$ was unsuccessful, but addition of methyl iodide to *cis*-$[PtEt_2(PMe_2Ph)_2]$ did occur. However, the initial product of oxidative addition decomposes in solution and we were unable to isolate a pure sample. The course of the reaction can be followed conveniently by n.m.r. spectroscopy. When the complex *cis*-$[PtEt_2(PMe_2Ph)_2]$ was dissolved in methyl iodide, a rapid reaction took place and an n.m.r. resonance from a methyl–platinum group appeared at τ 9·46. The peak is a triplet due to



(V)

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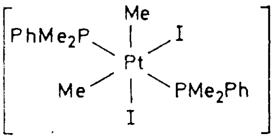
[22] B. L. Shaw and R. E. Stainbank, *J.C.S. Dalton*, 1972, 223.

[23] A. J. Cheney and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 3545.

[24] A. J. Cheney and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 3549.

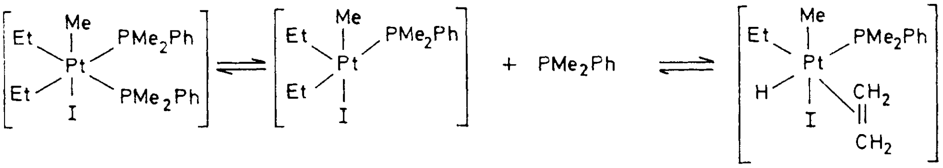
[25] W. S. McDonald, B. E. Mann, G. Raper, B. L. Shaw, and G. Shaw, *Chem. Comm.*, 1969, 1254.

coupling with phosphorus, ${}^3J$(PH) 7·3 Hz, with satellites due to coupling with ^{195}Pt, ${}^2J$(PtMe) 69·0 Hz. The methyl group is evidently *trans* to iodine, so that the stereochemistry (V) is indicated.[21] This peak slowly decayed, the half-life being 40 min at 33 °C, and a new methyl–platinum resonance appeared due to *trans*-[PtI(Me)($PMe_2Ph)_2$].[21] At the same time peaks due to methane (τ 9·78), ethane (τ 9·12), and ethylene (τ 4·66) appeared. Finally methyl iodide added to the complex *trans*-[PtI(Me)($PMe_2Ph)_2$] to give [$PtI_2(Me)_2(PMe_2Ph)_2$], (VI),[21] this reaction being complete in 24 h at 33 °C.



(VI)

The gases formed in this reaction were analysed by g.l.c. and shown to be methane, ethane, ethylene, and n-butane in molar proportions 1 : 2·6 : 3·0 : 0·3. The reaction probably proceeds by dissociation of a phosphine ligand giving a free co-ordination site,[16] followed by β-elimination of ethylene [equation (7)]. This intermediate can then eliminate either ethane (cleavage of PtH and PtEt bonds) or methane (cleavage of PtH and PtMe bonds), the former process evidently being favoured. The n-butane is probably formed in a competing reaction involving concerted elimination of two ethyl groups from platinum. No propane could be detected suggesting that ethyl groups are eliminated more readily than the methyl group.



(7)

It also seems that β-elimination takes place more readily from Pt^{IV} than from Pt^{II} complexes. Thus the complex *cis*-[$PtEt_2(PMe_2Ph)_2$] is quite stable in solution at room temperature, and decomposes only on heating above 100 °C when the products are ethylene, ethane, and benzene in molar proportions 1 : 1 : 0·4. The benzene presumably arises from decomposition of the initial product $Pt(PMe_2Ph)_2$ in a similar way to the reported decomposition of $Pt(PPh_3)_2$.[4,26]

It is interesting to compare the mechanism of the reaction of the ethylplatinum(IV) complex, with that of [$AuMe_2(Et)(PPh_3)$] which undergoes reductive elimination to give propane and ethane after dissociation of the phosphine ligand.[12] In this case concerted elimination with C–C bond formation takes place rather than β-elimination. Clearly the factors which influence the preferred mode of decomposition of transition-metal alkyl complexes are subtle, depending on the nature of the alkyl groups, the metal, and the other ligands present.[9]

Finally we note that the relative ease of elimination of some alkyl, acyl, and allyl groups, R, from platinum(IV) complexes is given by the series MeCO > CH_2=$CHCH_2$, Et > Me > $PhCH_2$ > CF_3 while a more limited series Et > Me > CF_3 can be deduced for elimination from Au^{III} complexes.[12,27]

EXPERIMENTAL

G.l.c. and mass spectra were obtained using a Pye series 104 gas chromatograph, with a 25% Apiezon L on Chromosorb P column at 45—48 °C, coupled to a Micromass 601 mass spectrometer. N.m.r. spectra were recorded using Perkin-Elmer R12B or Varian HA100 spectrometers.

The complexes *cis*-[$PtMe_2(PMe_2Ph)_2$] and [$PtCl(Me)_2$-(COMe)($PMe_2Ph)_2$] were prepared by literature methods,[21] and CD_3 analogues were prepared similarly.

Preparations.— cis-*Diethylbis(dimethylphenylphosphine)-platinum*(II). The complex *cis*-[$PtCl_2(PMe_2Ph)_2$] (0·50 g) was added to a solution of ethyl-lithium [from ethyl bromide (1·5 g) and lithium (0·5 g)] in diethyl ether (50 cm^3) at 0 °C. The solution was allowed to warm to room temperature, stirred for 0·5 h, then hydrolysed with ammonium chloride solution. The diethyl ether layer was dried ($MgSO_4$) and evaporated to give the product, which was recrystallised from pentane. Yield 0·24 g, m.p. 88—90 °C. N.m.r. (benzene): τ (MeP) 8·73 p.p.m. (doublet with ^{195}Pt satellites), ${}^2J + {}^4J$(PH) 7·2, ${}^3J$(PtH) 18·0 Hz; τ (Et) 8·15 p.p.m. (complex multiplet) (Found: C, 45·1; H, 6·0. Calc. for $C_{20}H_{32}P_2Pt$: C, 45·3; H, 6·0%).

Benzyl(bromo)dimethylbis(dimethylphenylphosphine)platinum(IV), (III). Benzyl bromide (1 cm^3) was added to a solution of the complex *cis*-[$PtMe_2(PMe_2Ph)_2$] (0·35 g) in diethyl ether. After 1 week at 0 °C colourless crystals of the *product* had separated. The crystals were filtered, washed with diethyl ether, and dried *in vacuo*. Yield 0·27 g, m.p. 135—138 °C (decomp.) (Found: C, 44·7; H, 5·4. Calc. for $C_{25}H_{35}BrP_2Pt$: C, 44·6; H, 5·2%). *Allyl(bromo)-dimethylbis(dimethylphenylphosphine)platinum*(IV), (IV), was prepared similarly from allyl bromide and the complex *cis*-[$PtMe_2(PMe_2Ph)_2$]. Yield 65%, m.p. 152—153 °C (decomp.), ν(C=C) at 1 615 cm^{-1} (Found: C, 40·7; H, 5·4. Calc. for $C_{21}H_{33}BrP_2Pt$: C, 40·5; H, 5·3%).

Reaction of Complex (IV) *with* $AgPF_6$.—A solution of complex (IV) (0·13 g) in CH_2Cl_2 (10 cm^3) was treated with $AgPF_6$ (0·06 g). The solution was filtered, the volume reduced to 5 cm^3, and diethyl ether (10 cm^3) added to precipitate the salt [$PtMe(PMe_2Ph)_3$]PF_6 (0·06 g), identified by its characteristic n.m.r. spectrum.[28]

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Reaction of cis-$[PtEt_2(PMe_2Ph)_2]$ *with* MeI.—(*a*) The complex *cis*-$[Et_2Pt(PMe_2Ph)_2]$ (0·15 g) was dissolved in MeI (1 cm^3). After 2 days the solvent was evaporated and the product was crystallised from CH_2Cl_2–diethyl ether to give $[PtI_2(Me)_2(PMe_2Ph)_2]$, (VI) (0·12 g), identified (m.p. and n.m.r.) by comparison with an authentic sample.[21] Pyrolysis above its melting point gave mostly MeI.

(*b*) The complex *cis*-$[PtEt_2(PMe_2Ph)_2]$ (0·15 g) was dissolved in MeI (1 cm^3). After 10 min at room temperature, the solvent was evaporated to give a pale yellow oil which could not be induced to crystallise by scratching. Crystallisation from methanol gave only the complex *trans*-$[PtI(Me)(PMe_2Ph)_2]$ (0·08 g), identified (m.p. and n.m.r.) by comparison with an authentic sample.[21]

Pyrolyses.—$[PtCl(CD_3)_2(COMe)(PMe_2Ph)_2]$, (II). Complex (II) was heated to 120 °C in a tube connected to the inlet system of a mass spectrometer. The gas evolved was identified as $>96\%$ pure $MeCOCD_3$ by its mass spectrum. The chief peaks were at *m/e* 61 ($MeCOCD_3$), 46 (CD_3CO), 43 (MeCO), 18 (CD_3), and 15 (Me). There was no peak at *m/e* 60 ($[^2H_2]Me_2CO$), and only trace peaks ($<4\%$) at *m/e* 45 (CD_2HCO) and 44 (CH_2DCO) indicating that less than 4% of the $MeCOCD_3$ had undergone end-to-end scrambling.[17]

$[PtCl(Me)_2(COMe)(PMe_2Ph)_2]$, (I). Weighed amounts of the sample (*ca.* 0·008 g) were heated in the sample chamber of a Perkin-Elmer DSC 1B differential scanning calorimeter which was calibrated using the heat of fusion (3·26 kJ mol^{-1}) of pure indium metal. Weight loss on pyrolysis: found (average of four results) 9·6 ± 0·4; acetone loss requires 9·8%.

Complex (IV). Weighed quantities of complex (IV) were sealed in glass capillary tubes. The tubes were heated at 160 °C for the required time period, then crushed in the inlet system of the g.l.c. which had previously been calibrated with known quantities of methane, ethane, propene, but-1-ene, and hexa-1,5-diene. In several runs the identity of the products was confirmed by recording their mass spectra. A larger-scale pyrolysis allowed isolation of the product *trans*-$[PtBr(Me)(PMe_2Ph)_2]$, identified by its m.p. and n.m.r. spectrum.[21]

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