

Fast-atom Bombardment (FAB) Mass Spectra of Nitrile or Cyanamide Complexes with the $\{M(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\}^{n+}$ (M=Fe or Re) Metal Sites. Application to Reactions Induced under FAB Conditions[†]

Luísa M. D. R. S. Martins, M. Fátima C. Guedes da Silva, Indalécio Marques, João J. R. Fraústo da Silva, M. Cândida N. Vaz and Armando J. L. Pombeiro*

Centro de Química Estrutural, Complexo I, IST, Av. Rovisco Pais, 1096 Lisboa codex, Portugal

The fast-atom bombardment (FAB) mass spectra, in 3-nitrobenzyl alcohol (NOBA) matrices, of the cyanamide or organonitrile complexes *trans*-[FeH(NCR)(dppe)₂][BF₄] (1; R=NH₂, NMe₂, NEt₂ or NC(NH₂)₂; dppe=Ph₂PCH₂CH₂PPh₂) and *cis*- or *trans*-[ReCl(NCR)(dppe)₂] (2; R=aryl), which have a diphosphinic {M(dppe)₂}ⁿ⁺ metal centre, are presented and discussed. Molecular ions have been detected for 1, [R=NH₂ or NC(NH₂)₂], and only for the *trans* isomers of 2 in agreement with the higher stability of their oxidized forms in comparison with those of the *cis* compounds. Possible fragmentation patterns are proposed, involving the stepwise elimination of ligands from the metal (NCR, H and dppe for 1; Cl, NCR and dppe for 2), preceding (for 1) the fragmentation of the diphosphine ligand which, nevertheless, for complexes 2, can also occur in the presence of the chloride ligand. This is interpreted on the basis of the relative electron donor ability of the ligands. Different fragmentation modes are observed for the dppe ligand, involving, e.g., dehydrogenation and loss of C₂H₄, Ph, PPh or P', in processes involving reductive or oxidative elimination steps. Rhenium fragment ions are more susceptible to oxygenation than the iron ones, in accord with the greater tendency of the former metal to reach higher oxidation states. The identification of reactions induced and monitored by FAB-MS was also essayed and although *trans*-[FeHCl(dppe)₂] (3) [the starting material for the synthesis of complexes (1) and NCNMe₂ do not react *per se* in solution, we have detected their reaction under FAB conditions, the spectra being interpreted by considering the addition of the substrate to fragment ions generated *in situ* from 3; a comparison with the solution chemistry is discussed and suggestions for its further development, towards lower metal oxidation state complexes, are presented on the basis of the FAB-MS reactions detected.

The application of mass spectrometric techniques to the investigation of structural properties of transition metal complexes is not yet a common practice, in spite of the rich information which, in principle, could be obtained. Various difficulties, such as their usually poor volatility and low thermal stability, as well as the low stability of their molecular ions and of the derived fragment ions, have often hampered the successful application of such techniques to those complexes. Even the use of FAB as a soft ionization technique (which, moreover, is readily accessible with existing mass spectrometers) has not yet become a standard procedure for the analysis of such a type of compound, in spite of the recognition⁵ of the convenience of such a technique in the field of coordination chemistry, allowing a considerable expansion of the range of compounds which can be examined. Examples are known⁶ of organometallic complexes for which FAB mass spectrometry constitutes the most convenient method for their structural characterization (apart from analysis by X-ray diffraction).

Moreover, the recent and quite promising investigation^{7,8} of ion/molecule reactions by FAB-MS coupled with mass-analysed ion kinetic energy (MIKE) spectrometry has allowed the detection and structural characterization of ionic organometallic species—e.g., highly reactive platinum(0) carbene intermediates in the reaction of a Pt(0)

complex with a diazo compound⁷—having short lifetimes (even below 10⁻⁵ s) and formed, in low concentration, as intermediates in reactions occurring under FAB conditions. A comparison with the same reaction in solution chemistry can then be attempted.

Hence, in view of the expected general relevance of FAB mass spectrometric studies to the investigation of transition metal complexes (which, nevertheless, has been demonstrated so far only in a rather limited number of cases) and following our interest on the synthesis, structural characterization and reactivity of coordination compounds with unsaturated small molecules, we have initiated a systematic investigation of such a type of compound by FAB. We now report the results obtained with some cyanamide and nitrile complexes of iron(II) or rhenium(I) having a diphosphine metal centre of the type {M(dppe)₂}ⁿ⁺ (M=Fe or Re, dppe=Ph₂PCH₂CH₂PPh₂) i.e. *trans*-[FeH(NCR)(dppe)₂][BF₄], 1, (R=NH₂, NMe₂, NEt₂ or NC(NH₂)₂) and *cis*- or *trans*-[ReCl(NCR)(dppe)₂], 2, (R=aryl). In addition, the reaction of NCNMe₂ with *trans*-[FeHCl(dppe)₂] (the starting material for the synthesis of complexes 1) under FAB conditions has also been investigated and compared with that occurring in solution chemistry.

EXPERIMENTAL

The fast-atom bombardment (FAB) mass spectrometric measurements were performed on a Trio 2000 spectrometer (Complexo I, I.S.T.). Positive-ion FAB mass spectra were

[†] Presented at the 2nd Meeting on Mass Spectrometry, organized by the Portuguese Society of Chemistry, Lisbon, 5–7 December 1995.

* Author for correspondence.

obtained by bombarding 3-nitrobenzyl alcohol (NOBA) matrices of the samples with 8 keV xenon atoms. Nominal molecular masses were calculated using the most abundant isotopes, i.e., ^{56}Fe (92%), ^{187}Re (63%) and ^{35}Cl (76%), and the expected natural abundance isotope cluster patterns were observed for the various ion clusters. However, further complexity due to addition (from the matrix) or loss of hydrogen was usually not taken into account. Mass calibration for data system acquisition was achieved using CsI.

For the study of the reaction of *trans*-[FeHCl(dppe)₂] with NCNMe₂, under FAB-MS conditions, a mixture of these two compounds [33 mg (0.037 mmol) and 3 μL (0.037 mmol) respectively] with the NOBA matrix (*ca.* 1 mL) was prepared, placed on the probe tip and then introduced immediately into the source.

The parent complexes *trans*-[FeHCl(dppe)₂]¹ and *trans*-[ReCl(N₂)(dppe)₂]² were prepared by published methods, whereas *trans*-[FeH(NCR)(dppe)₂][BF₄], **1**, (R = NH₂, NMe₂, NEt₂ or NC(NH₂)₂) were obtained by reacting *trans*-[FeHCl(dppe)₂] with the appropriate cyanamide, in tetrahydrofuran (THF) and in the presence of Ti[BF₄] as the chloride abstractor,³ and *cis*- or *trans*-[ReCl(NCR)(dppe)₂], **2**, (R = aryl) were formed by treatment of a toluene solution of *trans*-[ReCl(N₂)(dppe)₂] with the appropriate organonitrile⁴ (the experimental details of these preparations will be reported separately).

RESULTS AND DISCUSSION

FAB mass spectra of the complexes

Iron complexes. In the FAB mass spectra of the compounds *trans*-[FeH(NCR)(dppe)₂][BF₄], **1**, [R = NH₂, NMe₂, NEt₂ or NC(NH₂)₂] run in NOBA matrices, the corresponding molecular ions [FeH(NCR)(dppe)₂]⁺ are detected only for the cyanamide (NCR = NCNH₂) and the cyanoguanidine [NCR = NCNC(NH₂)₂] members at *m/z* 896 and 938, respectively. In the other cases, only derived fragment ions are observed, but similar fragmentation patterns are followed by all the complexes as indicated by the analogy of their spectra for *m/z* \leq 854, i.e., corresponding to the ion [FeH(dppe)₂]⁺, detected at *m/z* 854, and derived ionic fragments. This ion is detected in all cases and is formed upon loss of the appropriate cyanamide (NCR) group from the starting complex, **1**—see the proposed fragmentation pattern depicted in Scheme 1 for the dimethylcyanamide complex [FeH(NCNMe₂)(dppe)₂]⁺ as a typical example.

The elimination of the cyanamide ligand is followed by loss (as hydrogen) of the hydride ligand at [FeH(dppe)₂]⁺ to give the reduced iron (I) species [Fe(dppe)₂]⁺ (*m/z* 853) (reductive elimination of the latter ligand). This indicates the possible generation of a low oxidation state iron–diphosphine centre by reduction of a parent hydride complex, a process which may be of relevance in the understanding, for example, of biological nitrogen fixation by iron-nitrogenase. Although such a type of approach to the synthesis of electron-rich iron–diphosphine complexes has not yet been significantly explored, it has already been demonstrated electrochemically and in solution chemistry. In fact, upon cathodic-controlled-potential electrolysis of *trans*-[FeH(CNMe)(dppe)₂]⁺ in the presence of phenol (as a proton source), the isocyanide is reduced to dimethylamine,⁹ and the process is believed to occur through the intermediate formation of an iron(0) species of the type [Fe(CNMe)(dppe)₂]. Moreover, the related low oxidation

state iron–dinitrogen complex [Fe(N₂)(dmpe)₂] (dmpe = Me₂PCH₂CH₂PMe₂), in which N₂ can be protonated to ammonia, has been obtained by deprotonation of the iron(II)-hydride compound [FeH(N₂)(dmpe)₂]⁺ upon reaction with KOBu^t (Bu^t = C(CH₃)₃);¹⁰ however, in this case, the hydride ligand is removed as a proton rather than as hydrogen.

Elimination of the diphosphine ligand can occur at [Fe(dppe)₂]⁺ (*m/z* 853) to give [Fe(dppe)]⁺ (*m/z* 454). Hence, loss of the chelating diphosphine occurs only after the removal of the monodentate ligands, as is known¹¹ to occur in other cases, suggesting a greater coordination lability of the latter relative to the former ligands.

The molecular ion of the liberated diphosphine, dppe⁺, follows a fragmentation pathway analogous to that exhibited by a genuine sample of dppe, giving, upon Ph⁺ elimination, a fragment ion at *m/z* 321, assigned as [Ph₂PC₂H₄PPh]⁺, which, by PPh loss, generates [Ph₂PC₂H₄]⁺ (*m/z* 213) from which PPh₂⁺ (*m/z* 185) is formed upon ethylene elimination. Cyclization of PPh₂⁺ (with H₂ elimination) generates the 2,2'-biphenylphosphonium ion (*m/z* 183) which, by loss of phosphorus, forms the cyclic fragment ion at *m/z* 152; loss of Ph⁺ from PPh₂⁺ leads to PPh⁺ (*m/z* 108) which, on dehydrogenation, gives PC₆H₄⁺ (*m/z* 107) and PC₆H₃⁺ (*m/z* 106).

The diphosphine ligand itself can undergo partial fragmentation which is distinct from that observed when uncoordinated, and involving (i) dehydrogenation, e.g., at [Fe(dppe)₂]⁺ (*m/z* 853) to give a fragment ion at *m/z* 852 assigned to [Fe(dppe){Ph₂PC₂H₄PPh(C₆H₄)}]⁺ which can then again undergo hydrogen loss (*m/z* 851), (ii) ethylene elimination, e.g., at [Fe(dppe)]⁺ (*m/z* 454) to form a fragment ion at *m/z* 426 which conceivably is due to [Fe(PPh₂)₂]⁺, [FePh(PPh)(PPh₂)]⁺ or [Fe(PPh)(PPh₃)]⁺, (iii) phenyl (Ph⁺), PPh, PPh₂⁺ or P⁺ elimination from ligands derived from fragmentation of ligating dppe, (iv) rearrangements of (v) coupling processes within these ligands. Hence, phenyl elimination (type iii reaction) from the ion(s) at *m/z* 426 (see above) forms a fragment ion at *m/z* 349 assigned as [Fe(PPh)(PPh₂)]⁺ or [FeP(PPh₃)]⁺, which by removal of another phenyl group generates a fragment ion at *m/z* 272 possibly due to [Fe(PPh₂)]⁺ or [FeP(PPh₂)]⁺, whereas upon phosphorus loss it forms a fragment ion at *m/z* 318 assigned as [FePh(PPh₂)]⁺ or [Fe(PPh₃)]⁺. [Fe(PPh₂)]⁺ (*m/z* 241) can then be obtained, either by phosphorus loss from the ions at *m/z* 272, by phenyl elimination from those at *m/z* 318, or even upon PPh removal from those at *m/z* 349. Coupling (type iv reaction) of the two phenyl rings upon dehydrogenation (type i reaction), at [Fe(PPh₂)]⁺, forms the fragment ion at *m/z* 239 (see Scheme 1) from which the 2,2'-biphenylphosphonium cation (*m/z* 183) can be obtained upon decoordination from the iron metal. Moreover, phenyl elimination from [Fe(PPh₂)]⁺ forms [FePPh]⁺ (*m/z* 164) which, upon loss of phosphorus, gives [FePh]⁺ (*m/z* 133).

In addition, dppe loss from the abovementioned species at *m/z* 851 generates a fragment ion at *m/z* 453 assigned as [Fe{Ph(C₆H₄)PC₂H₄PPh(C₆H₄)}]⁺ or [Fe{Ph₂PC₂H₄P(C₆H₄)₂}]⁺, which, upon ethylene elimination (type ii reaction) followed by phenyl removal (type iii process), forms possibly [Fe(PPhC₆H₄)₂]⁺ (*m/z* 425) and [Fe(PC₆H₄)(PPhC₆H₄)]⁺ (*m/z* 348).

Rearrangement processes (type iv reactions) are possibly also involved in some of those pathways, such as those accounting for the formation of some of the abovementioned species at *m/z* 426, tentatively formulated as

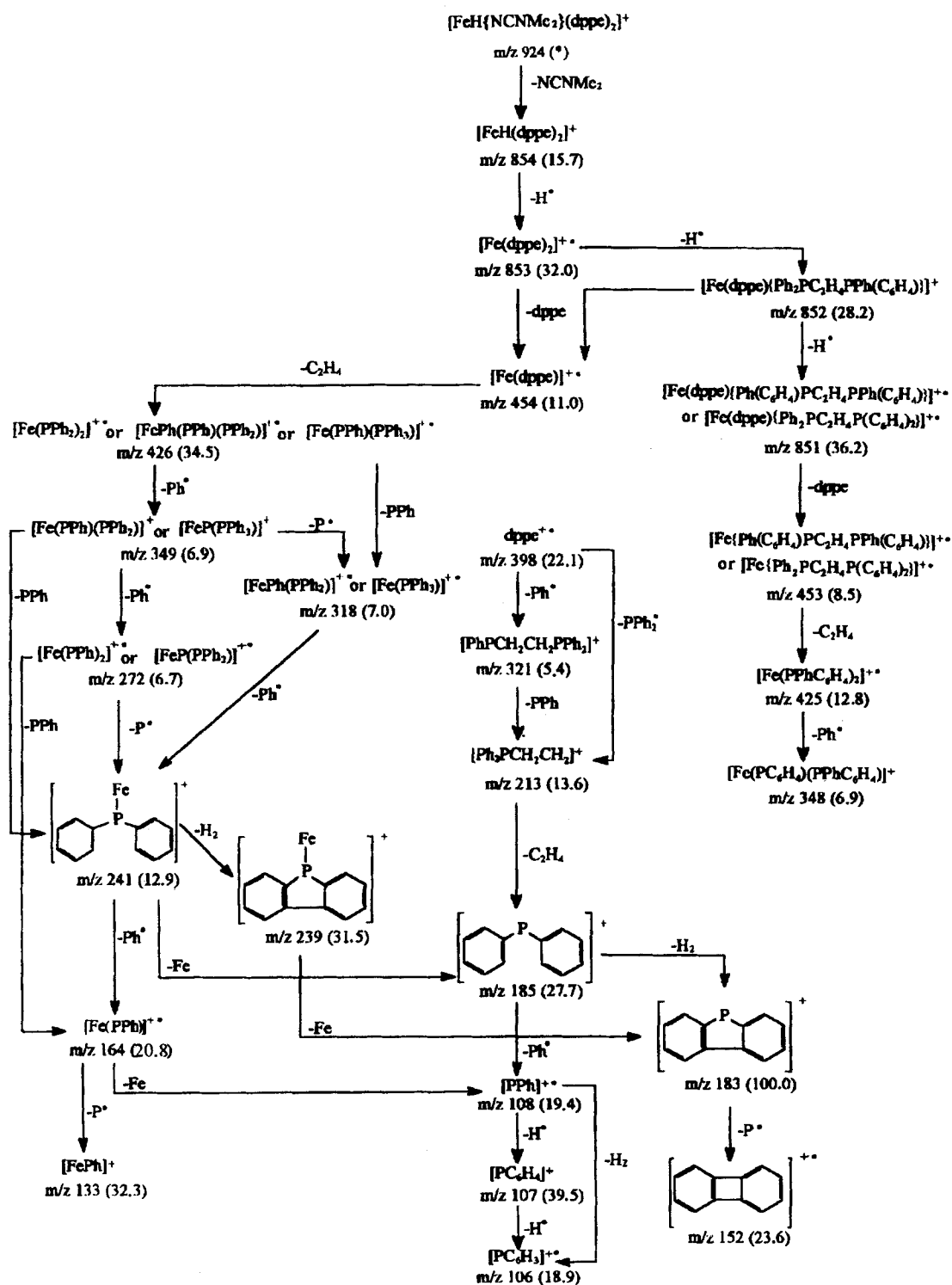
$[\text{Fe}(\text{PPh}_2)_2]^{2+}$, $[\text{FePh}(\text{PPh})(\text{PPh}_2)]^{2+}$ or $[\text{Fe}(\text{PPh})(\text{PPh}_3)]^{2+}$. In fact, the formation of these last two ions can be postulated as involving the transfer of a phenyl group from one of the PPh_2 ligands to the other one, in $[\text{Fe}(\text{PPh}_2)_2]^{2+}$, a process which can occur via the metal, as reported¹¹ for the complexes $[\text{PtL}_2(\text{dppe})_2]$ ($\text{L} = \text{Me}, \text{Et}$ or Ph), according to the following sequence:



Another point which deserves further consideration, in view of its significance in coordination chemistry, is the

variation of the metal formal oxidation state along the fragmentation pathways.

Although it is retained upon loss of a neutral ligand which donates an even number of electrons (such as a cyanamide or the diphosphine—see the corresponding steps in Scheme 1), a change can occur in other cases. In fact, the metal is reduced upon loss of a single-electron donor ligand as discussed above for the elimination, as hydrogen, of the hydride ligand in the iron(II) cation $[\text{FeH}(\text{dppe})_2]^+$ to form the iron(I) species $[\text{Fe}(\text{dppe})_2]^+$. Moreover, a change in the metal oxidation state can also result from the fragmentation



Scheme 1. Proposed FAB-MS fragmentation pattern for *trans*- $[\text{FeH}(\text{NCNMe}_2)(\text{dppe})_2][\text{BF}_4]$ in NOBA matrix. The relative intensities (% in relation to the m/z 183 peak) are indicated in parentheses. (*) Not observed.

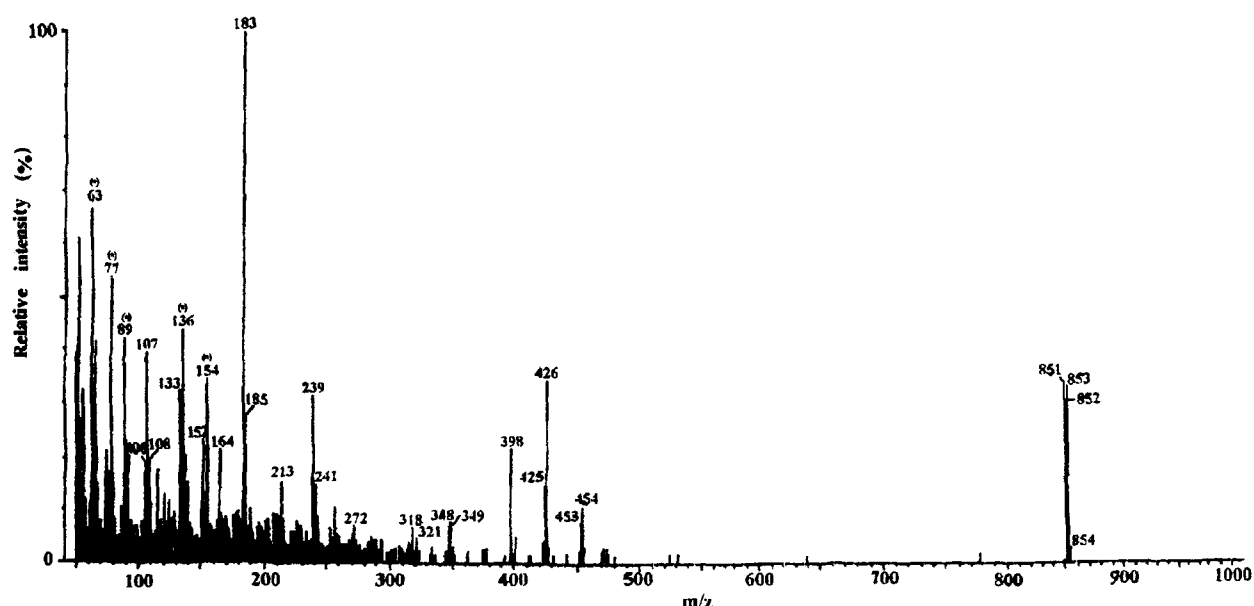
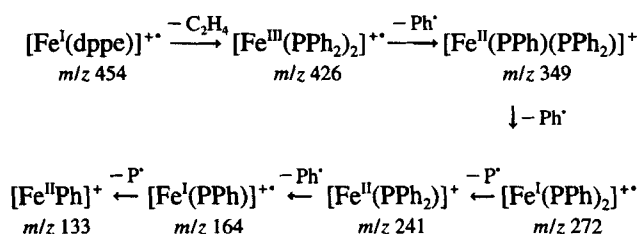


Figure 1. FAB mass spectrum of *trans*-[FeH(NCNMe₂)(dppe)₂][BF₄], in NOBA matrix. (*) Matrix peaks.

of the metal-ligating diphosphine, namely upon loss of a fragment (e.g., C₂H₄, Ph[•], PPh₂[•] or P[•]) from this or a derived ligand, in a formal redox elimination process. Examples are provided by the proposed following steps (taken from Scheme 1) in which the iron metal undergoes a sequence of oxidation and reduction processes:



Rhenium complexes. The rhenium complexes *cis*- and *trans*-[ReCl(NCR)(dppe)₂] (2, R=aryl), in NOBA matrices, exhibit similar FAB mass spectra, but with some significant differences from those described above for the iron compounds.

The molecular ions [ReCl(NCR)(dppe)₂]⁺⁺ are observed

only for the *trans* isomers, and interestingly this behaviour agrees with the slightly higher stability of these isomers relatively to the *cis* ones, as established¹² by electrochemical studies. They appear with the expected natural abundance isotope clusters due to the natural metal [¹⁸⁷Re (63%), ¹⁸⁵Re (37%)] and chloro [³⁵Cl (76%), ³⁷Cl (24%)] isotopes.

A typical FAB mass spectrum is depicted in Fig. 2 for *cis*-[ReCl(NCC₆H₄Cl-4)(dppe)₂], and the proposed general fragmentation pattern for the *cis* isomers is indicated in Scheme 2.

Similarly to the behaviour of the iron compounds, the fragmentation pathways of the rhenium complexes can be initiated by loss of the nitrile ligand to form [ReCl(dppe)₂]⁺⁺ (*m/z* 1018), followed by reductive elimination of the chloro-ligand (instead of the hydride in the case of the iron species) to give the reduced rhenium(I) ion [Re(dppe)₂]⁺ (*m/z* 983).

However, pathways different from those detected for the iron system also appear to occur for the rhenium complexes. Hence, the bidentate diphosphine can be lost even before the liberation of the monodentate chloro-ligand at [ReCl(dppe)₂]⁺⁺ (*m/z* 1018) to give [ReCl(dppe)]⁺⁺ (*m/z*

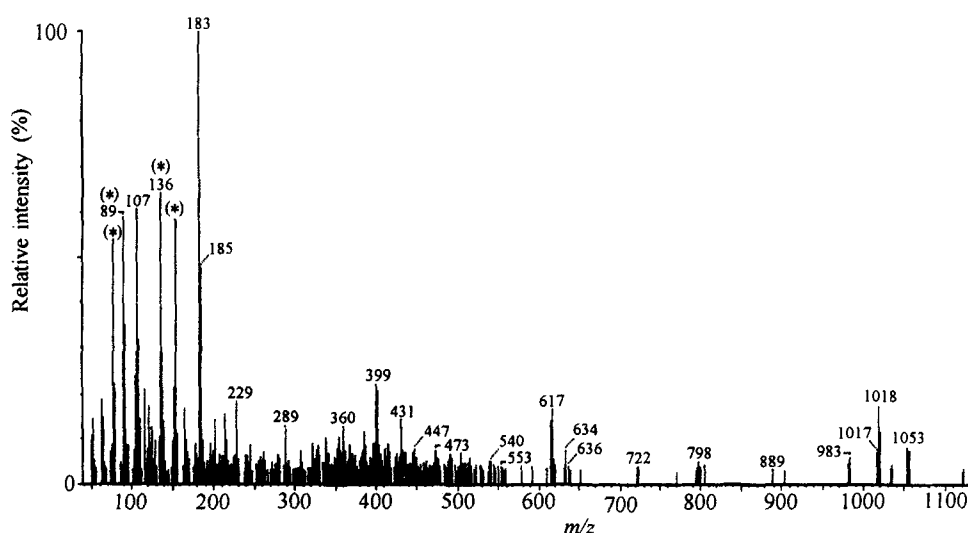
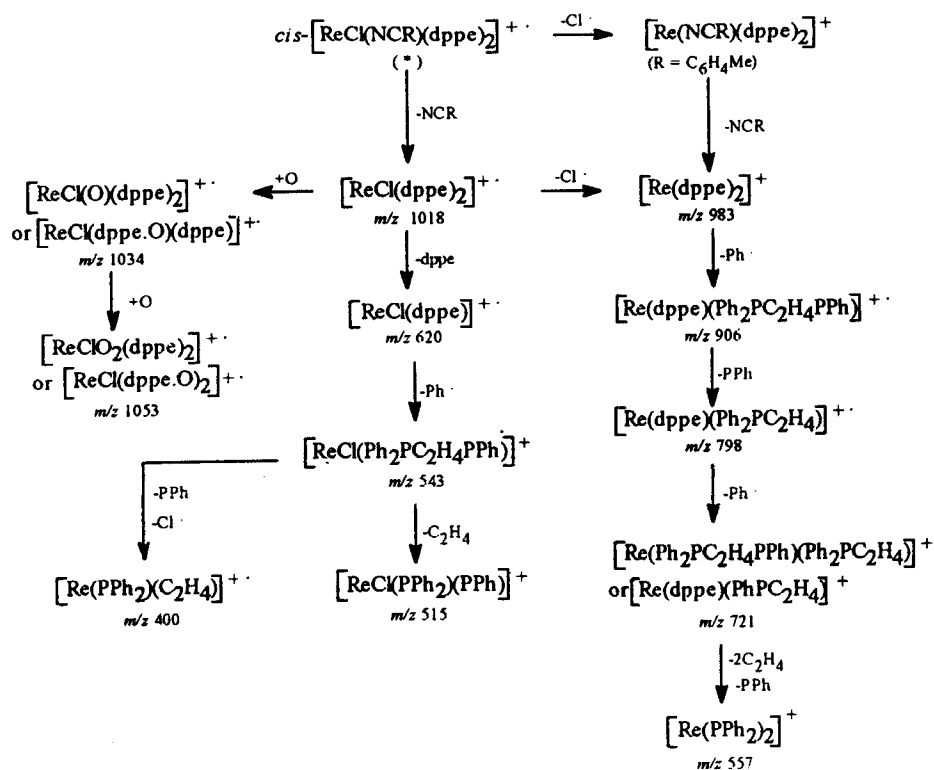


Figure 2. FAB mass spectrum of *cis*-[ReCl(NCC₆H₄Cl-4)(dppe)₂], in NOBA matrix. (*) Matrix peaks.



Scheme 2. Proposed FAB-MS fragmentation pattern for *cis*-[ReCl(NCR)(dppe)₂] (R=aryl) complexes, in NOBA matrix. (*) Not observed.

620). This behaviour would not be expected for the neutral rhenium(I) starting complex [ReCl(NCR)(dppe)₂]. However, its occurrence at the detectable cationic derived species [ReCl(dppe)₂]⁺ can be rationalised by the stronger net electron donor ability of the chloride relative to the diphosphine ligand, which thus stabilizes more effectively the oxidized rhenium(II) species. Such an oxidation effect does not occur with the iron complexes since they are already cationic, the detectable ions not being formed by oxidation. Nevertheless, the chloro-ligand can also be evolved, before the nitrile or the dppe, from the molecular ion to form [Re(NCR)(dppe)₂]⁺ although it is detected only in one case (R=C₆H₄Me-4).

Also in contrast with the common behaviour of the iron complexes, oxygenated rhenium ions, possibly [ReCl(O)(dppe)₂]⁺ and [ReClO₂(dppe)₂]⁺, are readily detectable at *m/z* 1034 and 1053 respectively. Although corresponding species with oxygenated dppe (instead of oxygenated metal), e.g. [ReCl(dppe·O)(dppe)]⁺ and [ReCl(dppe·O)₂]⁺, could also be postulated, the formation of the former oxo-rhenium(IV or VI) complexes is well accounted by the capacity of this metal to easily increase its oxidation state, a feature not exhibited by iron.

The molecular ion of the liberated diphosphine, dppe⁺, presents a fragmentation pattern similar to that of a genuine sample of the phosphine (see above), but the coordinated one appears to follow a fragmentation pathways distinct from those of the iron complexes.

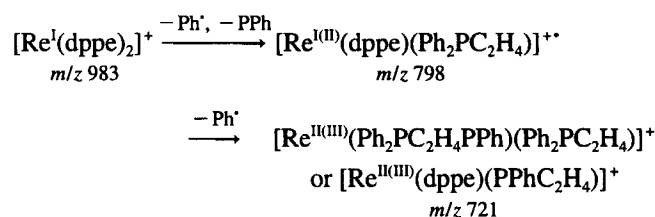
Hence, the fragmentation of the dppe ligand in the rhenium cations, in contrast to the iron ones, can be initiated even when the chloro-ligand has not yet been eliminated (see the above explanation for the enhanced stability of the Re–Cl bond). It can proceed via phenyl elimination from [ReCl(dppe)]⁺ (*m/z* 620) to give [ReCl(Ph₂PC₂H₄PPh)]⁺ (*m/z* 543) which possibly can follow two pathways: one involving the loss of PPh and Cl[•] to afford

[Re(PPh₂)(C₂H₄)]⁺ (*m/z* 400), and the other one occurring by ethylene elimination to form [ReCl(PPh₂)(PPh)]⁺ (*m/z* 515).

The diphosphines at [Re(dppe)₂]⁺ (*m/z* 983) also appear to be susceptible to fragmentation, possibly giving, through elimination of Ph[•], PPh and C₂H₄ groups, the fragment ion [Re(PPh₂)₂]⁺ (*m/z* 557).

Further fragmentation of the metal cations could not be unambiguously attributed due to the compact distribution of low intensity lines and complexity of the spectrum at *m/z* below *ca.* 550.

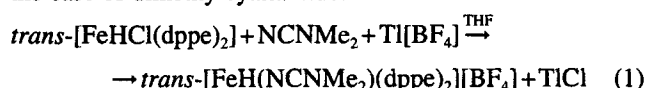
As mentioned for the iron complexes, the rhenium formal oxidation state can also vary along the dppe fragmentation, as suggested, e.g., by the following postulated sequence (see Scheme 2) although the metal oxidation state may not be assigned without ambiguity:



Reaction of *trans*-[FeHCl(dppe)₂] with NCNMe₂ under FAB-MS conditions

The chloro-complex *trans*-[FeHCl(dppe)₂], **3**, is the common starting material for the chemical synthesis, in tetrahydrofuran (THF) solution, of complexes **1** upon reaction with the appropriate cyanamide, in the presence of Ti[BF₄] as a chloride abstractor (in fact, without this salt the reaction does not occur in solution) —see Reaction (1), for

the case of dimethylcyanamide.

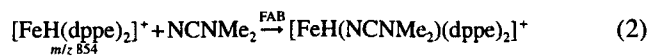


We have now attempted to carry out and monitor under FAB-MS conditions the reaction of **3** with NCNMe_2 , and compare it with that occurring in solution.

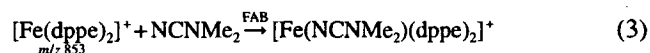
For this purpose, a mixture of these two species, in stoichiometric amounts, with the NOBA matrix was prepared, placed on the probe tip and then introduced immediately into the spectrometer source. The FAB mass spectrum obtained is shown in Fig. 3, and the proposed fragmentation pattern is depicted in Scheme 3.

Interestingly, the molecular ion (M^+) of the dimethylcyanamide complex $[\text{FeH(NCNMe}_2\text{)(dppe)}_2]^+$ and the ion derived by hydrogen loss, possibly $[\text{Fe(NCNMe}_2\text{)(dppe)}_2]^{2+}$, are detected at m/z 924 and 923, respectively (the extra peak at m/z 925 is due to the hydrogenated species $[M+H]^+$), in contrast with the FAB mass spectrum of a genuine sample of that complex (see Fig. 1) in which such ions are not observed.

Since the reaction, in solution, between $\text{trans-[FeHCl(dppe)}_2\text{)]}$ and NCNMe_2 requires the presence of a chloride abstractor (the TI^+ salt) which is absent in the FAB-MS experiment, the formation of the dimethylcyanamide complex in FAB conditions conceivably occurs only after the FAB activation of the starting material. However, the molecular ion $[\text{FeHCl(dppe)}_2]^{2+}$ is not expected to be more reactive than the parent neutral complex towards replacement of the chloride ligand by the cyanamide because the Fe-Cl bond should be strengthened as a result of the oxidation of the metal. Moreover, the derived and detected fragment ions $[\text{FeH(dppe)}_2]^+$ (m/z 854) and $[\text{Fe(dppe)}_2]^{2+}$ (m/z 853) would be prone to undergo ready addition of NCNMe_2 , in view of their coordinative and electronic unsaturation. In fact, these ions would account well for the formation of the abovementioned detected products, $[\text{FeH(NCNMe}_2\text{)(dppe)}_2]^+$ and $[\text{Fe(NCNMe}_2\text{)(dppe)}_2]^{2+}$ (Reactions (2) and (3), respectively).



FAB ↓ -H⁺



An overall comparison between the generation, in solution and under FAB-MS conditions, of the cyanamide complexes from $[\text{FeHCl(dppe)}_2]$ can then be attempted (see Scheme 4).

In solution chemistry, the unsaturated $[\text{FeH(dppe)}_2]^+$ complex is formed upon chloride abstraction (by TI^+), whereas under FAB conditions the TI^+ ion is not required, since the chloro-ligand is then eliminated from the molecular ion of the starting complex. In addition, hydrogen elimination from $[\text{FeH(dppe)}_2]^+$ occurs under FAB conditions, to give $[\text{Fe(dppe)}_2]^{2+}$, a species of iron(I) not obtained in solution chemistry and which allows the formation of $[\text{Fe(NCNMe}_2\text{)(dppe)}_2]^{2+}$, also not detected in solution. However, this last ion can be considered as the molecular ion of the 18-electron iron(0) complex $[\text{Fe(NCNMe}_2\text{)(dppe)}_2]$, thus suggesting its possible formation in solution chemistry, a point which deserves to be explored, by attempting the deprotonation of $[\text{FeH(NCNMe}_2\text{)(dppe)}_2]^+$ or its reductive dehydrogenation.

Moreover, cyanamide complexes with a single dppe ligand are possibly also obtained under FAB conditions, as indicated by the fragment ions at m/z 526 and 525, assigned to $[\text{FeH(NCNMe}_2\text{)(dppe)}]^+$ and $[\text{Fe(NCNMe}_2\text{)(dppe)}]^{2+}$, respectively. In principle, they can be formed either from elimination reactions (of dppe and, if necessary, of H) in related bis(diphosphine) complexes or from addition reactions (of NCNMe_2 and, if necessary, of H) to $[\text{Fe(dppe)}]^{2+}$ (m/z 454).

Fragmentation of the dppe ligand is also observed, according to pathways which relate to those discussed above for $[\text{FeH(NCNMe}_2\text{)(dppe)}_2]^+$. In addition, species derived from oxygenation (by the matrix) of the dppe, as ligand or uncoordinated, have also been detected, e.g., at m/z 868, assigned as $[\text{Fe(dppe)}\{\text{Ph}_2\text{PC}_2\text{H}_4\text{P(O)Ph}_2\}]^{2+}$, and at m/z 414 and 430, due to the mono- and the di-

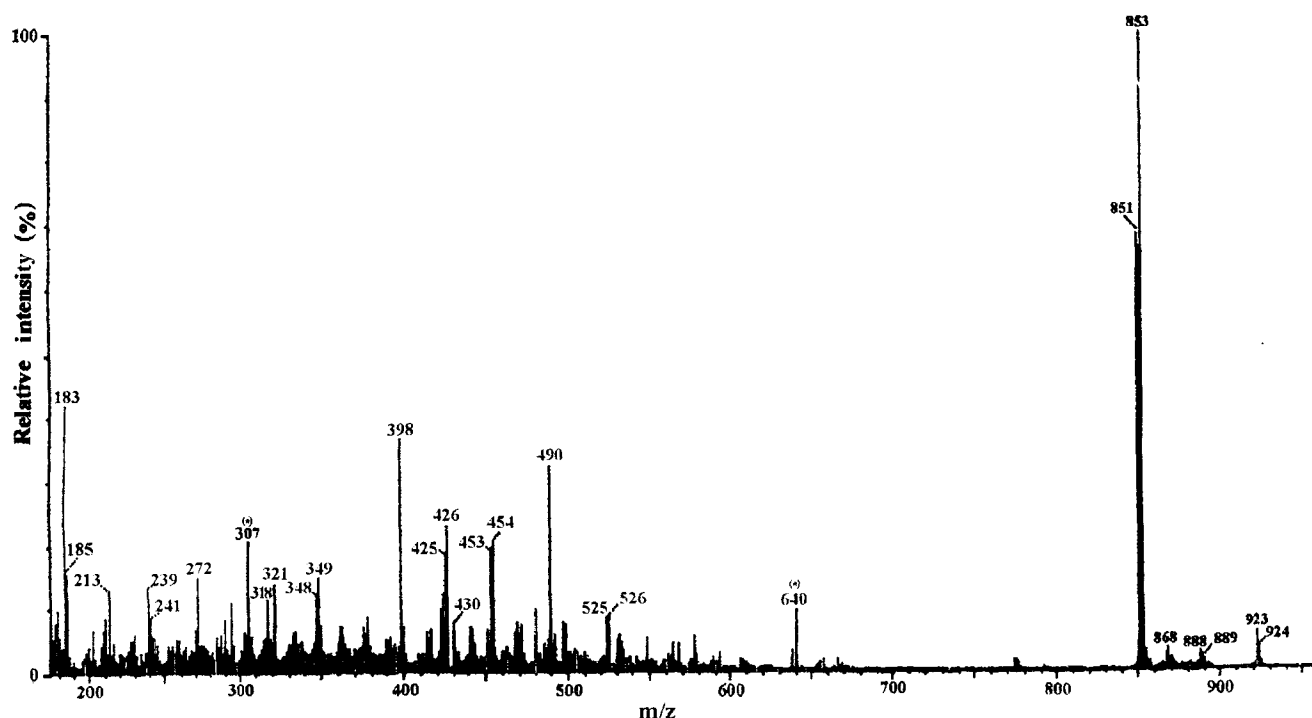
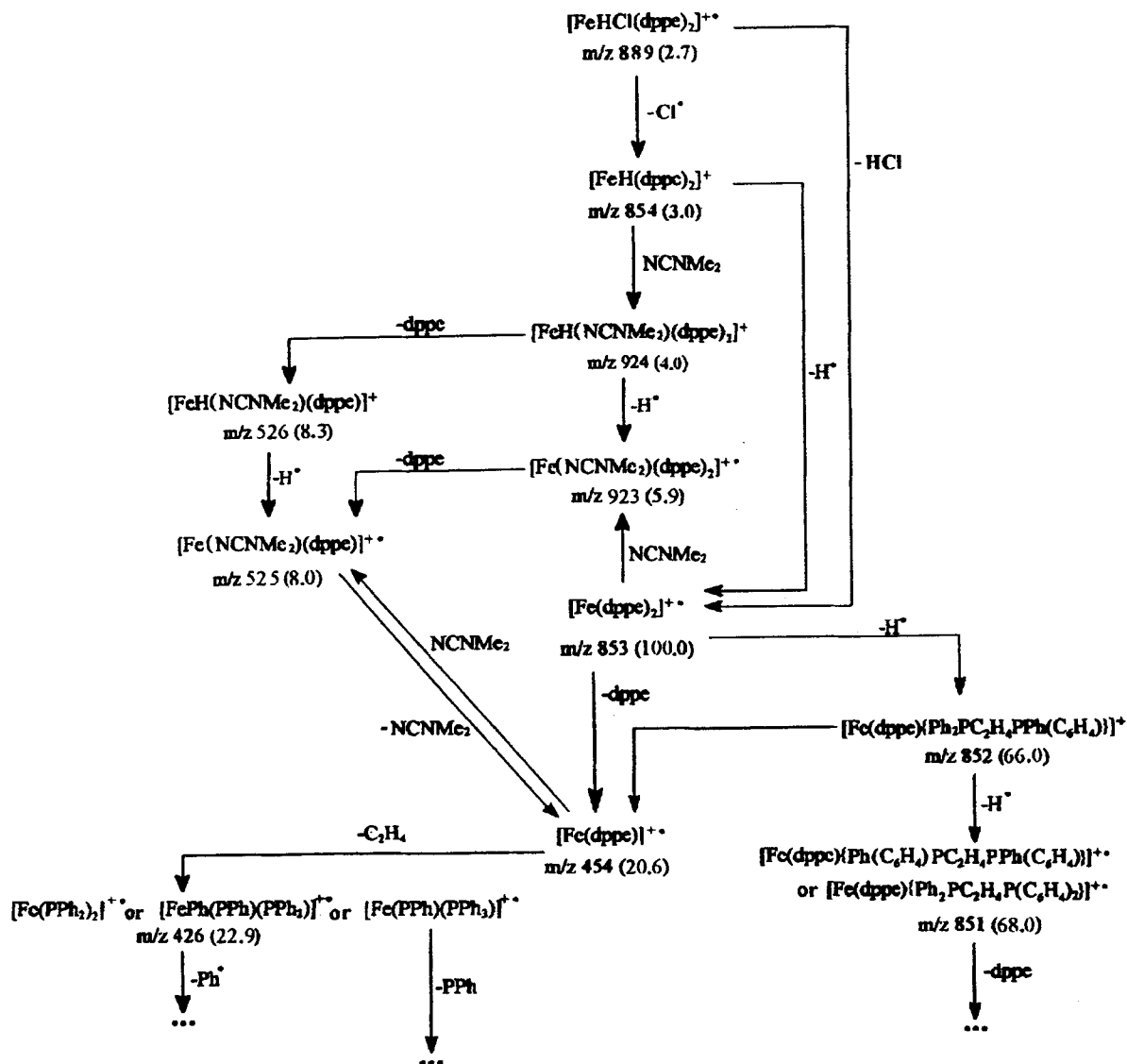


Figure 3. FAB mass spectrum of the system $\text{trans-[FeHCl(dppe)}_2\text{)]} + \text{NCNMe}_2$, in NOBA matrix.



Scheme 3. Proposed FAB-MS fragmentation pattern for the system *trans*- $[\text{FeHCl}(\text{dppe})_2] + \text{NCNMe}_2$ in NOBA matrix.

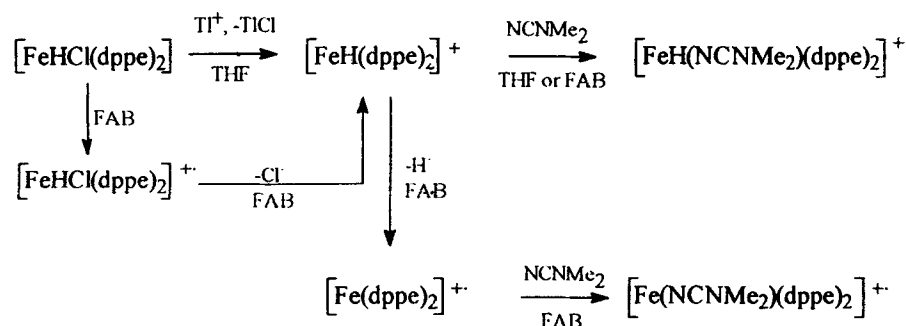
oxygenated diphosphine, i.e., $\text{Ph}_2\text{P}(\text{O})\text{C}_2\text{H}_4\text{PPh}_2^+$ and $\text{Ph}_2\text{P}(\text{O})\text{C}_2\text{H}_4\text{P}(\text{O})\text{Ph}_2^+$, respectively.

FINAL COMMENTS

The FAB mass spectrometric behaviour of some iron- and rhenium-phosphine complexes has been reported and some relevant features discussed in terms of the relative coordination lability and/or electron-donor capacity of their ligands (see, e.g., the order of the elimination of the ligands and/or

of their fragmentation), as well as of the ability of the metal to undergo a change in its oxidation state (see, for example, the formation of fragment ions involving a formal oxidation or reduction of the metal). Moreover, the relative stability of some isomeric molecular ions under FAB-MS conditions followed their relative stability in solution (*trans* vs. *cis* isomers of the rhenium complexes).

In the FAB-induced redox processes upon ligand elimination or fragmentation, the metal (either Fe or Re) has its formal oxidation state varying within the limits $+2 \pm 1$, thus



Scheme 4. Formation of dimethylcyanamide complexes of iron from the system $[\text{FeHCl}(\text{dppe})_2] + \text{NCNMe}_2$, in solution (THF) chemistry and in FAB-MS conditions.

presenting, in some cases, unusual values. Metal oxidation to higher levels, when it can encompass such a change (rhenium preferably to iron), can result from oxygenation.

The FAB-induced reactivity could also be compared with that exhibited by the complexes in solution, and the former can proceed without the use of auxiliary reagents indispensable in solution chemistry (see the formation of the cyanamide complexes of iron from the hydrido-chloride complex precursor). Moreover, a wider variety of possible reaction pathways can be detected by FAB-MS, leading to products not observed in solution chemistry but with potential significance for its development, in particular towards attempting the syntheses, in solution, of novel complexes with unusually low metal oxidation states whose existence has been demonstrated by the FAB technique.

Acknowledgements

The work has been partially supported by JNICT (National Board for Scientific and Technical Research) and the PRAXIS XXI programme.

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