Preparation and Thermal Decomposition of some (Butane-1,4-diyl)platinum(IV) Complexes

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The polymeric (butane-1,4-diyl)(platinum(IV) complexes $[\{PtXMe[(CH_2)_4]\}_n]$ (X = Br or I) have been prepared by reaction of $[Pt\{(CH_2)_4\}(cod)]$ (cod = cyclo-octa-1,5-diene) with MeBr or MeI, and react with ligands to give $[PtXMe\{(CH_2)_4\}L_2]$ [X = Br, L = PMe_2Ph; X = I, L = $\frac{1}{2}$(2,2′-bipyridine), PMe_2Ph, $PMePh_2$, $\frac{1}{2}$ $Ph_2PCH_2CH_2PPh_2$] or $[\{PtMe[(CH_2)_4]I(py)\}_2]$ when L = pyridine. The complexes $[PtXMe\{(CH_2)_4\}(PMe_2Ph)_2]$ have also been prepared by oxidative addition of MeX (X = I, Br, or Cl) to $[Pt\{(CH_2)_4\}(PMe_2Ph)_2]$, and $[Pt\{(CH_2)_4\}I_2(PMe_2Ph)_2]$ has been prepared from iodine and $[Pt\{(CH_2)_4\}(PMe_2Ph)_2]$. A study has been made of the products of thermal decomposition of the (butane-1,4-diyl)platinum(IV) complexes, and possible mechanisms of decomposition are discussed.

RECENT thermochemical studies have shown that the Pt–C σ bond is strong. Thus values of Pt–C bond energies have been obtained of 250 kJ mol^{-1} in *trans*-$[PtPh_2(PEt_3)_2]$,[1] 163 kJ mol^{-1} in $[PtMe_3(\eta\text{-}C_5H_5)]$,[2] 144 kJ mol^{-1} in *fac*-$[PtMe_3I(PMe_2Ph)_2]$,[3] and 112—124 kJ mol^{-1} in the strained ring compounds $[PtX_2\{(CH_2)_3\}L_2]$ (X = Cl or Br, L = nitrogen-donor ligand).[4] A mean value of the Pt–Me and Pt–COMe bond energies in $[PtMe_2(COMe)Cl(PMe_2Ph)_2]$ of 158 kJ mol^{-1} and a minimum value of the benzoylplatinum bond strength in $[Pt(COPh)Cl(PPh_3)_2]$ of 180 kJ mol^{-1} have also been estimated.[5,6] It is expected therefore that homolysis of Pt–C σ bonds would require a high activation energy, and it has been established that, under the relatively mild conditions needed to decompose many alkylplatinum complexes, alternative concerted mechanisms of decomposition are preferred.[3-5]

When the alkyl groups contain no β-hydrogen atoms decomposition has been shown to take place by a con-

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

[2] K. W. Eggar, *J. Organometallic Chem.*, 1970, **24**, 501.

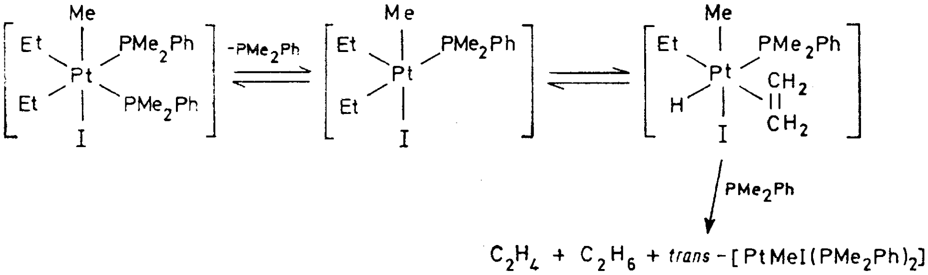
[3] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J.C.S. Dalton*, 1974, 2457.

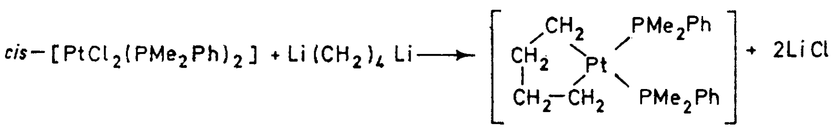
[4] P. W. Hall, R. J. Puddephatt, K. R. Seddon, and C. F. H. Tipper, *J. Organometallic Chem.*, 1974, **81**, 423.

[5] M. P. Brown, R. J. Puddephatt, C. E. E. Upton, and S. W. Lavington, *J.C.S. Dalton*, 1974, 1613.

[6] S. J. Ashcroft, A. Maddock, and G. Beech, *J.C.S. Dalton*, 1974, 462.

certed intramolecular reductive-elimination reaction,[3,5,7] but in the decomposition of the complex *fac*-$[PtMe_3I(PMe_2Ph)_2]$ to ethane and *trans*-$[PtMeI(PMe_2Ph)_2]$ the reductive elimination is accelerated if a phosphine or iodide ligand is dissociated first.[3,7] Thus the nature of the supporting ligands may be vital in determining the thermal stability of complexes of this type. If the alkyl groups contain a β-hydrogen atom then decomposition of both platinum(II) and platinum(IV) alkyls generally proceeds by the β-elimination mechanism.[5,8] For this reaction to take place there must be a vacant co-ordination site at the platinum centre, and Whitesides *et al.*[8] showed that the decomposition of dibutylbis(triphenylphosphine)platinum(II) to butene, butane, and ' $Pt(PPh_3)_2$ ' took place by dissociation of a phosphine ligand followed by β elimination of butene. A similar mechanism was proposed for the decomposition of the platinum(IV) complex $[PtMeEt_2I(PMe_2Ph)_2]$, which was thought to undergo loss of a phosphine ligand followed by β elimination of ethylene, and then loss of ethane or, less likely, methane [equation (1)].[5] A similar mechanism was suggested to account for the formation of propene in the thermal decomposition of the (propane-1,3-diyl)platinum(IV) complexes, $[PtX_2\{(CH_2)_3\}L_2]$ (X = halogen, L = nitrogen-donor ligand).[4]

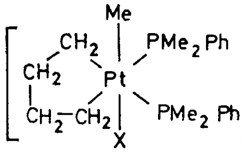

(1)


(2)

Whitesides and his co-workers [9] have recently shown that the heterocyclic compounds $[Pt\{(CH_2)_n\}(PPh_3)_2]$ (n = 4—6) are considerably more stable to β elimination than the butylplatinum(II) complexes studied earlier, and attributed this to the more rigid structure of the ring compounds which makes abstraction of the β-hydrogen atom by platinum more difficult. We now report an extension of our earlier studies of decomposition of acyclic alkylplatinum(IV) complexes [3,5] and of heterocyclic (propane-1,3-diyl)platinum(IV) complexes,[4] and include the preparation and thermal decomposition of some (butane-1,4-diyl)platinum(IV) complexes.

RESULTS AND DISCUSSION

Two routes have been used to prepare the (butane-1,4-diyl)platinum(IV) complexes. A series of complexes with dimethylphenylphosphine ligands was prepared by oxidative-addition reactions to (butane-1,4-diyl)bis(dimethylphenylphosphine)platinum(II), which in turn was prepared by reaction of *cis*-$[PtCl_2(PMe_2Ph)_2]$ with 1,4-dilithiobutane [equation (2)]. Methyl iodide, bromide, and chloride all reacted with $[Pt\{(CH_2)_4\}(PMe_2Ph)_2]$ and the respective products were shown to have structure (I) (X = I, Br, or Cl) by their n.m.r. spectra. Thus the methylphosphorus protons gave two doublets in the n.m.r. spectrum, indicating a structure with mutually *cis*-phosphine groups and with no plane of symmetry containing the PtP_2 group.[10] The methylplatinum protons gave a triplet, due to coupling with two equivalent ^{31}P atoms, with satellites due to coupling with ^{195}Pt and $^2J(PtH)$ 66—72 Hz, typical of a methylplatinum(IV) complex with the methyl group *trans* to halogen.[10,11] The data are consistent only with structure (I) and show that *trans* addition of each methyl halide has occurred. In these complexes, and in all other (butane-1,4-diyl)platinum complexes which we have studied, the ^1H n.m.r. signal of the $(CH_2)_4$ protons appeared as a broad peak with unresolved coupling, and gave no useful information about the stereochemistry of the complexes.


(I)

Iodine added to $[Pt\{(CH_2)_4\}(PMe_2Ph)_2]$ to give $[Pt\{(CH_2)_4\}I_2(PMe_2Ph)_2]$ of stereochemistry (II). Thus the methylphosphorus protons gave only one doublet in

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

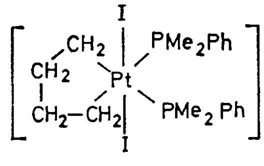
[8] G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 1972, **94**, 5258.

[9] J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1973, **95**, 4451.

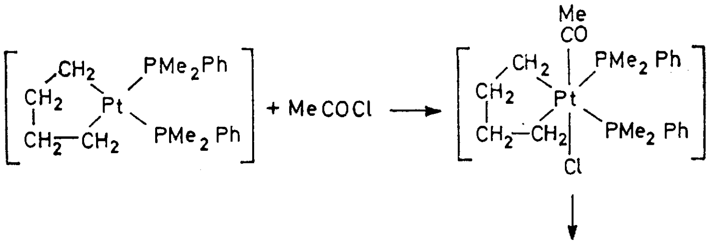
[10] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801.

[11] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

the n.m.r. spectrum indicating the presence of mutually *cis* chemically equivalent phosphine groups, consistent only with structure (II). Again *trans*-oxidative addition has occurred. Attempts to prepare similar adducts with chlorine or bromine were unsuccessful however and only the complexes *cis*-[$PtX_2(PMe_2Ph)_2$] (X = Cl or Br) were isolated. With acetyl chloride we were again unable to isolate the product of oxidative addition. When one equivalent of MeCOCl was added a compound was formed which could not be crystallised but which on hydrolysis gave hexan-2-one, identified by g.l.c. and m.s. The compound is therefore assumed to be *trans*-[$Pt(CH_2CH_2CH_2CH_2COMe)Cl(PMe_2Ph)_2$]. Addition of a further equivalent of MeCOCl to this gave *trans*-[$PtCl_2(PMe_2Ph)_2$], which then isomerised slowly to the *cis* isomer. It seems then that oxidative addition followed by reductive elimination occurred [equation (3)].



(II)

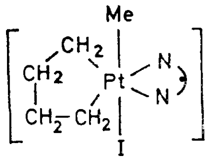


trans-[$Pt(CH_2CH_2CH_2CH_2COMe)Cl(PMe_2Ph)_2$] (3)

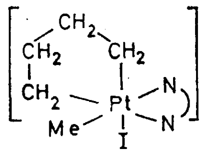
The second route to (butane-1,4-diyl)platinum(IV) complexes was *via* the intermediates [{$PtXMe[(CH_2)_4]$}$_n$] (X = Br or I). These complexes were precipitated when [Pt{$(CH_2)_4$}(cod)] (cod = *cis,cis*-cyclo-octa-1,5-diene) was dissolved in the corresponding methyl halide. They are expected to be tetrameric by analogy with the well known [$(PtMe_3I)_4$], but their insolubility precluded molecular-weight determination and it is possible that they exist in a more highly polymeric form. The polymeric structure in [{$PtXMe[(CH_2)_4]$}$_n$] was broken down on reaction with the ligand PMe_2Ph to give (I; X = I or Br), identical with the product formed by reaction of methyl iodide or bromide with [Pt{$(CH_2)_4$}$(PMe_2Ph)_2$], and the analogous methyldiphenylphosphine complex [PtMe{$(CH_2)_4$}I$(PMePh_2)_2$] was formed in a similar way. However, the reaction of [{$PtMe[(CH_2)_4]I$}$_n$] with triphenylphosphine led to reductive elimination and only [Pt{$(CH_2)_4$}$(PPh_3)_2$] could be isolated.[9,12] A similar trend has been observed in reactions of [$(PtMe_3I)_4$] with phosphines when PMe_2Ph and $PMePh_2$ gave the simple complexes [$PtMe_3I(PMe_2Ph)_2$] and [$PtMe_3I(PMePh_2)_2$] but PPh_3 gave mostly methyl iodide and *cis*-[$PtMe_2(PPh_3)_2$].[3]

Reaction of [{$PtMe[(CH_2)_4]I$}$_n$] with 2,2′-bipyridine (bipy) gave the expected complex [PtMe{$(CH_2)_4$}I(bipy)], but the n.m.r. spectrum contained two methylplatinum peaks with coupling constants ^2J(PtH) of 75.6 and 71.6 Hz. These values are consistent with methylplatinum(IV) complexes with the methyl group *trans* to halogen or to bipy respectively,[11,13] and so suggest that the product exists as a mixture of isomers, (III) and (IV). Reaction of pyridine (py) with [{$PtMe[(CH_2)_4]I$}$_n$] gave only a 1 : 1 adduct, which is presumably dimeric and analogous to the known dimer [{$PtMe_3I(py)$}$_2$].[14]

Thermal Decomposition of the Complexes.—The (butane-1,4-diyl)platinum(IV) complexes were pyrolysed by heating *in vacuo* to *ca.* 10 °C above the melting point. The volatile products were condensed immediately to prevent further reactions catalysed by the platinum-containing products. The results are given in the Table.



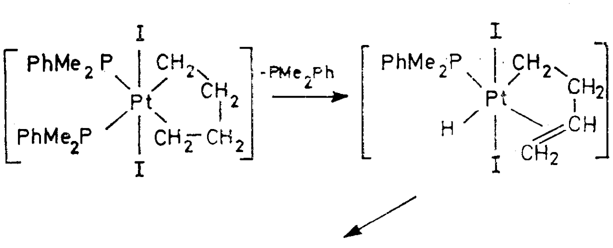
(III)



(IV)

$\widehat{N\ N}$ = 2,2′-bipyridyl

The simplest case is the decomposition of complex (II) which gave only a mixture of *cis*- and *trans*-[$PtI_2(PMe_2Ph)_2$] and but-1-ene, identified by its g.l.c. retention time and mass and n.m.r. spectra. The probable mechanism is shown in equation (4). The reaction involves dissociation of a ligand, followed by β elimination



[$PtI_2(PMe_2Ph)_2$] + $MeCH_2CH{=}CH_2$ (4)

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[12] C. G. Biefield, H. A. Eick, and R. H. Grubbs, *Inorg. Chem.*, 1973, **12**, 2166.

[13] D. E. Clegg, J. R. Hall, and G. A. Swile, *J. Organometallic Chem.*, 1972, **38**, 403.

[14] J. R. Hall and G. A. Swile, *J. Organometallic Chem.*, 1972, **42**, 479.

and then reductive elimination by cleavage of the Pt–H and Pt–CH$_2$ bonds in the intermediate. It is possible that an isomer with these bonds in mutually *cis* positions would be preferred to facilitate this process. As with the platinum(II) analogues,[9] no reductive elimination to give cyclobutane or ethene was observed.

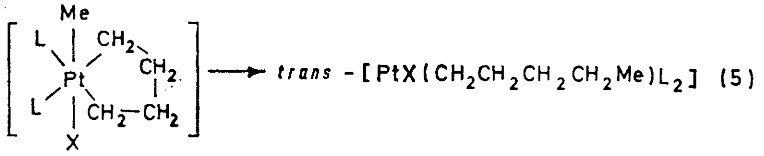
Decomposition of the (butane-1,4-diyl)methylplatinum(IV) complexes always led to a mixture of products, but two mechanisms were clearly important. The parent complex [{PtMe[(CH$_2$)$_4$]I}$_n$] and its complexes with py and bipy decomposed to give largely methane and butene (as a mixture of but-1-ene and *cis*- and *trans*-but-2-ene), and a mechanism similar to that in equation (4) is indicated, initiated by β elimination from the (butane-1,4-diyl)platinum group, but the presumed (but-3-en-1-yl)hydrido(methyl)platinum(IV) intermediate can decompose by reductive elimination of either methane (cleavage of Pt–H and Pt–Me bonds) or of but-1-ene (cleavage of Pt–H and Pt–butenyl bonds).

Volatile products of pyrolysis of (butane-1,4-diyl)platinum(IV) complexes

	Volatile products (%)									
Complex	Methane	But-1-ene	*trans*-But-2-ene	*cis*-But-2-ene	Butane	Pent-1-ene	*trans*-Pent-2-ene	*cis*-Pent-2-ene	Pentane	Others[a]
[Pt{(CH$_2$)$_4$}I$_2$(PMe$_2$Ph)$_2$]		100								
[{PtMe[(CH$_2$)$_4$]I}$_n$]	33	32	15	16	4					MeI
[PtMe{(CH$_2$)$_4$}I(bipy)]	13.5	40	13.5	14.5	6	3	4.5	4.5	0.5	MeI
[{PtMe[(CH$_2$)$_4$]I(py)}$_2$]	40	29	9.5	8	3	2	3.5	3.5	1.5	MeI, py
[PtMe{(CH$_2$)$_4$}Cl(PMe$_2$Ph)$_2$]	6	8[b]				86[b]				C$_6$H$_6$
[PtBrMe{(CH$_2$)$_4$}(PMe$_2$Ph)$_2$]	1	2[b]				97[b]				C$_6$H$_6$
[PtMe{(CH$_2$)$_4$}I(PMe$_2$Ph)$_2$]	14	21.5	3	2	0.5	46	6	6	1	C$_6$H$_6$
[PtMe{(CH$_2$)$_4$}I(PMePh$_2$)$_2$]		6	1.5	1.5		78	6	6.5		C$_6$H$_6$, MeI

[a] Not analysed quantitatively. [b] Total value for butenes or pentenes. The isomers were not separated by the column used.

In contrast to this behaviour, the phosphine complexes decomposed to give pent-1-ene as the major product, together with smaller quantities of isomeric pentenes and of methane and butenes. The platinum-containing products in each case could be identified as *trans*-[PtHXL$_2$] (X = Cl, Br, or I; L = PMe$_2$Ph or PMePh$_2$) by comparison of the i.r. spectra with those of authentic samples.[15] It seems that the first step in the decomposition must be concerted reductive elimination by cleavage of the Pt–CH$_3$ and one of the Pt–CH$_2$ bonds [equation (5)]. As expected,[8,16] the pentylplatinum(II) complex so formed undergoes β elimination of pent-1-ene to give *trans*-[PtHXL$_2$] as the final product. The butene and methane are presumably formed in a competing reaction as described earlier. When X = I, the complex with L = PMePh$_2$ gave considerably more pentene than when L = PMe$_2$Ph, suggesting that increased bulk or electron-withdrawing power of the ligand enhances decomposition of the platinum(IV) complex by reductive elimination rather than by β elimination. However, when L = PMe$_2$Ph, the complex with X = Br gave more pentene than when X = Cl or I, so that no clear trend is apparent.



(5)

We also examined the isotopic purity of the products formed by decomposition of [{Pt(CD$_3$)[(CH$_2$)$_4$]I}$_n$], formed by reaction of [Pt{(CH$_2$)$_4$}(cod)] with CD$_3$I, and of [Pt(CD$_3$){(CH$_2$)$_4$}I(PMe$_2$Ph)$_2$]. In each case the volatile products were separated by g.l.c. and the mass spectrum of each product was recorded. The pyrolysis of [{Pt(CD$_3$)[(CH$_2$)$_4$]I}$_n$] and of [Pt(CD$_3$){(CH$_2$)$_4$}I-(PMe$_2$Ph)$_2$] gave but-1-ene and some n-butane none of which contained deuterium, but the methane was mostly CD$_3$H, and CD$_3$I was also formed. The pentenes formed from [Pt(CD$_3$){(CH$_2$)$_4$}I(PMe$_2$Ph)$_2$] were all of isotopic composition C$_5$H$_7$D$_3$ (*m/e* 73). These results are in full agreement with those expected from the mechanisms proposed, but are not consistent with free-radical mechanisms.

The most important results of this work can be summarised thus. (1) The (butane-1,4-diyl)platinum(IV) complexes are, like the platinum(II) analogues, considerably more inert to thermal decomposition by β elimination than are similar acyclic compounds such as ethylplatinum(IV) complexes. (2) The complexes [PtMe{(CH$_2$)$_4$}IL$_2$] decompose largely by β elimination within the platinum(IV) complex when L is a nitrogen-donor ligand (*e.g.* L$_2$ = bipy), to give butene and methane, but by reductive elimination when L is a tertiary phosphine ligand to give, after β elimination from the pentylplatinum(II) complex formed, pentene and *trans*-[PtHIL$_2$] as the major products. (3) In the reductive elimination from [PtXMe{(CH$_2$)$_4$}(PR$_3$)$_2$] described above cleavage of the Pt–CH$_3$ bond and one of the Pt–CH$_2$ bonds takes place to give a pentylplatinum(II) intermediate, rather than cleavage of both Pt–CH$_2$ bonds to give cyclobutane. This effect may be due to the Pt–CH$_2$ bonds being stronger than the Pt–CH$_3$ bond, or, more likely, to the higher activation energy needed to close the C$_4$ ring to give the strained-ring product cyclobutane.

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[15] H. C. Clark and H. Kurosawa, *J. Organometallic Chem.*, 1972, **36**, 399.

[16] J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1968, 190.

EXPERIMENTAL

General techniques have been described previously.[3,5] Solutions of 1,4-dilithiobutane in diethyl ether were prepared by the method of West and Rochow [17] from lithium shot and 1,4-dibromobutane. The solutions were filtered under nitrogen before use in order to remove excess of lithium.

*(Butane-*1,4-*diyl)bis(dimethylphenylphosphine)platinum*(II).—1,4-Dilithiobutane [5 cm^3 of a solution prepared from Li (1.14 g) and 1,4-dibromobutane (5.53 g) in diethyl ether (40 cm^3)] was added to a suspension of *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] (0.5 g) in diethyl ether (10 cm^3). The solution was allowed to react at 0 °C for 16 h, then hydrolysed with ammonium chloride solution at 0 °C, and the dried ether layer was evaporated to yield the *product*, which was recrystallised from diethyl ether–hexane, yield 35%, m.p. 128—133 °C, ν(PtC) at 528 and 535 cm^{-1}. N.m.r. spectrum in benzene: δ(PCH$_3$) 1.27 p.p.m., doublet, $^2J + {}^4J$(PH) 7 Hz, ^3J(PtH) 18 Hz; δ[(CH$_2$)$_4$] 2.36 p.p.m., broad unresolved multiplet (Found: C, 45.35; H, 5.75. Calc. for C$_{20}$H$_{30}$P$_2$Pt: C, 45.55; H, 5.70%). In a reaction on a larger scale, from [PtCl$_2$(PMe$_2$Ph)$_2$] (3.95 g), the yield was 56%.

*(Butane-*1,5-*diyl)(cyclo-octa-*1,5-*diene)platinum*(II).— This complex was prepared in a similar way, but to minimise decomposition of the product the reaction mixture was stirred for only 2 h at -10 °C, yield 45%. It was recrystallised by allowing a solution in light petroleum (b.p. 30—40 °C) to evaporate slowly, m.p. 74 °C. N.m.r. spectrum in CH$_2$Cl$_2$: δ[(CH$_2$)$_4$] 1.29 p.p.m., broad unresolved multiplet; δ(CH) 4.78 p.p.m., ^2J(PtH) 38.4 Hz; δ(CH$_2$) 2.21 p.p.m., ^3J(PtH) 16.2 Hz (Found: C, 40.15; H, 5.55. Calc. for C$_{12}$H$_{20}$Pt: C, 40.1; H, 5.55%). The mass spectrum gave a parent ion at *m/e* 359 and peaks at *m/e* 303 $[P - \mathrm{C_4H_8}]^+$, 251 $[P - \mathrm{C_8H_{12}}]^+$, and 195 [Pt]$^+$, all with the correct isotope pattern.

*(Butane-*1,4-*diyl)iodo(methyl)platinum*(IV).—A solution of [Pt{(CH$_2$)$_4$}(cod)] (0.63 g) in methyl iodide (3 cm^3) was allowed to stand at room temperature for 3 d. The deposited crystals were washed thoroughly with CH$_2$Cl$_2$ and dried *in vacuo*, yield 0.49 g. The complex decomposed without melting at 195 °C (Found: C, 14.9; H, 2.55; Pt, 49.25. Calc. for C$_5$H$_{11}$IPt: C, 15.25; H, 2.80; Pt, 49.6%). The mass spectrum gave a parent ion at *m/e* 393 and other peaks at *m/e* 378 $[P - \mathrm{Me}]^+$, 337 $[P - \mathrm{C_4H_8}]^+$, 322 $[P - \mathrm{C_5H_{11}}]^+$, 266 $[P - \mathrm{I}]^+$, and 251 $[P - \mathrm{CH_3I}]^+$, all with the correct isotope pattern.

*Bromo(butane-*1,4-*diyl)methylplatinum*(IV).—A solution of [Pt{(CH$_2$)$_4$}(cod)] (0.32 g) in methyl bromide (2 cm^3) was allowed to stand in a sealed tube at room temperature for 1 month, during which time white crystals slowly formed. The tube was opened, the solvent was allowed to evaporate, and the crystals were washed thoroughly with CH$_2$Cl$_2$, yield 0.2 g. The complex decomposed without melting at 227 °C (Found: C, 17.55; H, 3.45; Pt, 56.7. Calc. for C$_5$H$_{11}$BrPt: C, 17.35; H, 3.20; Pt, 56.35%).

*(Butane-*1,4-*diyl)bis(dimethylphenylphosphine)iodo(methyl)platinum*(IV).—(a) The complex [Pt{(CH$_2$)$_4$}(PMe$_2$Ph)$_2$] (0.11 g) was dissolved in methyl iodide (2 cm^3). After 5 min the solvent was evaporated and the *product* was recrytallised from dichloromethane–hexane, yield 61%, m.p. 150—151 °C (decomp.), ν(PtC) at 530 and 546 cm^{-1}. N.m.r. spectrum in CH$_2$Cl$_2$: δ(PtCH$_3$) 0.60 p.p.m., triplet, ^3J(PH) 7.4 Hz, ^2J(PtH) 66.6 Hz; δ[(CH$_2$)$_4$] 1.66 p.p.m., broad unresolved multiplet; δ(PCH$_3$) 1.56 and 1.64 p.p.m., two doublets, each with $^2J + {}^4J$(PH) 7.4, ^3J(PtH) 8.4 Hz (Found: C, 37.75; H, 5.20. Calc. for C$_{21}$H$_{33}$IP$_2$Pt: C, 37.65; H, 4.95%).

(b) A solution of PMe$_2$Ph (0.04 g) in CH$_2$Cl$_2$ (1 cm^3) was added to a suspension of [PtMe{(CH$_2$)$_4$}I] (0.06 g) in CH$_2$Cl$_2$ (5 cm^3). The mixture was stirred at room temperature for 30 h when the precipitate slowly dissolved. The solution was filtered, the volume reduced to 1 cm^3, and methanol (10 cm^3) was added to precipitate the *product*, yield 100%. It was identical (m.p. and n.m.r.) with the product prepared by method (a).

The following *complexes* were prepared similarly: [PtBrMe{(CH$_2$)$_4$}(PMe$_2$Ph)$_2$], yield 96%; [PtMe{(CH$_2$)$_4$}I(PMePh$_2$)$_2$], yield 55%, m.p. 124 °C (decomp.), n.m.r. spectrum in CH$_2$Cl$_2$, δ(PtCH$_3$) 0.70 p.p.m., triplet, ^3J(PH) 7.8, ^2J(PtH) 67.8 Hz, δ[(CH$_2$)$_4$] 1.37 p.p.m., broad unresolved multiplet, δ(PCH$_3$) 2.17 p.p.m., doublet, ^2J(PH) 7.8, ^3J(PtH) 9.6 Hz (Found: C, 47.2; H, 4.75. Calc. for C$_{31}$H$_{37}$IP$_2$Pt: C, 46.9; H, 4.70%); [PtMe{(CH$_2$)$_4$}I(bipy)], yield 60%, m.p. 257 °C (decomp.), n.m.r. spectrum in CH$_2$Cl$_2$, δ(PtCH$_3$) 0.75 p.p.m., singlet, ^2J(PtH) 75.6 Hz, 1.49 p.p.m., singlet, ^2J(PtH) 71.6 Hz, δ[(CH$_2$)$_4$] 1.43 p.p.m., broad unresolved multiplet (Found: C, 32.8; H, 3.50; N, 5.10. Calc. for C$_{15}$H$_{19}$IN$_2$Pt: C, 32.8; H, 3.50; N, 5.10%); [{PtMe[(CH$_2$)$_4$]I(py)}$_2$], yield 70%, m.p. 220 °C (decomp.), n.m.r. spectrum in CH$_2$Cl$_2$, δ(PtCH$_3$) 1.24 p.p.m., singlet, ^2J(PtH) 72.0 Hz, 1.48 p.p.m., singlet, ^2J(PtH) 72.0 Hz, δ[(CH$_2$)$_4$] 1.41 p.p.m., broad unresolved multiplet (Found: C, 25.1; H, 3.35; N, 3.00; Pt, 42.35. Calc. for C$_{10}$H$_{16}$INPt: C, 25.4; H, 3.40; N, 2.95; Pt, 41.3%); and [PtMe{(CH$_2$)$_4$}I(Ph$_2$PCH$_2$CH$_2$PPh$_2$)], m.p. 154 °C (decomp.) (Found: C, 46.15; H, 4.50. Calc. for C$_{31}$H$_{35}$IP$_2$Pt: C, 47.15; H, 4.45%).

*Bromo(butane-*1,4-*diyl)bis(dimethylphenylphosphine)methylplatinum*(IV).—Methyl bromide (5 cm^3) was added to a solution of [Pt{(CH$_2$)$_4$}(PMe$_2$Ph)$_2$] (0.15 g) in diethyl ether (5 cm^3). After 48 h the white crystals which formed were filtered off and washed with diethyl ether, yield 0.10 g (77%), m.p. 162—164 °C (decomp.). N.m.r. spectrum in CH$_2$Cl$_2$: δ(PtCH$_3$) 0.48 p.p.m., triplet, ^3J(PH) 7.2, ^2J(PtH) 70.2 Hz; δ[(CH$_2$)$_4$] 1.46 p.p.m., complex multiplet; δ(PCH$_3$) 1.56 and 1.64 p.p.m., two doublets, $^2J + {}^4J$(PH) 8.4, ^3J(PtH) 8.4 Hz (Found: C, 40.25; H, 5.30. Calc. for C$_{21}$H$_{33}$BrP$_2$Pt: C, 40.5; H, 5.30%).

*(Butane-*1,4-*diyl)chlorobis(dimethylphenylphosphine)methylplatinum*(IV).—Methyl chloride (*ca.* 5 cm^3) was condensed into a Pyrex tube containing [Pt{(CH$_2$)$_4$}(PMe$_2$Ph)$_2$] (0.32 g). The tube was sealed, and the mixture allowed to stand at room temperature for 2 weeks. The tube was opened, the solvent allowed to evaporate, and the *product* was washed thoroughly with diethyl ether and dried *in vacuo*, yield 91%, m.p. 154—158 °C (decomp.). N.m.r. spectrum in CH$_2$Cl$_2$: δ(PtCH$_3$) 0.47 p.p.m., triplet, ^3J(PH) 7.2, ^2J(PtH) 72.2 Hz; δ[(CH$_2$)$_4$] 1.20 p.p.m., complex unresolved multiplet; δ(PCH$_3$) 8.40 and 8.46 p.p.m., two doublets, $^2J + {}^4J$(PH) 8, ^3J(PtH) 8 Hz (Found: C, 43.35; H, 5.70. Calc. for C$_{21}$H$_{33}$ClP$_2$Pt: C, 43.65; H, 5.70%).

*(Butane-*1,4-*diyl)bis(dimethylphenylphosphine)di-iodoplatinum*(IV).—A solution of iodine (0.048 g) in diethyl ether (5 cm^3) was added to a solution of [Pt{(CH$_2$)$_4$}(PMe$_2$Ph)$_2$] (0.10 g) in diethyl ether (5 cm^3). Orange crystals precipitated immediately. After leaving the solution for 16 h at 0 °C, the crystals were filtered off and recrystallised from dichloromethane–methanol, yield 48%, m.p. 214 °C (decomp.). N.m.r. spectrum in CH$_2$Cl$_2$: δ[(CH$_2$)$_4$] 4.48 p.p.m.,

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[17] R. West and E. G. Rochow, *J. Chem. Soc.*, 1953, 1739.

broad unresolved multiplet, J(PtH) 64 Hz; δ(PCH_3) 8.65 p.p.m., doublet, $^2J + {^4J}$(PH) 9.3, ^3J(PtH) 12.0 Hz.

Reaction of [{PtMe[$(CH_2)_4$]I}$_n$] *with Triphenylphosphine.*—The reaction of PPh_3 with a suspension of [{PtMe[$(CH_2)_4$]I}$_n$] in CH_2Cl_2 for 2 d gave an insoluble yellow product which could not be identified. The filtrate from the reaction was treated with methanol, and crystals of [Pt{$(CH_2)_4$}$(PPh_3)_2$], yield *ca.* 50%, were precipitated and identified by comparison with an authentic specimen prepared by reaction of PPh_3 with [Pt{$(CH_2)_4$}(cod)].[9]

Pyrolysis Experiments.—Complexes were pyrolysed *in vacuo* at *ca.* 10 °C above the melting point. Volatile products were usually collected immediately in a liquid-nitrogen-cooled trap, but in some cases the volatiles were allowed to remain in contact with the platinum-containing residue. The volatiles were analysed using a Pye 104 gas chromatograph with either Porasil B or Carbowax 20M columns, coupled to a Mikromass mass spectrometer.[3,5] Identification of products was made by comparison of retention times and mass spectra with those of authentic samples.

For the phosphine complexes the residues were identified by their i.r. and n.m.r. spectra; [$PtI_2(PMe_2Ph)_2$] formed from [$PtI_2(C_3H_6)(PMe_2Ph)_2$] existed as a *cis–trans* mixture.[18] The compounds *trans*-[$PtHX(PMe_2Ph)_2$] showed characteristic ν(PtH) bands at 2 140 (X = I), 2 181 (X = Br, lit.,[15] 2 185), and 2 200 cm^{-1} (X = Cl, lit.,[15] 2 195 cm^{-1}), as well as the characteristic triplets for the PCH_3 protons in the n.m.r. spectra.

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[18] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.