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A Mass Spectroscopic Study of Platinum Alkyl and Aryl Complexes

F. GLOCKLING, T. McBRIDE and R. J. I. POLLOCK
Department of Inorganic Chemistry, The Queen's University, Belfast BT9 5AG, U.K
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A mass spectroscopic study is reported on compounds of the type PtR_2L_2 where $L = PR_3$ or L_2 = a chelating diphosphine and R = alkyl or aryl. Various factors affecting fragmentation paths and ion abundances have been identified. Rearrangement processes occur in which organic groups are transferred to and from P and Pt, and a mechanism is proposed whereby polyphenyl ions are formed. The thermal decomposition of $PtAr_2(PPh_3)_2$ (Ar = Ph, m- and p-FC_6H_4) produces at 110–150° C yellow or red platinum cluster compounds.

Introduction

Although many main group and transition metal organometallic compounds have been examined mass spectroscopically[1–3] a systematic study of organoplatinum complexes has not previously been reported. In this work we have selected a number of tertiary phosphine platinum–dialkyls and –diaryls for examination and find that, with few exceptions, complexes with molecular weights up to 800 are sufficiently stable and volatile to produce clean mass spectra. The objectives in this work have been to determine how the nature of the phosphine and organic groups bonded to platinum influence the fragmentation behaviour, and to examine the relevance of mass spectrometry to recent work on the stability of transition metal–carbon bonds.[4]

Experimental

The compounds (Table I), prepared and purified as described in the preceding paper[5] or by literature methods,[6,7] were introduced into an MS902 mass spectrometer (at 70 eV) using a direct insertion probe. With three exceptions, the temperatures necessary to obtain strong spectra were well below the melting points of the compounds and thermal decomposition was avoided. In deriving ion abundances (Tables II–V) the ion current due to all Pt isotopes for each species have been summed and expressed as a percentage of the

TABLE I. Relative Ion Abundances.

	Ratio			
	$PtR_2L_2^{\cdot+}$	$PtRL_2^+$	$PtL_2^{\cdot+}$	$PtL(L\text{–}H)^+$
$PtMe_2(PMe_3)_2$	1	11.9		13.7
$PtMe_2(PEt_3)_2$	1	7.9	57.5	
$PtMe_2(PPh_3)_2$	1	12.6		10.5
$PtMe_2[(Ph_2P)_2CH_2]$	1	32.0	1.0	
$PtMe_2(Ph_2PCH_2)_2$	1	47.3		16.7
$PtEt_2[(Ph_2P)_2CH_2]$	–	1.0	2.6[a]	
$PtEt_2(Ph_2PCH_2)_2$	–	1.0	3.3[a]	
$PtPh_2(PMe_3)_2$	1	1.3	5.9	
$PtPh_2(PEt_3)_2$	1	7.6	364	
$PtPh_2(PPh_3)_2$	–	–	–	
$Pt(m\text{-}FC_6H_4)_2(PPh_3)_2$	–	–	–	
$Pt(p\text{-}FC_6H_4)_2(PPh_3)_2$	–	–	–	
$PtPh_2[(Ph_2P)_2CH_2]$	7.0	1	45.0	
$Pt(m\text{-}FC_6H_4)_2[(Ph_2P)_2CH_2]$	2.1	1	50.6	
$Pt(p\text{-}FC_6H_4)_2[(Ph_2P)_2CH_2]$	1.9	1	40.8	
$PtPh_2(Ph_2PCH_2)_2$	5.9	1	83.0	
$Pt(m\text{-}FC_6H_4)_2(Ph_2PCH_2)_2$	2.3	1	64.6	
$Pt(p\text{-}FC_6H_4)_2(Ph_2PCH_2)_2$	1.5	1	103	

[a] includes $PtHL_2^+$

total ion current excluding hydrocarbon ions below $Ph_2^{\cdot +}$, although these are referred to in the text where appropriate. A single mass number under m/e (Tables II–V) is used to denote a clean platinum isotope pattern, and is calculated on ^{195}Pt. Where an m/e range is quoted this covers all Pt isotopes and indicates overlap of two or more platinum isotope patterns resulting from $H\cdot$ or H_2 elimination processes. For phosphine and hydrocarbon ions a range is quoted when H, 2H etc. loss is observed for the listed ion.

Results and Discussion

Molecular Ions

All of the platinum dimethyl complexes produced molecular ions whereas neither of the platinum diethyl complexes did (Table I). Of the platinum– diphenyl and –di(fluorophenyl) complexes only those containing two triphenylphosphines, $PtAr_2(PPh_3)_2$, failed to show molecular ions, and indeed this group of three compounds did not produce any Pt-containing ions. The literature does not refer to their thermal stability but we find that at the temperature necessary (~ 150° C) to produce any ions in a mass spectrometer all three compounds decompose in vacuo forming yellow or red platinum cluster compounds.* The profound difference between the thermal stability of the $PtAr_2(PPh_3)_2$ compounds and the corresponding chelate complexes $PtAr_2(Ph_2PCH_2)_2$ and $PtAr_2[(Ph_2P)_2CH_2]$ is noteworthy and parent ion abundances were highest for this group. The failure of the diethylplatinum complexes to produce molecular ions is not due to thermal decomposition but to the facile loss of one ethyl radical.

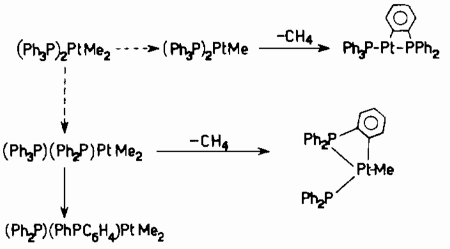
Fragmentation Processes

Apart from $PtAr_2(PPh_3)_2$ compounds the initial fragmentation step falls into two categories: those in which the molecular ion exclusively loses $R\cdot$ and those in which loss of $R\cdot$ is in competition with phosphine fragmentation. Further fragmentation of compounds with chelating phosphines is strikingly influenced by the size of the ring, and many processes are considered to involve loss of an ortho hydrogen atom from a Ph–P group. A major difference between $Pt(alkyl)_2L_2$ and $Pt(aryl)_2L_2$ compounds is that the latter readily eliminate biaryl, and this is a metastable supported process in several of the chelate complexes. With the exception of some $PtMe_2L_2$ compounds $PtL_2^{\cdot +}$ was by far the most abundant platinum-containing ion. A striking difference between complexes with chelating and monodentate phosphines was the absence of the $(chelate)^{\cdot +}$ ion whereas $PR_3^{\cdot +}$ was a major charge-carrier.

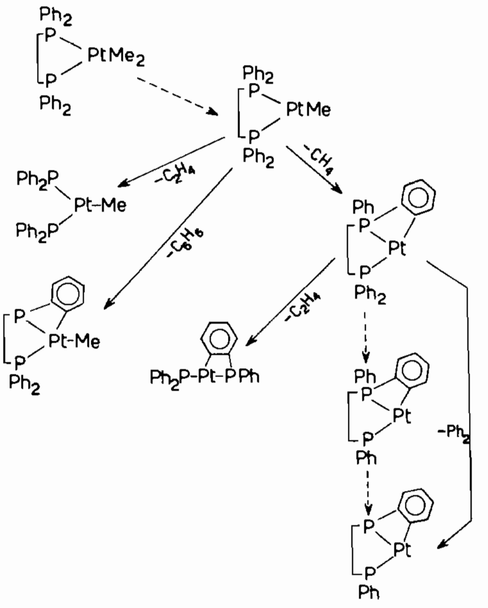
Doubly charged ions such as $(PtR_nL_2)^{2+}$, n = 0, 1, 2, were commonly observed and were often of considerable intensity e.g. $Pt(Ph_2PC_2H_4PPhC_6H_4)^{2+}$ carried 12% of the platinum-containing current. Loss of hydrogen from many of the fragments was a feature of all the mass spectra. Hydrocarbon ions were of low abundance in complexes containing only alkyl groups whereas all of the compounds containing phenyl groups produced high abundance ions due to $C_6H_6^{\cdot +}$, Ph^+ and $C_6H_4^{\cdot +}$ together with $Ph_2^{\cdot +}$. The latter might arise in part from transfer of phenyl groups from phosphorus to platinum followed by reductive elimination, and supporting evidence comes from the spectrum of $PtMe_2(PPh_3)_2$ where the ratio, $Ph_2:PPh_3$ is 0.8, whereas in free PPh_3 the ratio is only 0.2.[8] In the fragmentation diagrams (Schemes 1–3) solid arrows are used to denote elimination of even-electron fragments and broken arrows the elimination of odd-electron fragments. Metastable-supported transitions are indicated by including the neutral fragment against the arrow.

Dimethyl complexes

Fragmentation paths, including possible structures of Pt-containing ions are given in Schemes 1, 2 and ion abundances in Table II.



Scheme 1



Scheme 2

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* *J.C.S. Chem. Comm.*, 1973, 650.

TABLE II. Ion Abundances, $PtMe_2L_2$ Complexes.

m/e	Abundance	Assignment
$PtMe_2(PMe_3)_2$		
377	1.1	$PtMe_2(PMe_3)_2$
365–359	13.7	$PtMe(PMe_3)_2$
346	15.7	$Pt(CH_2PMe_2)(PMe_3)$
333–327	4.8	$PtMe_5P_2$
319–313	1.8	$PtMe_4P_2$
303–299	1.0	$PtMe_3P_2$
286	1.7	$Pt(CH_2P)(PMe)$
270	5.5	$Pt(CH_2PMe_2)$
259–251	2.1	$PtMe_2P$
240	1.8	$Pt(CH_2P)$
226	0.3	PtP
173.5	0.1	$Pt(PMe_3)_2{}^+$
91	6.9	PMe_4
76	15.2	PMe_3
61	18.9	PMe_2
47–45	9.4	PHMe
$PtMe_2(PEt_3)_2$		
461	0.4	$PtMe_2(PEt_3)_2$
446	3.0	$PtMe(PEt_3)_2$
431	21.5	$Pt(PEt_3)_2$
418–410	17.5	$PtEt_5MeP_2$
404–398	5.9	$PtEt_5P_2$
390–380	11.4	$PtEt_4MeP_2$
374–368	1.9	$PtEt_4P_2$
361–352	5.5	$PtEt_3MeP_2$
347–338	2.2	$PtEt_3P_2$
333–324	4.6	$PtEt_2MeP$
319–310	2.5	$PtEt_2P_2$
305–294	5.5	$PtEt_2MeP$
272–264	3.9	PtEtMeP
243–237	2.9	PtMeP
133–131	3.1	PEt_3Me
119–117	2.1	PEt_3H
105–103	0.6	PEt_2HMe
91–89	1.7	PEt_2H
75	0.7	PEtMe
62–60	3.2	$PEtH_2$
$PtMe_2(PPh_3)_2$		
749–745	0.1	$PtMe_2(PPh_3)_2$
734	1.2	$PtMe(PPh_3)_2$
718	1.0	$Pt(PPh_2C_6H_4)(PPh_3)$
672	0.6	$PtMe_2(PPh_2)(PPh_3)$
656	0.7	$PtMe(PPh_2)(C_6H_4PPh_2)$
630	0.1	$PtP_2C_{29}H_{25}$
610	0.6	$Pt(C_6H_4)PPh_4$
594	0.7	$PtMe_2(PPh_2)(C_6H_4PPh)$
568	0.2	$PtP_2C_{24}H_{23}$
548	0.2	$PtMe(C_6H_4)PPh_3$
532	0.5	$Pt(C_6H_4)_2PPh_2$
497	0.1	$PtP_2C_{19}H_{12}$
486	0.2	$Pt(PC_6H_4)(C_6H_4PPh)$
474–468	0.3	$PtMe(PPh_3)$
456	0.5	$Pt(C_6H_4)PPh_2$
411–407	0.2	$Pt(PPh)_2$
394	0.3	$PtMe(C_6H_4)PPh$
390	0.2	$PtP_2C_{10}H_{13}$
378	0.9	$PtP(C_6H_4)_2$
339–337	0.2	PPh_4
332	0.3	$PtPMe_2(C_6H_4)$
320–313	0.4	PtPMePh
302	0.8	$PtPC_6H_4$
277–275	0.6	$PMePh_3$
262	32.4	PPh_3
230–228	1.9	$Ph_2C_6H_4$
215	0.3	PMe_2Ph_2
200–199	2.1	$PMePh_2$
185–181	25.9	PPh_2
168–165	2.3	Ph_2CH_2
154–150	24.4	Ph_2
$PtMe_2[(Ph_2P)_2CH_2]$		
609	1.4	$PtMe_2(Ph_2PCH_2PPh_2)$
594	46.1	$PtMe(Ph_2PCH_2PPh_2)$
590	3.9	$PtP_2C_{26}H_{21}$
579	1.4	$Pt(Ph_2PCH_2PPh_2)$
565–561	0.4	$Pt(PPh_2)_2$
532	0.2	$PtMe_2(Ph_2PCH_2PPh)$
517–511	1.2	$PtMe(Ph_2PCH_2PPh)$
503–499	2.1	$Pt(Ph_2PCH_2PPh)$
489–484	0.9	$Pt(PPh_2)(PPh)$
470	1.2	$PtMe(PPh_3)$
457–453	3.3	$Pt(PPh_3)$
441–433	0.5	$PtMe(PhPCH_2PPh)$
427–420	1.6	$Pt(PhPCH_2PPh)$
411–407	1.4	$Pt(PPh)_2$
394	5.8	$PtMe(C_6H_4)PPh$
390	1.2	$PtP_2C_{10}H_{13}$
378	3.3	$PtP(C_6H_4)_2$
346	1.7	$PtP_2C_7H_5$
319–313	3.3	PtPMePh
302	6.2	$PtPC_6H_4$
289.5	3.9	$Pt(Ph_2PCH_2PPh_2)^+$
277	1.0	$PMePh_3$
263–261	1.5	$PHPh_3$
215	0.3	PMe_2Ph_2
201	1.1	$PHMePh_2$
185–183	2.9	PPh_2
154–150	2.2	Ph_2
$PtMe_2(Ph_2PCH_2)_2$		
623	0.8	$PtMe_2(Ph_2PC_2H_4PPh_2)$
608	39.4	$PtMe(Ph_2PC_2H_4PPh_2)$
592	13.9	$Pt(Ph_2PC_2H_4PPhC_6H_4)$
580	1.4	$PtMe(PPh_2)_2$
566–559	2.4	$Pt(PPh_2)_2$
530	0.3	$PtMe(Ph_2PC_2H_4PC_6H_4)$
519–511	1.0	$Pt(Ph_2PC_2H_4PPh)$
503–497	0.5	$PtMe(PPh_2)(PPh)$
486	3.2	$Pt(PPhC_6H_4)(PC_6H_4)$
457–453	1.7	$Pt(PPh_3)$
438	2.1	$Pt(PhPC_2H_4PC_6H_4)$
425–419	0.8	$PtMe(PPh)_2$
413–407	4.9	$PtPPh)_2$
394	0.3	$PtMe(C_6H_4)PPh$
390	0.3	$PtP_2C_{10}H_{13}$

TABLE II. (Cont.)

m/e	Abundance	Assignment
378	2.2	$PtP(C_6H_4)_2$
360	0.2	$PtP_2C_8H_7$
347	2.8	$PtP_2C_7H_6$
335–332	1.6	PtP_2Ph
302	0.7	$PtPC_6H_4$
296	11.1	$Pt(Ph_2PC_2H_4PPhC_6H_4)^+$
263–261	0.9	$PHPh_3$
257.5	0.6	$Pt(PhPC_2H_4PPhC_6H_4)^+$
243	0.6	$Pt(PPhC_6H_4)(PC_6H_4)^+$
201	0.3	$PHMePh_2$
185–183	3.5	PPh_2
154–152	2.5	Ph_2

For the PPh_3 and $(Ph_2PCH_2)_2$ complexes fragmentation occurs by initial loss of a methyl radical followed by methane elimination. This behaviour closely parallels that of $PtX_2(PR_3)_2$ compounds (where X = halide and R = Et or Ph) since elimination of $X\cdot$ is followed by loss of HX.[9] By contrast the 4-membered chelate complex, $PtMe_2[(Ph_2P)_2CH_2]$ successively loses two methyl radicals. The difference is probably attributable to a proximity effect in that the small P–Pt–P bond angle in $PtMe[(Ph_2P)_2CH_2]^+$ will limit the approach between the ortho hydrogen atoms of the phenyl groups and the methyl group. In all of the compounds containing phenyl bonded to phosphorus, elimination of alkane occurs at some stage in the fragmentation, and these are considered to parallel reactions of neutral molecules in involving an ortho hydrogen atom and forming a Pt–C bond.[10] (See proposed structures in Schemes 1–3).

The subtle interplay of factors determining methyl or methane elimination from $PtMeL_2^+$ is further illustrated for L = PMe_3 and PEt_3 (reactions 1 and 2).

$$PtMe_2(PMe_3)_2^{\cdot+} \xrightarrow{-Me} PtMe(PMe_3)_2^+ \xrightarrow{-CH_4} Pt(PCH_2Me_2)(PMe_3)^+ \qquad (1)$$

$$PtMe_2(PEt_3)_2^{\cdot+} \xrightarrow{-Me} PtMe(PEt_3)_2^+ \xrightarrow{-Me} Pt(PEt_3)_2^{\cdot+} \qquad (2)$$

These processes appear to contradict the proposal of the preceding paragraph, but in the case of the PEt_3 complex reaction (3) involving ethane elimination takes place rather than the CH_4 elimination of reaction (1)

$$PtMe(PEt_3)_2^+ \xrightarrow{-C_2H_6} Pt(PEt_2CH_2)(PEt_3)^+ \qquad (3)$$

For $PtMe_2$ complexes with trimethyl- or triethyl-phosphine so many alternative structures may be written for fragment ions that fragmentation schemes are not included; even the product ion in reaction (3) cannot be formulated unambiguosly.

Diethyl complexes

Ion abundances for the two compounds examined are listed in Table III.

Since β-elimination is a well established process these compounds were studied in anticipation that successive ethylene loss would produce a platinum dihydride species. This was not observed although in the spectrum of $PtEt_2[(Ph_2P)_2CH_2]$ the ion at m/e 580 was unambiguously assigned to a monohydride ion formed by reaction (4).

TABLE III. Ion Abundances, $PtEt_2L_2$ Complexes.

m/e	Abundance	Assignment
$PtEt_2[(Ph_2P)_2CH_2]$		
637	–	$PtEt_2(Ph_2PCH_2PPh_2)$
608	13.8	$PtEt(Ph_2PCH_2PPh_2)$
584–575	35.8	$PtH(Ph_2PCH_2PPh_2)$
565–561	0.4	$Pt(PPh_2)_2$
503–499	3.4	$Pt(Ph_2PCH_2PPh)$
489–484	1.2	$Pt(PPh_2)(PPh)$
470	0.3	$PtMe(PPh_3)$
459–453	2.3	$Pt(PPh_3)$
427–420	1.7	$Pt(PhPCH_2PPh)$
411–407	1.2	$Pt(PPh)_2$
394	0.9	$Pt(PPh_2CH_2)$
390	0.5	$PtP_2C_{10}H_{13}$
378	3.3	$PtP(C_6H_4)_2$
346	1.7	$Pt(PhPCH_2P)$
335–332	0.5	PtP_2Ph
319–313	1.2	$Pt(PMePh)$
302	6.1	$PtPC_6H_4$
290	3.3	$PtH(Ph_2PCH_2PPh_2)^+$
262	9.7	PPh_3
250.5	0.1	$Pt(Ph_2PCH_2PPh)^+$
201–199	1.4	$PHMePh_2$
185–183	6.8	PPh_2
154–150	4.4	Ph_2
$PtEt_2(Ph_2PCH_2)_2$		
651	–	$PtEt_2(Ph_2PC_2H_4PPh_2)$
622	12.5	$PtEt(Ph_2PC_2H_4PPh_2)$
596–588	41.2	$Pt(Ph_2PC_2H_4PPh_2)$
568–559	2.2	$Pt(PPh_2)_2$
519–509	0.8	$Pt(Ph_2PC_2H_4PPh)$
486	3.6	$Pt(PPhC_6H_4)(PC_6H_4)$
457–453	1.0	$Pt(PPh_3)$
438	1.9	$Pt(PhPC_2H_4PC_6H_4)$
422	0.3	$PtP_2C_{13}H_9$
413–407	4.9	$Pt(PPh)_2$
381–375	2.5	$PtPPh_2$
350–345	2.4	PtP_2CH_2Ph
335–332	1.7	PtP_2Ph
311	0.2	$PtEt(Ph_2PC_2H_4PPh_2)^+$
302	6.3	$PtPC_6H_4$
296.5	9.3	$Pt(Ph_2PC_2H_4PPh_2)^+$
263–261	0.8	$PHPh_3$
258	0.9	$Pt(Ph_2PC_2H_4PPh)^+$
243	0.5	$Pt(PPhC_6H_4)(PC_6H_4)^+$
185–183	3.8	PPh_2
154–151	3.2	Ph_2

$$PtEt[(Ph_2P)_2CH_2]^+ \rightarrow PtH[(Ph_2P)_2CH_2]^+ + C_2H_4 \quad (4)$$

For the complex $PtEt_2(Ph_2PCH_2)_2$ ethylene loss from $PtEt(Ph_2PCH_2)_2^+$ was metastable supported, but the resulting isotope pattern (m/e 596–588) clearly showed that ethyl radical loss was also occurring. Thus three fragmentation processes could account for the observations (reaction 5).

$$PtEt(Ph_2PCH_2)_2^+ \begin{cases} \xrightarrow{-C_2H_5\cdot} Pt(Ph_2PCH_2)_2^{\cdot+} \\ \xrightarrow{-C_2H_4} PtH(Ph_2PCH_2)_2^+ \\ \xrightarrow{-C_2H_4} PtEt(Ph_2P)_2^+ \end{cases} \quad (5)$$

In neither diethylplatinum complex was a molecular ion observed; $PtEtL_2^+$ was the second most abundant Pt-containing ion, and with one exception rupture of Pt–Et bonds was complete before Pt-phosphine fragmentation began.

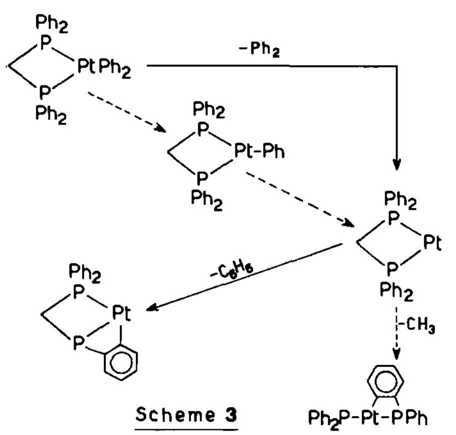
Diaryl complexes

An illustrative fragmentation path is shown in Scheme 3 and ion abundances in Table IV. Since a number of the phosphine ligands contained phenyl groups two series of compounds were examined, viz. $PtPh_2L_2$ and $Pt(m,p,\text{-}FC_6H_4)_2L_2$, thus allowing the origin of eliminated phenyl groups to be determined.

Initial fragmentation involves cleavage of Ar· from the parent ion and loss of the second aryl group is in competition with P–C bond cleavage, especially with trialkylphosphine complexes. In contrast to the platinum dialkyls the diaryls eliminate Ar_2 in a concerted process which is metastable supported for several compounds (Table VI). In the spectrum of $Pt(m,p,\text{-}FC_6H_4)_2[(Ph_2P)_2CH_2]$ a broad metastable peak centred at 435 can be ascribed to two processes (reactions 6 and 7).

$$Pt(C_6H_4F)_2[(Ph_2P)_2CH_2]^{\cdot+} \xrightarrow{m^*,436} Pt[(Ph_2P)_2CH_2]^{\cdot+} + C_{12}H_8F_2 \quad (6)$$

$$Pt[(Ph_2P)_2CH_2]^{\cdot+} \xrightarrow{m^*,434} Pt(Ph_2PCH_2PC_6H_4)^{\cdot+} + C_6H_6 \quad (7)$$



Scheme 3

TABLE IV. Ion Abundances, $Pt(aryl)_2L_2$ Complexes.

m/e	Abundance	Assignment
$PtPh_2(PMe_3)_2$		
501	5.7	$PtPh_2(PMe_3)_2$
425–421	7.6	$PtPh(PMe_3)_2$
408	0.9	$PtPh(PMe_2CH_2)(PMe_2)$
404	0.4	$PtP_2C_{11}H_{15}$
395–391	0.5	$PtPh(PMe_2)_2$
365–361	0.5	$PtPh(PMe)_2$
347	33.9	$Pt(PMe_3)_2$
333–329	8.7	$Pt(PMe_3)(PMe_2)$
319–313	2.3	$Pt(PMe_2)_2$
302	0.9	$Pt(PMe_2)(PMe)$
286	1.1	$Pt(PMe)(PCH_2)$
270	7.3	$Pt(PMe_2CH_2)$
259–251	2.8	$PtPMe_2$
244–238	2.5	$PtPMe$
154–151	14.4	Ph_2
139	4.5	$PHMe_2Ph$
91	5.8	PMe_4
$PtPh_2(PEt_3)_2$		
585	0.04	$PtPh_2(PEt_3)_2$
509–505	0.3	$PtPh(PEt_3)_2$
479–473	0.3	$PtPh(PEt_3)(PEt_2)$
450–443	0.1	$PtPh(PEt_2)_2$
434–425	14.3	$Pt(PEt_3)_2$
417	0.3	$Pt(PEt_3)(PEt_2Me)$
406–395	15.2	$Pt(PEt_3)(PEt_2H)$
389	0.4	$Pt(PEt_2Me)(PEt_2H)$
378–367	15.8	$Pt(PEt_2H)_2$
361	0.3	$Pt(PEt_2Me)(PEtH_2)$
350–339	9.0	$Pt(PEt_2H)(PEtH_2)$
322–309	5.0	$Pt(PEtH_2)_2$
305–301	0.8	$PtPPh$
292.5	0.2	$PtPh_2(PEt_3)_2^+$
287–279	3.1	$PtPEt_2$
258–252	2.7	$PtPEt$
195–194	1.4	PEt_3Ph
167–165	0.1	PEt_2HPh
154–150	23.1	Ph_2
118–117	3.6	PEt_3
90	3.9	PEt_2H
$PtPh_2[(Ph_2P)_2CH_2]$		
733	1.2	$PtPh_2(Ph_2PCH_2PPh_2)$
656	0.2	$PtPh(Ph_2PCH_2PPh_2)$
579	7.8	$Pt(Ph_2PCH_2PPh_2)$
565–561	0.7	$Pt(PPh_2)_2$
503–498	0.7	$Pt(Ph_2PCH_2PPh)$
489–484	1.2	$Pt(PPh_2)(PPh)$
470	0.6	$PtPC_{19}H_{16}$
459–453	0.9	$Pt(PPh_3)$
426–420	0.8	$Pt(PhPCH_2PPh)$
412–406	1.0	$Pt(PPh)_2$
394	0.7	$Pt(PPh_2CH_2)$
390	0.4	$PtP_2C_{10}H_{13}$
382	0.6	$Ph_2(C_6H_4)_3$
378	1.8	$PtP(C_6H_4)_2$
366.5	0.5	$PtPh_2(Ph_2PCH_2PPh_2)^+$
349–345	0.8	$Pt(PhPCH_2P)$

TABLE IV. (Cont.)

m/e	Abundance	Assignment
306	1.3	$Ph_2(C_6H_4)_2$
302	2.8	$PtPC_6H_4$
262	1.1	PPh_3
230	4.5	$Ph_2C_6H_4$
200–199	4.8	$PMePh_2$
185–181	3.8	PPh_2
167–165	2.3	$C_{13}H_{11}$–$C_{13}H_9$
154–150	59.4	Ph_2
$Pt(m\text{-}FC_6H_4)_2[(Ph_2P)_2CH_2]$		
769	0.2	$Pt(C_6H_4F)_2(Ph_2PCH_2PPh_2)$
750	0.02	$Pt(C_6H_4F)(C_6H_4)(Ph_2PCH_2PPh_2)$
674	0.1	$Pt(C_6H_4F)(Ph_2PCH_2PPh_2)$
655	0.03	$Pt(C_6H_4)(Ph_2PCH_2PPh_2)$
598–592	0.1	$Pt(C_6H_4F)(Ph_2PCH_2PPh)$
579	5.2	$Pt(Ph_2PCH_2PPh_2)$
564	0.4	$Pt(PPh_2)(PPhC_6H_4)$
503–498	0.5	$Pt(Ph_2PCH_2PPh)$
489–485	0.7	$Pt(PPh_2)(PPh)$
470	0.3	$PtPC_{19}H_{16}$
459–453	0.5	$Pt(PPh_3)$
426–420	0.5	$Pt(PhPCH_2PPh)$
412–407	0.6	$Pt(PPh)_2$
394	0.5	$Pt(PPh_2CH_2)$
390	0.3	$PtP_2C_{10}H_{13}$
384.5	0.2	$Pt(C_6H_4F)_2(Ph_2PCH_2PPh_2)^+$
378	1.0	$PtP(C_6H_4)_2$
302	2.0	$PtP(C_6H_4)$
289.5	0.1	$Pt(Ph_2PCH_2PPh_2)^+$
280	0.8	$PPh_2(C_6H_4F)$
266	5.1	$C_{18}H_{12}F_2$
262	8.7	PPh_3
248	0.7	$C_{18}H_{13}F$
203–199	1.2	$PPh(C_6H_4F)$
190–188	41.8	$(C_6H_4F)_2$
172–168	21.5	PhC_6H_4F
154–150	7.2	Ph_2
$Pt(p\text{-}FC_6H_4)_2[(Ph_2P)CH_2]$		
769	0.7	$Pt(C_6H_4F)_2(Ph_2PCH_2PPh_2)$
750	0.07	$Pt(C_6H_4F)(C_6H_4)(Ph_2PCH_2PPh_2)$
674	0.3	$Pt(C_6H_4F)(Ph_2PCH_2PPh_2)$
655	0.07	$Pt(C_6H_4)(Ph_2PCH_2PPh_2)$
597	0.08	$Pt(C_6H_4F)(Ph_2PCH_2PPh)$
579	14.2	$Pt(Ph_2PCH_2PPh_2)$
564	1.6	$Pt(PPh_2)(PPhC_6H_4)$
503–498	1.5	$Pt(Ph_2PCH_2PPh)$
489–485	2.3	$Pt(PPh_2)(PPh)$
470	1.0	$PtPC_{19}H_{16}$
457–453	1.2	$Pt(PPh_3)$
426–420	1.3	$Pt(PhPCH_2PPh)$
412–407	1.7	$Pt(PPh)_2$
394	1.6	$Pt(PPh_2CH_2)$
390	0.6	$PtP_2C_{10}H_{13}$
384.5	0.3	$Pt(C_6H_4F)_2(Ph_2PCH_2PPh_2)^+$
378	3.2	$PtP(C_6H_4)_2$
302	5.2	$PtP(C_6H_4)$
280	0.9	$PPh_2(C_6H_4F)$

TABLE IV. (Cont.)

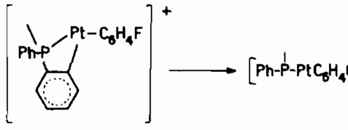
m/e	Abundance	Assignment
266	1.2	$C_{18}H_{12}F_2$
262	2.5	PPh_3
248	0.3	$C_{18}H_{13}F$
203–199	2.1	$PPh(C_6H_4F)$
190–188	35.4	$(C_6H_4F)_2$
172–168	16.2	PhC_6H_4F
154–150	4.5	Ph_2
$PtPh_2(Ph_2PCH_2)_2$		
747	1.0	$PtPh_2(Ph_2PC_2H_4PPh_2)$
670	0.2	$PtPh(Ph_2PC_2H_4PPh_2)$
593	13.5	$Pt(Ph_2PC_2H_4PPh_2)$
565	3.1	$Pt(PPh_2)_2$
516	0.3	$Pt(Ph_2PC_2H_4PPh)$
490–483	2.7	$Pt(PPh_2)(PPh)$
459–449	1.3	$Pt(PPh_3)$
438	0.3	$Pt(PhPC_2H_4PC_6H_4)$
412–407	2.5	$Pt(PC_6H_4)_2$
382	0.4	$Ph_2(C_6H_4)_3$
378	1.7	$PtP(C_6H_4)_2$
373.5	0.6	$PtPh_2(Ph_2PC_2H_4PPh_2)^+$
347	1.9	$PtP_2C_7H_6$
335–332	0.9	PtP_2Ph
306	1.1	$Ph_2(C_6H_4)_2$
302	3.3	$PtPC_6H_4$
296.5	1.5	$Pt(Ph_2PC_2H_4PPh_2)^+$
291–289	0.6	$PEtPh_3$
263–261	1.7	$PHPh_3$
257.5	0.3	$Pt(PhPC_2H_4PPhC_6H_4)^+$
230–228	4.2	$Ph_2C_6H_4$
185–178	7.2	PPh_2
170–165	3.0	$C_{13}H_{14}$–$C_{13}H_9$
154–151	46.7	Ph_2
$Pt(m\text{-}FC_6H_4)_2(Ph_2PCH_2)_2$		
783	0.5	$Pt(C_6H_4F)_2(Ph_2PC_2H_4PPh_2)$
764	trace	$Pt(C_6H_4F)(C_6H_4)(Ph_2PC_2H_4PPh_2)$
688	0.2	$Pt(C_6H_4F)(Ph_2PC_2H_4PPh_2)$
669	0.1	$Pt(C_6H_4)(Ph_2PC_2H_4PPh_2)$
593	15.0	$Pt(Ph_2PC_2H_4PPh_2)$
565	2.5	$Pt(PPh_2)_2$
516	0.2	$Pt(Ph_2PC_2H_4PPh)$
490–483	1.9	$Pt(PPh_2)(PPh)$
459–449	0.8	$Pt(PPh_3)$
440–436	0.2	$Pt(PhPC_2H_4PPh)$
418	0.1	$C_{30}H_{20}F_2$
412–407	1.5	$Pt(PC_6H_4)_2$
400	0.1	$C_{30}H_{21}F$
391.5	0.5	$Pt(C_6H_4F)_2(Ph_2PC_2H_4PPh_2)^+$
378	0.8	$PtP(C_6H_4)_2$
360	0.1	$C_{24}H_{15}F_3$
347	1.0	$Pt(C_6H_4PCH_2P)$
342	0.9	$C_{24}H_{16}F_2$
335–332	0.5	PtP_2Ph
324	0.8	$C_{24}H_{17}F$
302	1.4	$PtPC_6H_4$
296.5	2.3	$Pt(Ph_2PC_2H_4PPh_2)^+$
280–277	1.7	$PPh_2(C_6H_4F)$

TABLE IV. (Cont.)

m/e	Abundance	Assignment
266	18.1	$C_{18}H_{12}F_2$
262	1.0	PPh_3
248–244	6.3	$C_{18}H_{13}F$
221–219	6.0	$P(C_6H_4F)_2$
203–199	3.0	$PPh(C_6H_4F)$
190–188	10.1	$(C_6H_4F)_2$
185–183	2.8	PPh_2
172–168	15.7	PhC_6H_4F
154–150	3.8	Ph_2
$Pt(p\text{-}FC_6H_4)_2(Ph_2PCH_2)_2$		
783	0.4	$Pt(C_6H_4F)_2(Ph_2PC_2H_4PPh_2)$
764	0.02	$Pt(C_6H_4F)(C_6H_4)(Ph_2PC_2H_4PPh_2)$
688	0.2	$Pt(C_6H_4F)(Ph_2PC_2H_4PPh_2)$
669	0.01	$Pt(C_6H_4)(Ph_2PC_2H_4PPh_2)$
611	0.01	$Pt(C_6H_4F)(Ph_2PC_2H_4PPh)$
593	24.3	$Pt(Ph_2PC_2H_4PPh_2)$
565	3.6	$Pt(PPh_2)_2$
516	0.3	$Pt(Ph_2PC_2H_4PPh)$
490–483	2.4	$Pt(PPh_2)(PPh)$
459–449	1.0	$Pt(PPh_3)$
440–436	0.4	$Pt(PhPC_2H_4PPh)$
418	1.0	$C_{30}H_{20}F_2$
412–407	2.1	$Pt(PC_6H_4)_2$
400	0.7	$C_{30}H_{21}F$
391.5	0.7	$Pt(C_6H_4F)_2(Ph_2PC_2H_4PPh_2)^+$
378	1.1	$PtP(C_6H_4)_2$
347	1.4	$Pt(C_6H_4PCH_2P)$
342	2.2	$C_{24}H_{16}F_2$
335–332	0.7	PtP_2Ph
324	1.9	$C_{24}H_{17}F$
305.5	0.4	$Pt(C_6H_4F)(Ph_2PC_2H_4PPh)^+$
302	2.1	$PtPC_6H_4$
296.5	3.6	$Pt(Ph_2PC_2H_4PPh_2)^+$
280	0.6	$PPh_2(C_6H_4F)$
266	13.2	$C_{18}H_{12}F_2$
262	0.7	PPh_3
248	5.0	$C_{18}H_{13}F$
221	0.6	$P(C_6H_4F)_2$
203–199	2.6	$PPh(C_6H_4F)$
190–188	11.9	$(C_6H_4F)_2$
185–183	2.8	PPh_2
172–168	9.0	PhC_6H_4F
154–150	2.9	Ph_2

Biaryl ions were of high abundance and are formed mainly by Pt–C bond cleavage. This follows since in $Pt(C_6H_4F)_2L_2$ compounds the abundance of $C_{12}H_8F_2{}^{\cdot +}$ was 5 to 10 times that of $Ph_2{}^{\cdot +}$, suggesting that concerted reductive elimination is a dominant process.[4] In the spectra of the fluorophenyl compounds low abundance ions were observed due to C–F bond cleavage even from the molecular ion. No significant correlations emerged between ion abundances in the *m*-fluoro, *p*-fluoro and phenyl complexes.

Although only the compounds with L = PPh_3 discussed earlier were thermally unstable some of the non-platinum containing ions produced in other cases suggest some degree of pyrolytic decomposition combined with migration of groups from phosphorus to platinum and vice versa. For example in the spectra of $Pt(C_6H_4F)_2(Ph_2PCH_2)_2$ ions were observed with up to five C_6 units, but containing with one exception only 0–2 fluorine atoms $[C_6H_4X(C_6H_4)_nC_6H_4X, X=H \text{ or } F, n=0–3]$. Formation of ions of this type may involve transfer of C_6H_4 units followed by insertion into the Pt–C_6H_4F bond (e.g. reaction 8).



(8)

In the case of $Pt(C_6H_4F)_2(Ph_2PCH_2)_2$ the ion $C_{18}H_{12}F_2{}^{\cdot +}$ was more abundant than $C_{12}H_8F_2{}^{\cdot +}$.

In the methylphenyl complex, $PtMePh(Ph_2PCH_2)_2$ cleavage of the Pt–C bonds was competitive and there was evidence for thermal disproportionation since molecular ions corresponding to $PtMe_2(Ph_2PCH_2)_2$ and $PtPh_2(Ph_2PCH_2)_2$ were present in low abundance (Table V). Introducing an intimate mixture of the two

TABLE V. Ion Abundances, $PtMePh(Ph_2PCH_2)_2$.

m/e	Abundance	Assignment
747	trace	$PtPh_2(Ph_2PC_2H_4PPh_2)$
719	trace	$PtPh_2(PPh_2)_2$
685	0.8	$PtMePh(Ph_2PC_2H_4PPh_2)$
670	2.4	$PtPh(Ph_2PC_2H_4PPh_2)$
642	0.2	$PtPh(PPh_2)_2$
623	0.4	$PtMe_2(Ph_2PC_2H_4PPh_2)$
608	16.1	$PtMe(Ph_2PC_2H_4PPh_2)$
596–591	23.9	$Pt(Ph_2PC_2H_4PPh_2)$
580	0.5	$PtMe(PPh_2)_2$
565	3.1	$Pt(PPh_2)_2$
517–513	0.8	$Pt(Ph_2PC_2H_4PPh)$
489–483	5.5	$Pt(PPh_2)(PPh)$
457–453	1.7	$Pt(PPh_3)$
438	1.8	$Pt(PhPC_2H_4PC_6H_4)$
411–407	4.6	$Pt(PPh)_2$
379–375	3.1	$PtMe(PhPC_2H_4P)$
347	2.3	$PtP_2C_7H_6$
342.5	0.5	$PtMePh(Ph_2PC_2H_4PPh_2)^+$
302	6.7	$PtPC_6H_4$
296.5	7.2	$Pt(Ph_2PC_2H_4PPh_2)^+$
263–261	2.1	$PHPh_3$
257.5	0.7	$Pt(Ph_2PC_2H_4PPh)^+$
244.5	0.7	$Pt(PPh_2)(PPh)^+$
230–226	1.1	$Ph_2(C_6H_4)$
213–212	2.2	$P(C_2H_4)Ph_2$
201	1.5	$PHMePh_2$
185–183	5.6	PPh_2
154–152	4.6	Ph_2

symmetrical compounds into the mass spectrometer under the same conditions did not produce $\mathrm{PtMePh(Ph_2PCH_2)_2}^{\cdot +}$. A broad, distorted metastable peak centred at 539 is probably due to reactions 9 and 10.

$$\mathrm{PtMePh(Ph_2PCH_2)_2}^{\cdot +} \xrightarrow{\mathrm{m^*,540}} \mathrm{PtMe(Ph_2PCH_2)_2}^{+} + \mathrm{Ph}\cdot \quad (9)$$

$$\mathrm{Pt(Ph_2PCH_2)_2}^{\cdot +} \xrightarrow{\mathrm{m^*,538}} \mathrm{Pt(PPh_2)_2}^{\cdot +} + \mathrm{C_2H_4} \quad (10)$$

Phosphine fragmentation

Fragmentation of phosphine groups without prior cleavage of Pt–C bonds was observed in some cases, though no clear pattern was discernable: for $\mathrm{PtMe_2(PPh_3)_2}$ the molecular ion carried 0,1% of the ion current compared to 0.6% for $\mathrm{PtMe_2(PPh_2)(PPh_3)}^+$. Coordination to platinum also influenced the fragmentation of the phosphine, for example in the free phosphine $\mathrm{(Ph_2P)_2CH_2}$ elimination of $\mathrm{CH_2}$ is metastable supported[11] whereas in its platinum diaryl complexes, the ion $\mathrm{Pt[(Ph_2P)_2CH_2]}^{\cdot +}$ eliminates a methyl radical, presumably forming a 4-membered $\mathrm{PtPC_2}$ ring. Migration of both alkyl and aryl groups from platinum to phosphorus is clearly demonstrated by the appearance of mixed phosphine ions. Thus $\mathrm{PMe_2Ph}^{\cdot +}$ is present in the spectrum of $\mathrm{PtPh_2(PMe_3)_2}$ and $\mathrm{PPh_2C_6H_4F}^{\cdot +}$ in the spectrum of $\mathrm{Pt(C_6H_4F)_2(Ph_2PCH_2)_2}$ Transfer of organic groups between phosphorus atoms is apparent in all the spectra, and these processes may occur through initial transfer to platinum. For example in the spectrum of $\mathrm{PtMe_2(Ph_2PCH_2)_2}$ the ion $\mathrm{PPh_3}^{\cdot +}$ may result in part from the reactions:
$\mathrm{Pt(PPh_2)_2}^{\cdot +} \rightarrow \mathrm{PfPh(PPh)(PPh_2)}^{\cdot +} \rightarrow \mathrm{Pt(PPh)(PPh_3)}^{\cdot +} \rightarrow \mathrm{PPh_3}^{\cdot +}$, although $\mathrm{PPh_3}^{\cdot +}$ is present in the spectrum of the free phosphine. Migration of two groups from platinum to phosphorus must also occur since the ion $\mathrm{(P(C_6H_4F)_2}^{+}$ is observed in the spectra of $\mathrm{Pt(}m,p\mathrm{-FC_6H_4)_2(Ph_2PCH_2)_2}$.

Phosphonium ions e.g. $\mathrm{PMe_2Ph_2}^+$ from $\mathrm{PtMe_2(PPh_3)_2}$; $\mathrm{PEt_3Me}^+$ from $\mathrm{PtMe_2(PEt_3)_2}$ also result from the transfer of alkyl and aryl groups from platinum to phosphorus. For $\mathrm{PEt_3}$ and $\mathrm{(Ph_2PCH_2)_2}$ complexes ethylene elimination was commonly metastable supported (Table VI) and occurred from a variety of fragment ions. With $\mathrm{PtPh_2(PEt_3)_2}$ this was only observed after cleavage of both phenyl groups whereas the chelating phosphine complexes lost ethylene competitively with Pt–C bond cleavage. In the case of $\mathrm{PtMe_2(Ph_2PCH_2)_2}$ loss of $\mathrm{C_2H_4}$ and $\mathrm{C_6H_6}$ from the phosphine are both metastable supported and occur in competition with elimination of methyl groups. This compound also shows a metastable peak for radical elimination from a doubly charged ion (reaction 11).

$$\mathrm{Pt(Ph_2PC_2H_4PPhC_6H_4)}^{\cdot 2+} \rightarrow \mathrm{Pt(Ph_2PC_2H_4PC_6H_4)}^{2+} + \mathrm{Ph}\cdot \quad (11)$$

TABLE VI. Metastable Supported Transitions.

	m*
$PtMe_2(PMe_3)_2$	
$\mathrm{PtMe(PMe_3)_2}^{+} \rightarrow \mathrm{Pt(PMe_2CH_2)(PMe_3)}^{+} + \mathrm{CH_4}$	331
$PtMe_2(PPh_3)_2$	
$\mathrm{PtMe(PPh_3)_2}^{+} \rightarrow \mathrm{Pt(PPh_2C_6H_4)(PPh_3)}^{+} + \mathrm{CH_4}$	702
$\mathrm{PtMe_2(PPh_2)(PPh_3)}^{+} \rightarrow \mathrm{PtMe(PPh_2)(PPh_2C_6H_4)}^{+} + \mathrm{CH_4}$	640
$PtMe_2[(Ph_2P)_2CH_2]$	
$\mathrm{PtMe(Ph_2PCH_2PPh_2)}^{+} \rightarrow \mathrm{PtMe(Ph_2PCH_2PC_6H_4)}^{+} + \mathrm{C_6H_6}$	448
$\mathrm{C_{13}H_{12}PPt}^{+} \rightarrow \mathrm{PtP(C_6H_4)_2}^{+} + \mathrm{CH_4}$	363
$PtMe_2(Ph_2PCH_2)_2$	
$\mathrm{PtMe(Ph_2PC_2H_4PPh_2)}^{+} \rightarrow \mathrm{Pt(Ph_2PC_2H_4PPhC_6H_4)}^{+} + \mathrm{CH_4}$	576
$\mathrm{PtMe(Ph_2PC_2H_4PPh_2)}^{+} \rightarrow \mathrm{PtMe(PPh_2)_2}^{+} + \mathrm{C_2H_4}$	553
$\mathrm{Pt(Ph_2PC_2H_4PPhC_6H_4)}^{+} \rightarrow \mathrm{Pt(PPh_2)(PPhC_6H_4)}^{+} + \mathrm{C_2H_4}$	537
$\mathrm{PtMe(Ph_2PC_2H_4PPh_2)}^{+} \rightarrow \mathrm{PtMe(Ph_2PC_2H_4PC_6H_4)}^{+} + \mathrm{C_6H_6}$	462
$\mathrm{Pt(PhPC_2H_4PC_6H_4)}^{+} \rightarrow \mathrm{Pt(PPh)(PC_6H_4)}^{+} + \mathrm{C_2H_4}$	384
$\mathrm{Pt(Ph_2PC_2H_4PPhC_6H_4)}^{+} \rightarrow \mathrm{Pt(PhPC_2H_4PC_6H_4)}^{+} + \mathrm{C_{12}H_{10}}$	324
$\mathrm{Pt(Ph_2PC_2H_4PPhC_6H_4)}^{\cdot 2+} \rightarrow \mathrm{Pt(PhPC_2H_4PPhC_6H_4)}^{2+} + \mathrm{C_6H_5}\cdot$	224
$PtEt_2[(Ph_2P)_2CH_2]$	
$\mathrm{PtEt(Ph_2PCH_2PPh_2)}^{+} \rightarrow \mathrm{PtH(Ph_2PCH_2PPh_2)}^{+} + \mathrm{C_2H_4}$	553
$\mathrm{PtH(Ph_2PCH_2PPh_2)}^{+} \rightarrow \mathrm{Pt(Ph_2PCH_2PPh)}^{+} + \mathrm{C_6H_6}$	434
$PtEt_2(Ph_2PCH_2)_2$	
$\mathrm{PtEt(Ph_2PC_2H_4PPh_2)}^{+} \rightarrow \mathrm{C_{26}H_{25}P_2Pt}^{+} + \mathrm{C_2H_4}$	567
$\mathrm{Pt(Ph_2PC_2H_4PPhC_6H_4)}^{+} \rightarrow \mathrm{Pt(PPh_2)(PPhC_6H_4)}^{+} + \mathrm{C_2H_4}$	537
$\mathrm{Pt(PhPC_2H_4PC_6H_4)}^{+} \rightarrow \mathrm{Pt(PPh)(PC_6H_4)}^{+} + \mathrm{C_2H_4}$	384
$\mathrm{Pt(Ph_2PC_2H_4PPhC_6H_4)}^{+} \rightarrow \mathrm{Pt(PhPC_2H_4PC_6H_4)}^{+} + \mathrm{C_{12}H_{10}}$	324
$\mathrm{Pt(Ph_2PC_2H_4PPhC_6H_4)}^{\cdot 2+} \rightarrow \mathrm{Pt(PhPC_2H_4PPhC_6H_4)}^{2+} + \mathrm{C_6H_5}\cdot$	224
$PtPh_2(PMe_3)_2$	
$\mathrm{Pt(PMe_3)_2}^{\cdot +} \rightarrow \mathrm{Pt(PMe_2)(PMe_3)}^{+} + \mathrm{CH_3}\cdot$	318
$PtPh_2(PEt_3)_2$	
$\mathrm{Pt(PEt_3)_2}^{\cdot +} \rightarrow \mathrm{Pt(PEt_3)(PEt_2H)}^{\cdot +} + \mathrm{C_2H_4}$	377
$\mathrm{Pt(PEt_3)(PEt_2H)}^{\cdot +} \rightarrow \mathrm{Pt(PEt_2H)_2}^{\cdot +} + \mathrm{C_2H_4}$	349
$\mathrm{Pt(PEt_2H)_2}^{\cdot +} \rightarrow \mathrm{Pt(PEt_2H)(PEtH_2)}^{\cdot +} + \mathrm{C_2H_4}$	321
$\mathrm{Pt(PEt_2H)(PEtH_2)}^{\cdot +} \rightarrow \mathrm{Pt(PEtH_2)_2}^{\cdot +} + \mathrm{C_2H_4}$	293
$PtPh_2[(Ph_2P)_2CH_2]$	
$\mathrm{Pt(Ph_2PCH_2PPh_2)}^{\cdot +} \rightarrow \mathrm{Pt(PPh_2)(PPhC_6H_4)}^{+} + \mathrm{CH_3}\cdot$	549
$\mathrm{PtPh_2(Ph_2PCH_2PPh_2)}^{\cdot +} \rightarrow \mathrm{Pt(Ph_2PCH_2PPh_2)}^{\cdot +} + \mathrm{C_{12}H_{10}}$	457
$\mathrm{Pt(Ph_2PCH_2PPh_2)}^{\cdot +} \rightarrow \mathrm{Pt(Ph_2PCH_2PC_6H_4)}^{\cdot +} + \mathrm{C_6H_6}$	434
$\mathrm{Pt(FC_6H_4)_2[(Ph_2P)_2CH_2]}$, *m*- and *p*-	
$\mathrm{Pt(Ph_2PCH_2PPh_2)}^{\cdot +} \rightarrow \mathrm{Pt(PPh_2)(PPhC_6H_4)}^{+} + \mathrm{CH_3}\cdot$	549

TABLE VI. (Cont.)

	m*
$PtPh_2(Ph_2PCH_2)_2$	
$Pt(Ph_2PC_2H_4PPh_2)^{\cdot+} \rightarrow Pt(PPh_2)_2^{\cdot+} + C_2H_4$	538
$PtPh_2(Ph_2PC_2H_4PPh_2)^{\cdot+} \rightarrow Pt(Ph_2PC_2H_4PPh_2)^{\cdot+} + C_{12}H_{10}$	471
$Pt(PPh_2)_2^{\cdot+} \rightarrow Pt(PPh_2)(PC_6H_4)^{\cdot+} + C_6H_6$	420
$Pt(FC_6H_4)_2(Ph_2PCH_2)_2$, m - and p -	
$Pt(Ph_2PC_2H_4PPh_2)^{\cdot+} \rightarrow Pt(PPh_2)_2^{\cdot+} + C_2H_4$	538
$Pt(C_6H_4F)_2(Ph_2PC_2H_4PPh_2)^{\cdot+} \rightarrow Pt(Ph_2PC_2H_4PPh_2)^{\cdot+} + (C_6H_4F)_2$	449
$Pt(PPh_2)_2^{\cdot+} \rightarrow Pt(PPh_2)(PC_6H_4)^{\cdot+} + C_6H_6$	420
$Pt(PPh_2)(PC_6H_4)^{\cdot+} \rightarrow Pt(PC_6H_4)_2^{\cdot+} + C_6H_6$	343
$PtMePh(Ph_2PCH_2)_2$	
$PtMe(Ph_2PC_2H_4PPh_2)^{+} \rightarrow Pt(Ph_2PC_2H_4PPhC_6H_4)^{+} + CH_4$	576
$PtPh(Ph_2PC_2H_4PPh_2)^{+} \rightarrow Pt(Ph_2PC_2H_4PPhC_6H_4)^{+} + C_6H_6$	523
$Pt(PPh_2)_2^{\cdot+} \rightarrow Pt(PPh_2)(PC_6H_4)^{\cdot+} + C_6H_6$	420
$Pt(PhPC_2H_4PC_6H_4)^{+} \rightarrow Pt(PPh)(PC_6H_4)^{+} + C_2H_4$	384
$Pt(Ph_2PC_2H_4PPhC_6H_4)^{\cdot 2+} \rightarrow Pt(PhPC_2H_4PPhC_6H_4)^{2+} + C_6H_5^{\cdot}$	224

In all compounds containing PPh groupings the lowest mass platinum-containing ion was $PtPC_6H_4^+$ whereas in alkylphosphine complexes it was $PtPCH_2^+$. Only in $PtMe_2(PMe_3)_2$ was the simpler PtP^+ ion identified in low abundance.

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