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Fast-atom bombardment (FAB) mass spectra of coordination complexes: aggregation processes in the mass spectra of Group 11 alkynyl complexes

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Abstract

The FAB mass spectra of m$(C_2Ph)(PPh_3)$ (m = Cu, Ag, Au) and $C_2\{Au(PR_3)\}_2$ (R = Ph, *m*-tolyl) have been studied and the fragmentation routes determined by a combination of MIKES and B^2/E techniques. A particular feature in the spectra of both types of complex is the presence of aggregate ions containing up to twelve metal atoms. For m$(C_2Ph)(PPh_3)$, these ions have the compositions $[m_a(C_2Ph)_b(PPh_3)_c]^+$ ($a \geq b \geq c$; for Cu, $a = 1$–4; Ag, 1–3; Au, 1–4), although $[Cu_5(C_2Ph)_3(PPh_3)_3]^+$ was detected in the B^2/E scan. Fragmentation involves loss of PPh_3, Ph or C_2Ph groups. For $C_2\{Au(PR_3)\}_2$, loss of PR_3 is the predominant fragmentation mode. In general, the ions are derived from several, rather than one, higher nuclearity ions. In both series, many ions can be considered to be formed by addition of $[m(PR_3)]^+$ cations to neutral oligometric M_n species; these ions are isolobal with protonated M_n ions.

Introduction

The presence of ions at higher mass than the nominal parent ion in the mass spectra of inorganic and organometallic molecules is indicative of ion-molecule aggregation processes [1]. Several examples of this phenomenon have been reported recently, for example, with simple salts of Mg, Hg, Pb [2] and uranyl [3], mixed ligand complexes of magnesium [4], allylpalladium complexes [5], and $Pt(PPh_3)_4$ [6]. We have briefly described the occurrence of aggregate ions in the FAB mass spectra of the C_2 complexes $C_2\{Au(PR_3)_2\}_2$ (R = Ph, *m*-tol) [7]. This paper describes the latter results in more detail and also includes the results of a more extensive study of the complexes m$(C_2Ph)(PPh_3)$ (m = Cu, Ag, Au). *

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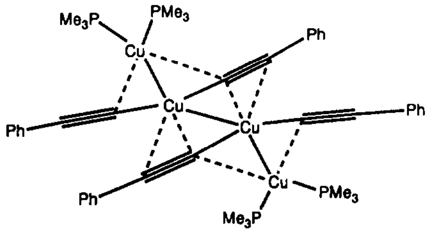
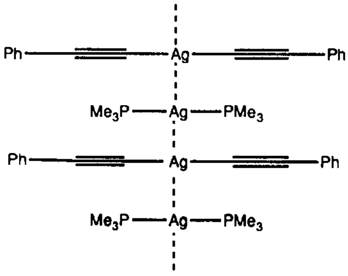
* In this paper, the symbol m is used to denote a metal atom, with M reserved for the molecular ion.



(1)

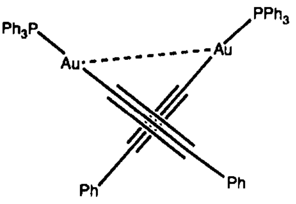


(2)

Results and discussion

Complexes $m(C_2Ph)(PPh_3)$ *(*$m = Cu, Ag, Au$*)*

Unfortunately structural studies of two of the three complexes studied in this work have not yet been determined. For copper, the related complex $\{Cu(C_2Ph)(PMe_3)\}_4$ has structure **1**, in which two $[Cu(PMe_3)_2]^+$ cations interact with dinuclear anionic $[Cu_2(C_2Ph)_4]^{2-}$ species [8]. For the silver analogue $\{Ag(C_2Ph)(PMe_3)\}_2$ (**2**), linear chains of $[Ag(PMe_3)_2]^+$ cations and $[Ag(C_2Ph)_2]^-$ anions are found with Ag···Ag separations of 3.03 Å [9]. Finally, for $Au(C_2Ph)(PPh_3)$ (**3**), two mononuclear molecules interact in the solid state to form a weak Au···Au bond (3.38 Å) such that the two $PAuC_2$ chains are nearly orthogonal [10]. The common feature of the solid state structures of these three molecules is the presence of secondary interactions leading to extended structures.



(3)

$Ph_3P\text{-}Cu\text{-}C{\equiv}C\text{-}Ph$

(4)

$Ph_3P\text{-}Ag\text{-}C{\equiv}C\text{-}Ph$

(5)

The positive ion FAB mass spectra of the three complexes $m(C_2Ph)(PPh_3)$ (m = Cu (**4**), Ag (**5**), Au (**3**)) are collected in Table 1. There are some similarities but also important differences, so that the three spectra will be discussed individually.

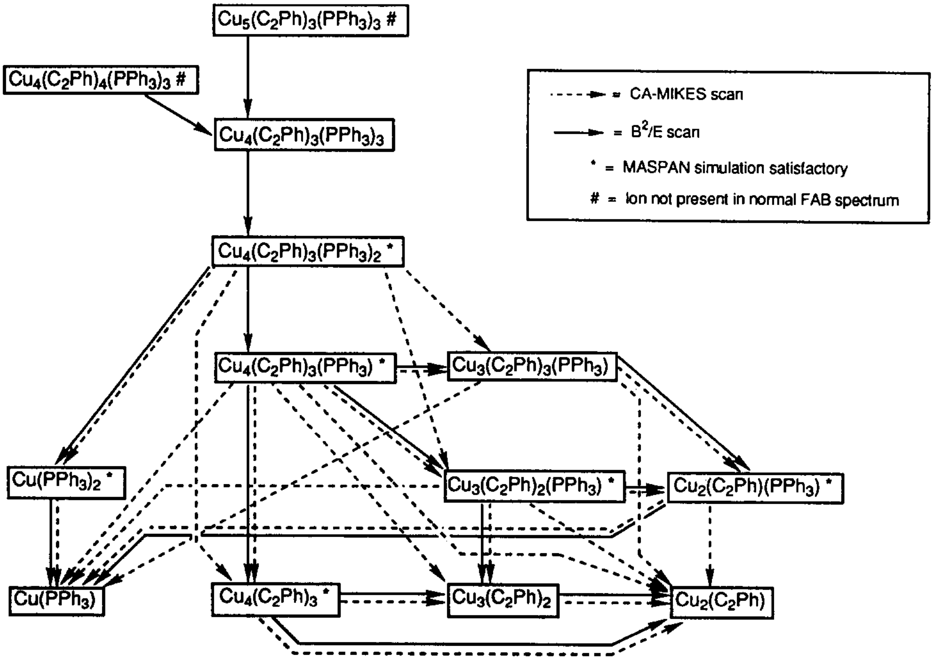
(a) m = Cu (4). The majority of the ions present in the mass spectra of the copper complex have been studied by MIKES [11] and B^2/E analyses [12], with confirmation of ion compositions using MASPAN ion envelope simulations [13]. The inter-relationships thus determined are shown in Scheme 1. There were often weak ions which are found in the MIKES and B^2/E studies which were not present in the normal FAB mass spectrum (see Fig. 1); where these can be assigned, they have also been incorporated in Scheme 1.

There is an apparent relationship between the observed ions and the tetrameric units found in the solid state structure of $\{Cu(C_2Ph)(PMe_3)\}_4$. The most stable and

Table 1

FAB mass spectra (positive ion; *m/z* and relative intensities) of $m(C_2Ph)(PPh_3)$ (m = Cu, Ag, Au)

Ion	Cu		Ag		Au	
$m_4(C_2Ph)_3(PPh_3)_3$	1343	2				
$m_4(C_2Ph)_3(PPh_3)_2$	1081	15			1615	2
$m_4(C_2Ph)_3(PPh_3)$	819	75				
$m_4(C_2Ph)_3$	557	30				
$m_3(PPh_3)_3P$?					1408	4
$m_3(C_2Ph)_3(PPh_3)$	753	9				
$m_3(C_2Ph)_2(PPh_3)_2$			1049	0.4	1317	12
$m_3(C_2Ph)_2(PPh_3)$	655	33	787	2	1055	3
$m_3(C_2Ph)_2$	393	12				
$m_2(C_2Ph)(PPh_3)_2$			841	5	1019	75
$m_2(C_2Ph)(PPh_3)$	489	28	579	5	757	4
$m_2(C_2Ph)$	227	20	317	8		
$m(C_2Ph)(PPh_3)$	426	4			560	18
$m(C_2Ph)(PPh_2)$	349	4			483	3
$m(PPh_3)_2$	587	100	631	100	721	68
$m(PPh_3)(PPh_2)$			554	2	644	5
$m(PPh_3)$	325	46	369	65	459	100
$m(PPh)$					305	6
$mO(PPh_3)_2$	603	10	647	4	737	6
$mO(PPh_3)$	341	4	385	4	475	4



Scheme 1. Major inter-ionic relationships for $Cu(C_2Ph)(PPh_3)$ (4) as established by CA/MIKES, B^2/E and simulation of ion isotope patterns.

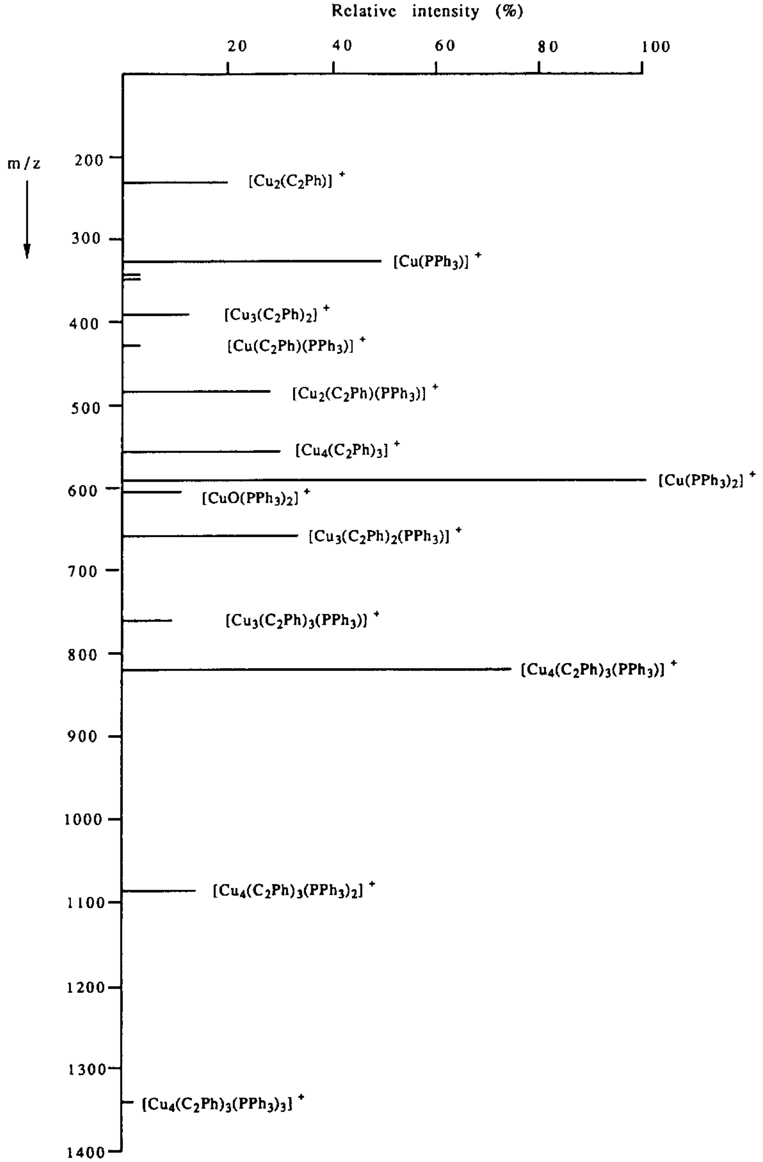


Fig. 1. FAB mass spectrum of $Cu(C_2Ph)(PPh_3)$ (4).

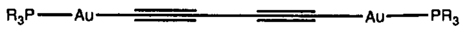
abundant ions are $[Cu_4(C_2Ph)_3(PPh_3)]^+$ and $[Cu(PPh_3)_2]^+$. In most cases, ions have the formulation $[Cu_a(C_2Ph)_b(PPh_3)_c]^+$ ($a = 1$–4, $b = 0$–3, $c = 0$–3; $a \geq b \geq c$). The base peak is $[Cu(PPh_3)_2]^+$, well known as a stable linear two-coordinate cation. Major fragmentation routes involve loss of PPh_3, $Cu(C_2Ph)$, C_2Ph or Cu fragments. The ions $[Cu_m(C_2Ph)_n(PPh_3)_3]^+$ ($m = 5$, $n = 3$; $m = 4$, $n = 4$) are apparently formed independently (no parent ions could be detected in the metastable B^2/E scan) while the extensive fragment ions observed at lower m/z values clearly arise from several higher mass ions (no comment can be made on the direct formation of these fragment ions). Only in the case of $[Cu_x(C_2Ph)_{x-1}]^+$ ($x = 2$–4) were PPh_3-free ions observed; $[Cu(PPh_3)_n]^+$ ions ($n = 1, 2$) were abundant, the latter being the base peak.

(b) m = Ag (5). In this case, the highest mass ion at m/z 1049 corresponds to $[Ag_3(C_2Ph)_2(PPh_3)_2]^+$; other ions are formed by loss of Ph, PPh_3 or C_2Ph units, the former occurring from $[Ag(PPh_3)_2]^+$, the base peak. The only PPh_3-free ion is $[Ag_2(C_2Ph)]^+$.

(c) m = Au (3). For this complex, relatively strong polynuclear ions were found containing up to four gold atoms. The fragmentation is more complex than that found for the Cu and Ag analogues; ions containing more C_2Ph groups than PPh_3 ligands are present and in this case $[Au(PPh_3)]^+$ is the base peak. The formulation of several ions requires the presence of Ph groups; in one case, $[Au(PPh)]^+$ is formed. Monitoring of the ions $[Au(C_2Ph)(PPh_3)]^+$, $[Au_2(C_2Ph)(PPh_3)_2]^+$ and $[Au(PPh_3)_2]^+$ showed that the intensities of the latter two ions increased as that of $[M]^+$ decreased as a function of time. This suggests that a decomposition/aggregation process may be involved in the formation of some of the aggregate ions. By this we mean that appreciable concentrations of reactive fragments produced by decomposition of the organometallic in the matrix may build up, further reaction of these fragments then leading to the formation of some of the aggregate ions.

The formulation of the aggregate ions in the spectra of **4** and **5** corresponds to the addition of $m(PPh_3)$ moieties to the molecular ion. The isolobal relationship between $[m(PPh_3)]^+$ and H^+ is well known and we propose that these ions have a similar isolobal relationship to the protonated M^+ ions found in conventional organic (and some organometallic) FAB mass spectra. The addition of successive $m(C_2Ph)$ fragments to the ions $[m(C_2Ph)(PPh_3)]^+$ (m = Cu, $n = 0, 1$; m = Ag, Au, $n = 1, 2$) suggests that the copper-containing aggregate ions are stabilised by the presence of an extra Cu atom, while the Ag and Au aggregates are more effecetively stabilised by additional $m(PPh_3)$ groups. From the MIKES and B^2/E studies it can be seen that in terms of metastable decompositions, there are a large number of competing pathways for the fragmentation of the higher mass ions. For a given high mass ion, loss of m, $m(C_2Ph)$ or PPh_3 is possible; most of the possible fragment ions have appreciable stabilities. The flexibility of the metal coordination spheres in the gas phase is evident.

Some evidence of oxidation occurring during the FAB ionisation process is found in the presence of ions such as $[mO(PPh_3)]^+$ ($n = 1, 2$). A B^2/E scan on the Cu ion established that there is no precursor to this ion, so that it is apparently formed directly by addition of O to $[Cu(PPh_3)_2]^+$ during or after the ionisation process. It is not possible to determine the site of O atom addition, since neither $[OPPh_3]^+$ nor $[MO]^+$ ions are present.



(6) R = Ph
(7) R = *m*-tol

Complexes $C_2\{Au(PR_3)_2\}_2$ (R = Ph (6), m-*tol (7))*

The spectra of these two complexes are collected in Table 2, from which their richness can be seen immediately. The highest mass ions correspond to aggregates containing between ten and twelve gold atoms. The spectra are conveniently

Table 2

FAB mass spectra (positive ion; m/z and relative intensities) of $C_2\{Au(PR_3)_2\}_2$ ($\equiv$ M; R = Ph, *m*-tol)

Ion	Ph		*m*-tol	
M_6-9PR_3	3294	0.2		
M_5-2PR_3			4522	0.001
M_5-3PR_3			4218	0.001
M_5-6PR_3	3138	0.1	3306	0.001
M_5-7PR_3	2876	0.8		
M_5-8PR_3	2614	0.3		
$M_4+2Au(PR_3)-4PR_3$	3638	0.2		
$M_4+2Au(PR_3)-5PR_3$	3376	0.1		
$M_4+Au(PR_3)-2PR_3$	3703	0.1		
$M_4+Au(PR_3)-4PR_3$	3179	0.5		
$M_4+Au(PR_3)-5PR_3$	2917	0.3	3084	0.01
$M_4+Au(PR_3)-6PR_3$	2655	0.1	2781	0.001
$M_4+Au(PR_3)-7PR_3$	2393	0.2	2477	0.01
M_4			4104	0.001
M_4-R	3691	0.1	4012	0.001
M_4-PR_3			3800	0.01
$M_4-PR_3-PR_2$			3587	0.004
M_4-2PR_3			3496	0.02
M_4-5PR_3	2458	0.3	2580	0.01
M_4-6PR_3	2196	1.4		
$M_3+3Au(PR_3)-3PR_3$	3417	0.1		
$M_3+3Au(PR_3)-6PR_3$	2631	0.1		
$M_3+2Au(PR_3)-3PR_3$	2958	0.2		
$M_3+2Au(PR_3)-4PR_3$	2696	0.6		
$M_3+2Au(PR_3)-5PR_3$	2434	0.3		
$M_3+Au(PR_3)-2PR_3$	2761	1.3		
$M_3+Au(PR_3)-3PR_3$	2499	1.5	2670	0.06
$M_3+Au(PR_3)-4PR_3$	2237	1	2364	0.1
$M_3+Au(PR_3)-5PR_3$	1975	0.5		
M_3-2PR_3	2302	0.3		
M_3-3PR_3	2040	1	2166	0.05
M_3-4PR_3	1778	1	1863	0.1
$M_2+2Au(PR_3)-2PR_3$	2278	0.8	2446	0.02
$M_2+Au(PR_3)-PR_3$	2081	11	2249	3.0
$M_2+Au(PR_3)-2PR_3$	1819	2	1946	0.4
$M_2+Au(PR_3)-3PR_3$	1557	3	1641	2
$M_2+Au(C_2)$	2105	1		
M_2			2052	0.01
M_2-PR_3	1622	2	1748	2
$M_2-Au(PR_3)-PR_3-PR_2$	979	11		
$M+2Au(PR_3)-PR_3$	1598	1	1724	0.3
$M+2Au(PR_3)-3PR_3$			1116	0.05
$M+Au(PR_3)+O$	1417	18	1543	3
$M+Au(PR_3)$	1401	66	1527	34
$M+Au(PR_3)-Me$			1512	2
$M+Au(PR_3)-PR_3$	1139	15	1223	5
$M+Au(PR_3)-2PR_3$	876	6	919	2
$M+Au(PR_2)$	1324	6	1436	3
$M+AuR$			1314	1
$M+Au(C_2)$			1248	1
$M+Au-R$			1132	0.5
MH	943	7	1027	17

Table 2 (continued)

Ion	Ph		*m*-tol	
$M-R$	865	2	935	1
$Au_2(PR_3)_2$	917	5	1001	5
$Au_2(PR_3)_2-R$	841	5	911	2
$Au_2(PR_3)$			697	1
$Au_2(PR_2)$	578	5		
$C_2Au(PR_3)_2$	745	1	829	2
$C_2Au(PR_3)$	483	5	525	4
$OAu(PR_3)_2$	737	2	821	2
$Au(PR_3)_2$	721	49	805	41
$Au(PR_3)_2-R$			714	2
$Au(PR_3)+R$			591	2
$OAu(PR_3)$	475	4	517	3
$Au(PR_3)$	459	100	501	100
$Au(PR_2)$			410	3

analysed in terms of the formation of ions of composition $[\{aM + bAu(PR_3)\} - cPR_3]^+$ ($a = 1$–6, $b = 0$–3, $c = 0$–7). Some further fragmentation is evident at lower mass numbers, which takes the form of loss of R, PR_3, Au, AuC_2 or $Au(PR_3)$ groups. The protonated molecular ions $[C_2\{Au(PR_3)_2\}_2 + H]^+$ are not particularly abundant (7 and 17%, respectively) and from the B^2/E studies (see below) it can be seen that the observed ion intensities for $[M]^+$ are in part due to the decomposition of higher mass ions which contain this fragment. The proton probably originates from the matrix. The mass spectrum of the clathrate complex $C_2\{Au(PR_3)\}_2 \cdot C_6H_6$ (R = *m*-tol), where a weak interaction between solvent and complex is seen in the X-ray determined structure [7], is identical to that of the unsolvated compound. No Au $\cdots$ Au interaction is found in either form in the solid state. We suggest therefore that the aggregates seen in the FAB mass spectra reflect the favoured formation of gold-containing clusters in the gas phase. It is likely that bonding interactions of relatively low energy are involved which do not occur in the solid or solution phase.

Figure 2 illustrates the mass spectrum of the P(*m*-tolyl)$_3$ complex (**7**) with major peaks labelled to correspond with the MIKES and B^2/E studies, the results of which are summarised in Scheme 2. The latter presents the inter-relationships established for most of the high-mass ions. Again we find that some of the ionic compositions are characteristic of adduct formation by addition of $Au(PR_3)$ groups. As found for the phenylacetylide complexes discussed above, the aggregates consist of "cationated" neutral species. In **6** and **7**, the added cations are Au^+ and $[Au(PR_3)]^+$. In general, the neutral species comprise the parent molecule together with further units of either Au or Au_2C_2. The formulation of several ions requires the presence of more than one extra Au or $Au(PR_3)$ unit; this feature, coupled with the observation of the ions $[Au_2(PR_3)_2]^+$ (which are not formed from M^+) suggests that Au $\cdots$ Au interactions may be involved in these larger aggregates.

The results of the metastable studies show that a myriad of decomposition pathways are available for the high mass ions. This appears to be due to the fact that the ionic species formed by loss of the various constituents of the aggregates

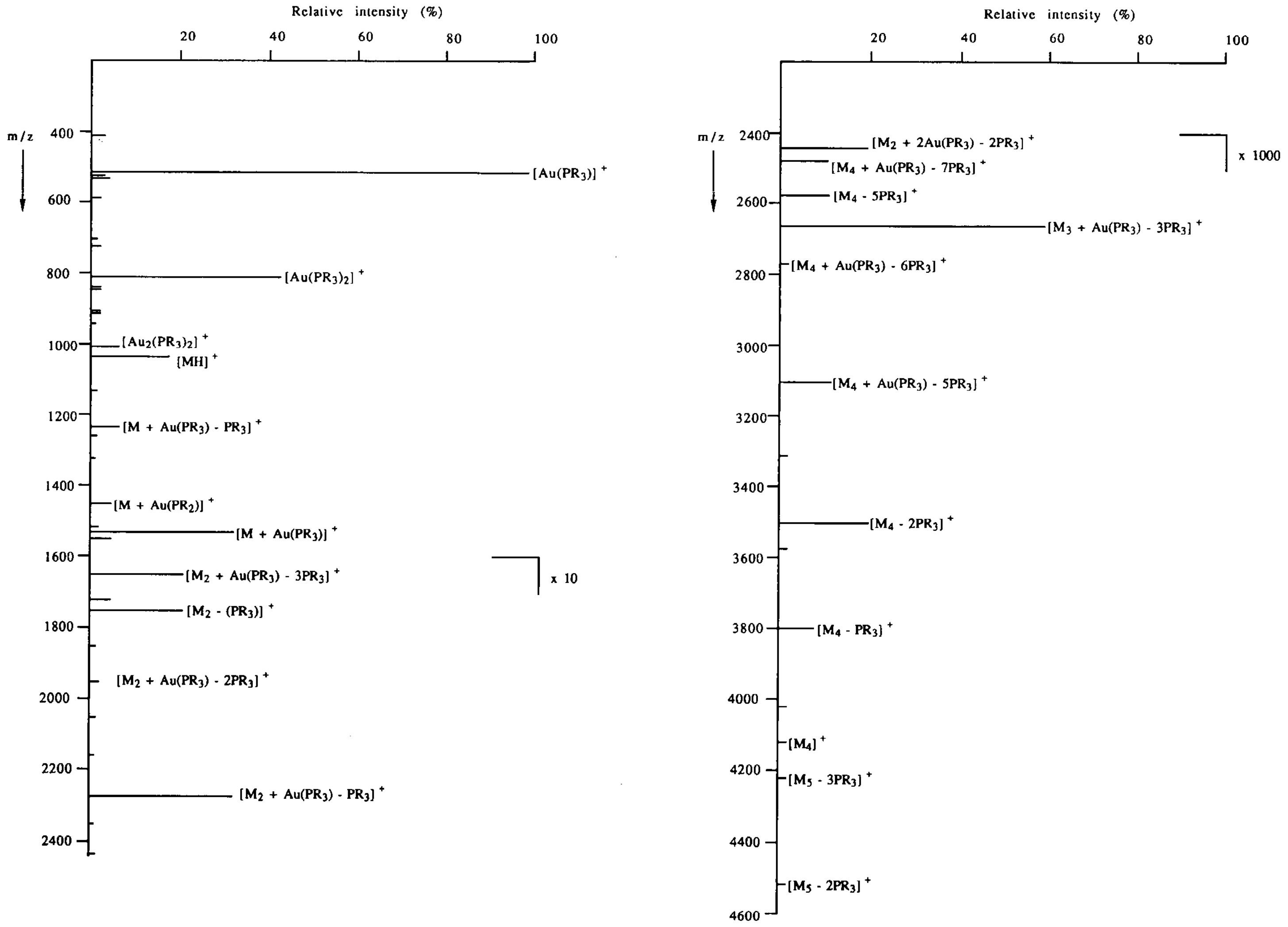
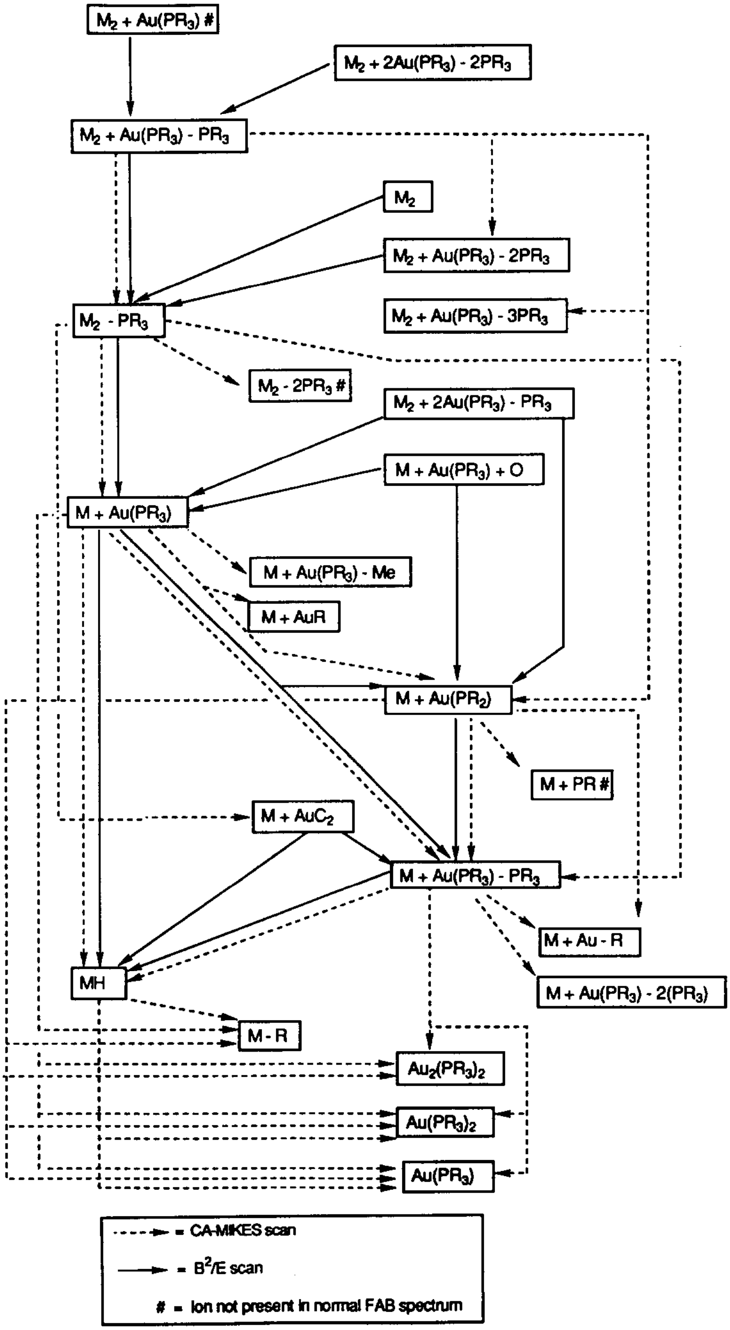


Fig. 2. FAB mass spectrum of $C_2\{Au[P(C_6H_4Me\text{-}m)_3]\}_2$ (7).



Scheme 2. Major inter-ionic relationships for $C_2\{Au[P(C_6H_4Me\text{-}m)_3]\}_2$ (7) as established by CA/MIKES and B^2/E spectra.

(Au, C_2, PR_3, R, Me) are not particularly unstable. We are not able to comment extensively on the formation of the higher mass ions; however, daughter ions that have weak parent ions in the B^2/E spectra and yet are of reasonable abundance

(> 2%) in the regular FAB spectra may be good candidates for the formation of primary aggregates. Examples are $[\{M_2 + Au(PR_3)\} - PR_3]^+$, $[M_2 - PR_3]^+$ and $[M + Au(PR_3)]^+$; others, such as $[\{M + Au(PR_3)\} - PR_3]^+$, are probably formed primarily through fragmentation. Unfortunately, these effects are difficult to quantify as a result of decreasing instrumental sensitivity at high mass numbers. It is clear, however, that we are not seeing the formation of a single, particularly large or stable aggregate, but rather of several aggregate ions of varying size which then undergo fragmentation.

From the studies of phenylacetylide and ethynediyl complexes described above, we can make some further comments about the FAB ionisation mechanism. There are three types of desorption/ionisation phenomena occurring in FAB mass spectrometry:

(i) Solids may be desorbed directly as clusters. This is a sputtering phenomenon and occurs from the solid state. Examples include the cesium halides [14] and TiO_2 [15].

(ii) Desorption as ions. This occurs when

$$E_{(\text{molecule})} < E_{(\text{FAB complex})}$$

and is often found with ionic complexes, such as $[Ru(CCHR)(PR_3)_2(\eta\text{-}C_5H_5)][PF_6]$ [16]. The inequality relates to the overall energetics for the process

$$\text{molecule}_{(\text{matrix})} \rightarrow [\text{ion}]^+_{(\text{gas phase})}$$

This is effectively a transfer of the ionic species to the gas phase, and allows the determination of the composition of both cations and anions by positive and negative ion spectra, respectively. In addition, neutral species with low ionisation energies may also be desorbed in this fashion. The "FAB complex" is any ensemble which may be formed chemically from the original precursor (including those formed by reaction with the matrix).

(iii) Desorption as a FAB complex. This process occurs when

$$E_{(\text{molecule})} > E_{(\text{FAB complex})}$$

Some recent results [17] suggest that it is the stability of the FAB complex in the selvedge region which ensures that this is the predominant species desorbed. This type of mechanism may be further divided into

(a) Desorption of the primary FAB complex, such as $[M + \text{matrix}]^+$, $[M + H]^+$, $[M - H]^+$, $[M + O]^+$. Most organometallics are desorbed in this manner.

(b) Desorption of a secondary FAB complex, where

$$E_{(\text{primary FAB complex})} > E_{(\text{secondary FAB complex})}$$

This process is illustrated in the present study where we see the formation of a variety of ensembles of multi-molecule aggregates, often in competing reactions.

The major factor which determines which mechanism will predominate is the nature of the equilibria occurring between the gas phase, selvedge region and the matrix.

Mixed-metal species

Aggregation processes occurring during the FAB ionisation process can sometimes be confirmed by running spectra of mixtures of similar components. Preliminary studies have shown that the FAB mass spectra of equimolar mixtures of $m(C_2Ph)(PPh_3)$ (m = Ag, Au) produces ions containing both metals, *e.g.* $[AgAu(C_2Ph)(PPh_3)_2]^+$, which fragments to $[AgAu(C_2Ph)(PPh_3)]^+$, both ions having relatively high abundances. Further studies of these and related systems may give more information about the reactions which lead to the aggregated species.

Experimental

Complexes

The complexes $m(C_2Ph)(PPh_3)$ (m = Cu [18], Ag [19], Au [20]) and $C_2\{Au(PR_3)_2\}_2$ (R = Ph, *m*-tol) [17] were made by cited methods. The Cu and Ag samples could only be synthesised successfully from their respective phenylacetylide polymers.

Spectroscopy

FAB mass spectra were obtained by use of a VG ZAB 2HF instrument equipped with a FAB source with 3-nitrobenzyl alcohol as matrix (exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV). Samples were dissolved in CH_2Cl_2 and then suspended in the matrix.

Collision-activated mass-analyzed ion kinetic energy spectra (CA/MIKES) were recorded with helium introduced in the second field-free region at an analyzer pressure of 2×10^{-7} Torr. Isotopic simulations were performed on a VAX 11/780 computer using the MASPAN program [13]. The accuracy of nominal masses greater than 1500 a.m.u. is $< \pm 2$ a.m.u. The accuracy of the CA/MIKES and B^2/E analyses in this region is ± 5 a.m.u. No differences were found in the spectra of $Ag(C_2Ph)(PPh_3)$ when either Ar or Xe was used as the FAB ionising gas. No changes were observed in the spectra of $Au(C_2Ph)PPh_3)$ when recorded as a function of contact time with matrix. When the spectra were recorded as a function of the time the sample spent in the source, changes were found in all of the samples. Generally, most effects were seen on the intensities of the higher mass ions. For example, the peaks at m/z 1408 and 1019 in the spectrum of $Au(C_2Ph)(PPh_3)$ decreased more rapidly than the other peaks in the spectrum (approx. 20% reduction after 4 min in the source). The tables report all assignable peaks in reproducible spectra. In the context of matrix reactivity, we note here that the clear matrix solution of **5** was invariably blackened after removal from the source.

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