
Mass Spectral Behavior of Some Homoleptic and Mixed Aryldichalcogenide Bis(Diphenylphosphino)Ferrocenenickel(II), Palladium(II), and Platinum(II), and Bis(Diisopropylphosphino)Ferrocenepalladium(II) Complexes

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The mass spectral behavior of a number of organometallic complexes containing the Group 10 metals Ni, Pd, and Pt, together with various thiolate ligands were studied. For Pd, two main types of complexes, differing by the substituents on the phosphorus atom were studied. Types I and II were substituted with bis(diphenylphosphino)ferrocene and bis(diisopropylphosphino)ferrocene ligands, respectively. The Ni complexes, except for one, and the Pd Type I complexes had no molecular radical cations ($M^{+\cdot}$) in their EI spectra. On the other hand, all the Pt complexes showed intense $M^{+\cdot}$ ions in their EI spectra indicating that these complexes were more stable as radical cations than those of Ni and Pd. The FAB and MALDI spectra of all the complexes displayed intense quasi-molecular ions (MH^+) and the fragmentations in both modes were similar. The MALDI spectra of several complexes displayed only $M^{+\cdot}$ ions while one gave evidence of both MH^+ and $M^{+\cdot}$ ions. Several Pd Type II complexes yielded intense $M^{+\cdot}$ in their EI spectra. (J Am Soc Mass Spectrom 2005, 16, 94–99) © 2004 American Society for Mass Spectrometry

Group 10 diphenylphosphinoferrocene (dppf) dichloro complexes, $M(dppf)Cl_2$, particularly the Pd analogs, are known to have been used in various catalytic reactions including the cross-coupling of primary and secondary alkyl Grignard and alkylzinc reagents with organic halides [1]. In studies of the synthesis, structural determination, and stabilities of a series of organochalcogens of similar Group 10 metal complexes [2, 3], mass spectrometry played a very important role. Henderson et al. [4] and Traeger [5] have used electrospray ionization (ESI) extensively as a mild technique to elucidate the structures of thiosalicylic metal complexes and to study other transition-metal coordination complexes. It has been known since the inception of fast atom

bombardment (FAB) as an ionization technique, that it can be used for the analysis of transition-metal coordination complexes [6, 7]. We also found that FAB ionization is equally capable of producing MH^+ ions of the Group 10 metal complexes [2, 3]. For example, arylchalcogenide ligand complexes like thiosalicylic acid and aryldichalcogenide ligands, such as 1,2-benzenedithiol and 3,4-toluenedithiol, readily show (MH^+) ions in their FAB spectra, hence FAB mass spectrometry provides a very facile structural characterization tool for metal complexes of these ligands.

In a report on diethyldithiocarbamatonicel(II) thiolato complexes [8], we observed that these complexes are thermally unstable and that electron impact (EI), as well as field ionization (FI), mass spectrometry yielded spectra that show no ions representing the molecular masses. But FAB ionization readily provided MH^+ ions. The diethyldithiocarbamatonicel complexes, $Ni(dtc)(PBU_3)(SR)$ ($dtc =$

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diethyldithiocarbamate, $R = C_6H_5, C_6H_4Cl-4$), in solution slowly form the dimeric compound $[Ni(dtc)]_2-(\mu-SR)_2$, a product that is similarly formed by the energetic EI conditions.

Mixed aryldichalcogenide bis(diphenylphosphino)ethanenickel(II) complexes are similarly found to have a gradation of stabilities in their mass spectra [3] depending on the nature of the aryldichalcogenide ligand. The stable complexes are the ones with homoleptic sulfur and as the ligands change to mixed chalcogenide ligands, so does the thermal stability of the complexes [3].

In the present study, we compare the behavior of the bis(diphenylphosphino)ferrocene (dppf) and bis(diisopropylphosphino)ferrocene (dippf) complexes mentioned above with those containing the bis(diphenylphosphino)ethane ligand, and observe what happens when the Ni is changed to other Group 10 metals.

Our aim was to compare the EI, FAB, and matrix-assisted laser desorption ionization (MALDI) mass spectral behavior as well as their behavior with respect to the central metal atom. We found that the ferrocene-anchored diphosphino ligands showed minor changes in the fragmentation profile of these complexes. Much of what we describe here is on the behavior of the complexes under EI and FAB ionization conditions. More elaborate studies have been carried out on their behavior under MALDI conditions. The results of these studies will be reported in a subsequent paper.

Experimental

Materials and Methods

All solvents were of analytical grade but were dried by procedures described previously [9]. 2-Mercaptophenol (Merck, Johannesburg, South Africa), and 3-nitrobenzyl alcohol (NBA, Aldrich, Dorset, England, UK), were used as received. Cesium iodide, α -cyano-4-hydroxycinnamic acid, sodium iodide, and polyethylene glycol (PEG) for mass spectrometry were obtained from Aldrich and were also used as received. The starting materials, $Ni(dppf)Cl_2$ and $Ni(dippf)Cl_2$, were prepared by published procedures [10, 11]. All the complexes that were used in this study were also synthesized by published procedures [12].

Mass Spectrometry

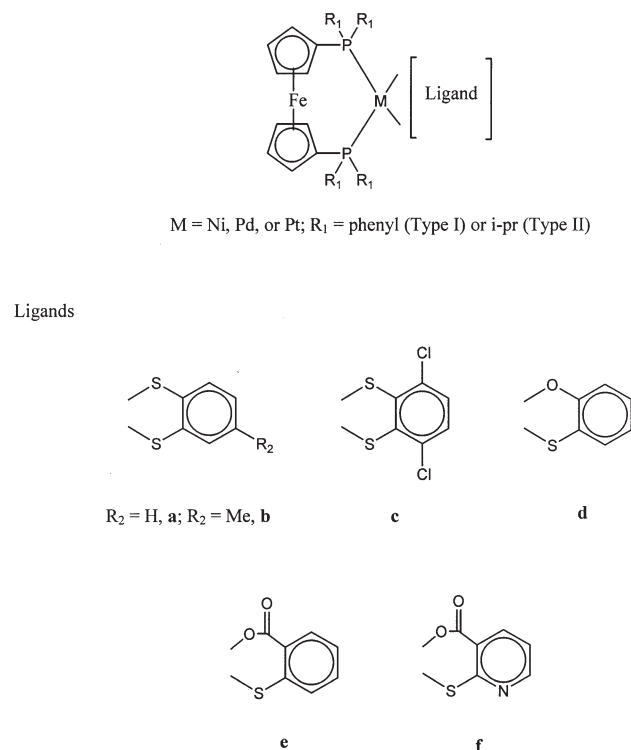
The EI and FAB mass spectrometry of all the compounds was performed on a JMS-HX100 EBE spectrometer (JEOL, Akishima, Japan). EI spectra were obtained at electron energy of 70 eV, an emission current of 100 μA and acceleration voltage of 5 kV. The ion source temperature was 250 °C and the temperature of the EI direct insertion probe (DIP) was programmed from 50 °C to 250 °C at 32 °C/min. FAB spectra of all the compounds were obtained with NBA as the matrix. Argon fast atoms were used to bombard the samples, dissolved in the matrix, on a stainless steel probe tip.

The ion source temperature was kept below 100 °C to prevent decomposition of the compounds. The mass spectrometer was calibrated using CsI.

MALDI mass spectrometry experiments were performed on a QTOF Ultima (Micromass Inc., Manchester, England). Nitrogen was introduced into the ion source to produce a pressure of 0.36 mbar. Desorption is by a nitrogen laser operating at 337 nm and 10 Hz. The MALDI plate has an 8×12 array of sample wells plus one lock mass well for each cluster of four sample wells. For high resolution mass accurate spectra, the TOF analyzer was operated in the W mode with a resolving power of at least 14,000. The matrix used was α -cyano-4-hydroxycinnamic acid as a 2 mg/ml solution in 50:50 acetonitrile:methanol. For calibration, a 2/1/1 mixture of PEG 200/600/1000 was used together with sodium iodide, and this solution was also used in the lock mass wells. A few sample crystals were added to 15 μl of the matrix solution, then 1 μl of the mixture was deposited and evaporated in a sample well. Spectra were accumulated until a satisfactory signal/noise ratio had been obtained or for a period up to 2 min.

Results and Discussions

Two main types of complexes, differing by the substituents on the phosphorus atoms, were studied. Type I had bis(diphenylphosphino)ferrocene (dppf) whilst Type II had bis(diisopropylphosphino) ferrocene (dippf) ligand. There were also variations of metals and thiolato ligands. For Type I, the metals were Ni (1), Pd (2), and



Scheme 1. Compounds studied.

Table 1. Nominal and exact masses of the most intense peaks in the M^{+} or MH^{+} clusters of aryldichalcogenide bis(diphenylphosphino)ferrocenenickel(II), **1**

Complex	EI	FAB	MALDI	
			Measured	Calculated
1a	N.O.	753	N.O.	753.0202 (MH^{+})
1b	766	767	766.0269 (M^{+})	766.0280
1c			819.9360 (M^{+})	819.9345
	N.O.	821 (^{58}Ni)	820.9418 (MH^{+})	820.9423

Pt (**3**); for Type II, the metal was Pd (**4**). The general formula for the complexes and a description of the thiolato ligands are given in Scheme 1. Thus, four series of complexes were studied in total, the results of which are described below.

Nickel Series

Three complexes (**1a–1c**) of Aryldichalcogenide bis(diphenylphosphino)ferrocenenickel(II), **1**, were studied. Using the three ionization techniques we found that only **1b** gave a molecular radical cation (M^{+}) in EI mode while **1a**, **1b**, and **1c** had ions in the molecular ion region of their FAB and MALDI spectra. Table 1 gives the masses of the most intense peaks in the molecular ion clusters of the complexes in the EI, FAB, and MALDI spectra. Unfortunately, the MALDI spectrum of Complex **1a** did not have M^{+} or MH^{+} ions at $m/z = 752$ or 753 , respectively, although a MH^{+} ion was observed in the FAB spectrum. Accurate masses were obtained with the MALDI-QTOF instrument which demonstrated that complex **1b** surprisingly produced an M^{+} instead of an MH^{+} , whereas complex **1c** was observed to yield a MH^{+} ion as well as a M^{+} ion (Figure 1).

The most prominent peak in the EI spectra of all the complexes was that at m/z 586. This fragment, $[\text{dppfS}]^{+}$, was found at m/z 587 in the FAB spectrum of **1a** and **1c** as the protonated species. We suggest that the positive charge on these complexes is centered on the dppf moiety which retains the charge on fragmentation. It is therefore apparent that both m/z 586 and 587 are the result of fragmentation of the M^{+} and MH^{+} ions followed by rearrangement to produce the $[\text{dppfS}]^{+}$ and its protonated species, respectively. It is clear why in the three complexes, only **1b** produced a M^{+} in the EI mode whereas in the case of the analogous dppe complexes, all of them gave M^{+} ions [1, 2] with a gradation of stabilities. The difference between the dppf and dppe Ni complex spectra could be explained in terms of the charge center. It seems that the chalcogen atoms stabilize the charge on Ni, thus strengthening the Ni chalcogen bonds with a concomitant increase in the stability of the M^{+} ions. In the dppf analogs, however, the charge center seems to shift to the Fe in the ferrocene moiety and away from the chalcogens. The Ni chalcogen bonds are thus weakened and fragmentation takes place at these points rather more easily to produce the $[\text{dppf}]^{+}$ ion at $m/z = 554$ which eliminates a phenyl and a diphenylphosphino (PPh_2) groups to give the ions $[\text{dppf-Ph}]^{+}$ at $m/z = 477$ and $[\text{dppf-Ph}_2\text{P}]^{+}$ at $m/z = 369$.

The FAB mass spectral fragmentations were similar for **1a**, **1b**, and **1c** and are typified by the proposed fragmentation pattern in Scheme 2. In the FAB spectra, there is a prominent peak at $m/z = 612$. This could be produced as a result of fragmentation of the MH^{+} ion to form $[\text{dppfNi}]^{+}$. The absence of this ion in the EI spectra is most likely due to a weak phosphorus-Ni bond which fragments after the formation of the $[\text{dppfNi}]^{+}$ ion. A

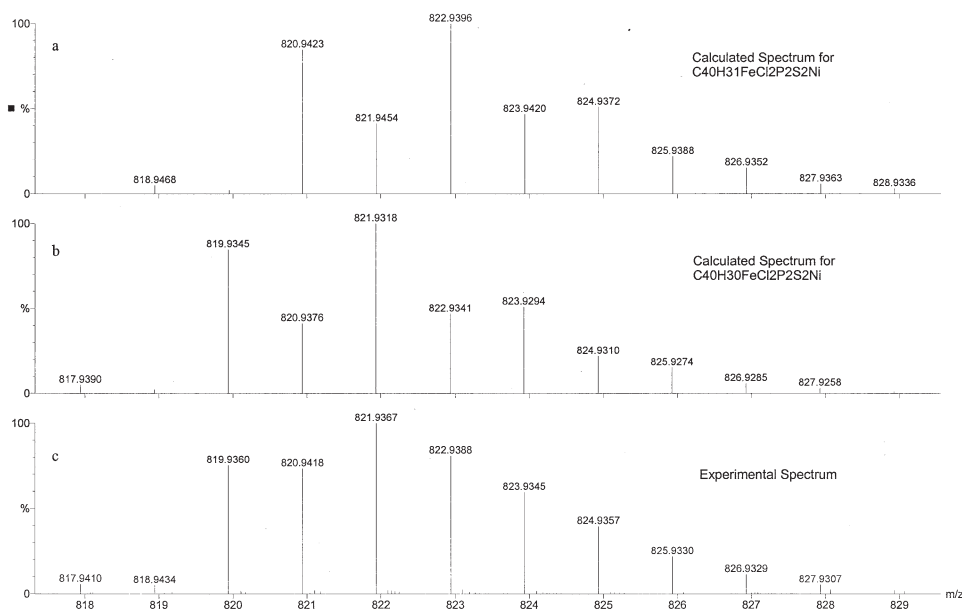
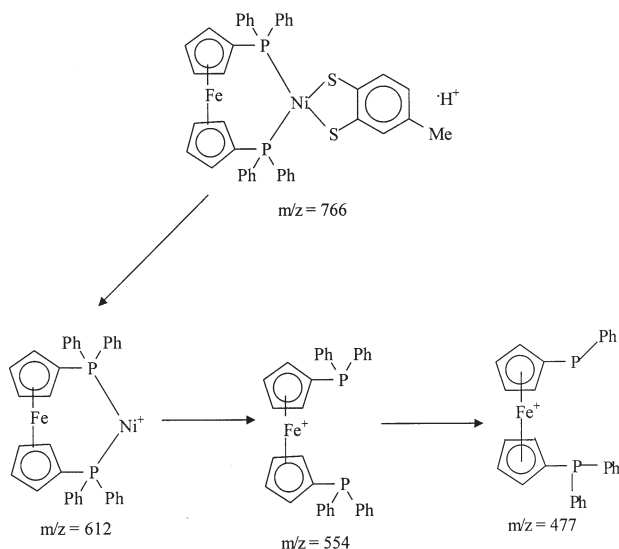


Figure 1. MALDI and simulated mass spectra of Compound **1c**.



Scheme 2. Proposed fragmentation for FAB-generated MH^+ ions of aryldichalcogenide bis(diphenylphosphino)ferrocene-nickel(II) complex, **1b**.

similar explanation is offered for the irreversibility of redox behavior of $Ni(dppf)Cl_2$ as oxidation leads to the decomposition of the oxidized species [13]. The fragment ions at $m/z = 554$ and $m/z = 477$ were also observed in the FAB spectra, though their intensities were low.

Palladium Series Type I

In the $dppf$ Pd complexes, the spectra and fragmentation patterns were similar to those of the Ni complexes. The EI mass spectra were devoid of M^+ ions. As in the case of series I complexes, Table 2 shows the nominal masses of the most intense ions in MH^+ clusters in the FAB spectra. The MALDI spectra of these complexes were not acquired. As was in the case of the Ni complexes, all the molecular ions eliminated the respective aryldichalcogenide ligands to produce $[dppfPd]^+$ ($m/z = 660$) and followed a fragmentation pattern similar to that in Scheme 2.

Platinum Series

For the $dppf$ Pt complexes, there were ions representing the intact complexes in the EI (Figure 2), the FAB

Table 2. Nominal masses of the most intense ion in the MH^+ clusters of the aryldichalcogenide bis(diphenylphosphino)ferrocene-palladium(II) complexes, **2**

Complex	FAB
2a	801
2b	815
2c	871
2d	785
2e	N.O.
2f	814

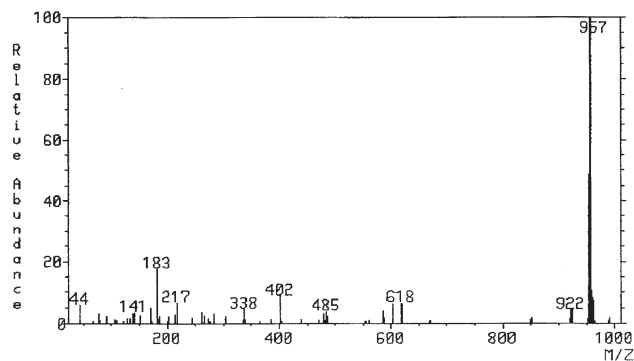


Figure 2. EI mass spectrum of **3c**.

(Figure 3) and MALDI spectra (not shown) of all complexes (Table 3). Ions that were similar to those found in the spectra for the Ni and Pd complexes were $[(dppf)Pt]^+$ ($m/z = 749$) and $[(dppf)PtS]^+$ ($m/z = 781$). There were, however, some observed differences between these Pt complexes and those of the first two. The first of these are formed by the loss of CO_2 from **3e** and **3f**. They were the only two compounds that did not undergo serial fragmentation to yield $[dppf]^+$. Most of the fragmentation pattern differences were found in the FAB spectra. For example, all the dithiolato ligand complexes **3a** ($m/z = 890$), **3b** ($m/z = 904$) and **3c** ($m/z = 958$) lost a phenyl group from the MH^+ ions.

Compared to the Ni and Pd complexes, the stability of the Pt complexes was generally higher. Removing an electron from any of these complexes, particularly if the positive charge resides on the Group 10 metal, results in the weakening of the metal-phosphorus bond. The extent of the metal-phosphorus bond weakening would thus determine the stability of the metal-containing fragment ion. From the reversible redox behavior observed for $Pt(dppf)Cl_2$ [11], it is evident that the loss of an electron to form a $[Pt(dppf)Cl_2]^+$ ion does not affect the stability of the Pt-P bond and hence the rational for stable fragments for the Pt compounds in this study.

Palladium Series Type II

When the substituent on the phosphorus atom in the phosphine ligand was changed from phenyl to isopro-

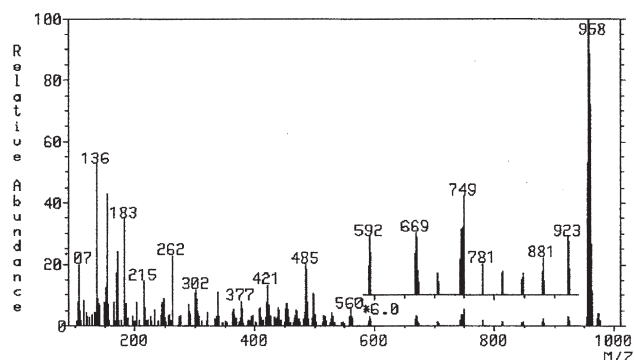


Figure 3. FAB mass spectrum of **3c**.

pyl, there was less fragmentation evident in the mass spectra. This was studied only for Pd, but the trend could be expected to be similar for Pt due to the better stability of dppf Pt complexes described above. All three dithiolato complexes (**4a**, **4b**, **4c**) and the oxothiolato complex (**4d**) gave $M^{+\cdot}$ ions in the EI mode. Complexes **4e** and **4f** that contain CO_2 as part of the thiolato ligands readily eliminated CO_2 to give low intensity ions at $m/z = 632$ and 633 , respectively. In contrast to the EI spectra, all six complexes had either $M^{+\cdot}$ or MH^+ ions in their FAB and MALDI spectra (Table 3), (Table 4). There is evidence from the FAB spectrum of **4b** to suggest that there are two fragmentation pathways for these compounds (Scheme 3). The first is the loss of the thiolato ligand to produce $[dippfPd]^+$ ($m/z = 524$), which is the pathway of all the dppf complexes. This is followed by the loss of an isopropyl group to give the ion at $m/z = 481$. The second pathway is unique to **4b** and starts with a loss of an isopropyl group from the MH^+ ion ($m/z = 679$) to produce a much weaker ion at $m/z = 635$; this is followed by the loss of the dithiolato ligand to form the $[dippfPd]^+$ fragment. It is observed in the spectra of many of the compounds that the $[dippfPd]^+$ goes on to eliminate neutral propene to give an ion at $m/z = 439$. In comparison to the dppf complexes, the dippf analog showed no tendency to lose the Group 10 metal. This is a sign that the more basic phosphine (dippf) stabilizes the interaction between the metal and the phosphine ligand in the Pd complexes. The ability of **4b** to form a stable MH^+ ion at $m/z = 679$ seems to be aided by the electron releasing methyl substituent on the dithiolato ligand in strengthening the Pd-S.

Conclusions

For Type I complexes, the Pt analogs were found to be the most stable of the three metals. Their EI spectra showed molecular ion clusters. Those containing the carboxyl group did not have any molecular ions because of the ease of CO_2 elimination. The FAB and MALDI spectra were very similar. However, several of the compounds exhibited either $M^{+\cdot}$ or MH^+ clusters,

Table 3. Nominal and exact masses of the most intense ion of $M^{+\cdot}$ and MH^+ clusters of the aryldichalcogenide bis(diphenylphosphino)ferroceneplatinum(II) complexes, **3**

Complex	EI	FAB	MALDI	
			Measured	Calculated
3a	889	890	889.0469 ($M^{+\cdot}$)	889.0418
3b	903	904	903.0640 ($M^{+\cdot}$)	903.0574
3c	957	958	957.9609 (MH^+)	957.9717
3d	873	874	873.0643 ($M^{+\cdot}$)	873.0646
3e	N.O.*	902	902.0748 (MH^+)	902.0674
3f	N.O.*	903	903.0635 (MH^+)	903.0626

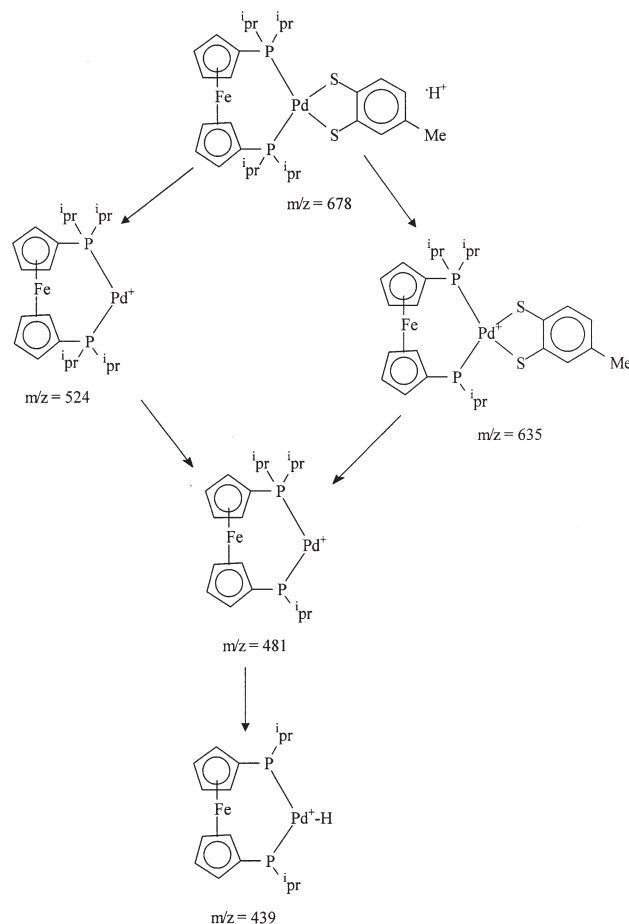
*The molecular ion is not observed as it readily fragments to give the $[M - CO_2]^{+\cdot}$ radical cation.

Table 4. Nominal and exact masses of the most intense peak of $M^{+\cdot}$ and MH^+ clusters of the aryldichalcogenide bis(diisopropylphosphino)ferrocene-palladium(II) complexes, **4**

Complex	EI	FAB	MALDI	
			Measured	Calculated
4a	664	665	664.0508 ($M^{+\cdot}$)	664.0438
4b	678	679	678.0621 ($M^{+\cdot}$)	678.0587
4c	734	735	733.9697 ($M^{+\cdot}$)	733.9641
4d	648	648	648.0746 ($M^{+\cdot}$)	648.0667
4e	N.O.*	677	677.0691 (MH^+)	677.0695
4f	N.O.*	678	678.0667 (MH^+)	678.0646

*The molecular ion is not observed as it readily fragments to give the $[M - CO_2]^{+\cdot}$ radical cation.

or both, in their MALDI spectra. Apart from **4e** and **4f**, Pd Type II complexes gave $M^{+\cdot}$ ions in EI indicating that these are more stable than the Type I analogs, and in FAB and MALDI all showed either $M^{+\cdot}$ or MH^+ ion clusters. The MALDI spectrum of Compound **1c** indicated the presence of both the $M^{+\cdot}$ and the MH^+ ion clusters.



Scheme 3. Proposed fragmentation for FAB-generated MH^+ ions of aryldichalcogenide bis(diphenylphosphino)ferrocene-palladium(II) complex, **4b**.

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