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ESI/MS^n in the structural characterisation of some nitrido-Re heterocomplexes

Michela Tubaro[a,*], Ester Marotta[a], Pietro Traldi[a], Cristina Bolzati[b], Marina Porchia[b], Fiorenzo Refosco[b], Francesco Tisato[b]

[a] *ISTM—C.N.R., Via Marzolo, 1, Padua 35131, Italy*
[b] *ICIS—C.N.R., Corso Stati Uniti, 4, Padua 35127, Italy*

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Abstract

Six different nitride-containing rhenium heterocomplexes with a mixed coordination sphere comprising heterodiphosphines (PNP) and dithiocarbamates (DTC) or halides (X) have been studied by means of electrospray mass spectrometry and collisional experiments. Two compounds are neutral intermediates of the type [Re(N)Cl_2(PNP)], and four are cationic species of general formula [Re(N)(DTC)(PNP)]$^+$, obtained after treatment of the intermediate species with dithiocarbamate. Both Cl-containing intermediates do not show the formation of molecular ions, being the $[M - Cl]^+$ and $[M - 2Cl]^+$ ions the only species detected in the ESI spectra. This behaviour, already observed for some Cl-containing Pt complexes, has been explained by Re–Cl bond cleavage activated by the high positive charge density present on the ESI droplet surface. However, the four mixed heterocomplexes display only the molecular cation with no detectable fragmentation. Further MS^n spectra of all compounds show instead specific fragmentation processes, mainly related to the different outer sphere substituents. Comparison with the fragmentation profiles of isostructural technetium complexes evidence similar primary cleavage followed by quite different decomposition pathways.

Keywords: ESI/MS^n spectra; Structural characterisation; Nitrido-Re heterocomplexes

1. Introduction

The metastable isotope ^{99m}Tc is the radiodiagnostic of election in Nuclear Medicine because of its almost ideal physical properties for nuclear imaging ($t_{1/2} = 6.06$ h, pure γ-emission of $E_\gamma = 140$ keV) and easy availability at relatively low cost through the commercial ^{99}Mo/^{99m}Tc generator [1,2].

Nuclear Medicine stays among the diagnostic modalities the clinicians can adopt to visualise organs and tissues and related abnormalities. More commonly identified techniques such as X-ray and Computed Tomography cover more than 50% of total imaging investigations followed by echography, which makes use of ultrasounds and covers ca. 25%. Nuclear Medicine and Magnetic Resonance Imaging (MRI), which utilise nuclear radioactivity and nuclear spin relaxation property, respectively, share the residual market [3].

The recent advent of the β-emitting radionuclides ^{186}Re ($t_{1/2} = 3.8$ days, $E_{\beta max} = 1.07$ MeV) and ^{188}Re ($t_{1/2} = 0.7$ days, $E_{\beta max} = 2.11$ MeV) as candidates for the application of injectable radiopharmaceuticals to the therapy of malignant and degenerative diseases [4], has made coordination chemistry with group 7 elements technetium and rhenium very attractive.

These investigations aim primarily at the knowledge of the molecular structure of ^{99m}Tc- and $^{188/186}$Re-based agents produced at very low concentrations (micromolar scale or 'non-carrier added' level, *nca*). This can be conveniently achieved through the comparison of their chemical properties with those of the corresponding compounds prepared at the millimolar level ('carrier added', *ca*) with the long-lived β-emitting isotope ^{99}Tc and with the naturally occurring mixture of non-radioactive Re isotopes. ^{99}Tc and Re complexes can be fully characterised by standard analytical and spectroscopic methods. It is straightforward that the possibility to establish without uncertainty the chemical identity of a specific tracer is of vital importance for the elucidation of its biological behaviour.

* Corresponding author. Tel.: +39-049-8295691; fax: +39-049-8295621.
E-mail address: mslab@adr.pd.cnr.it (M. Tubaro).

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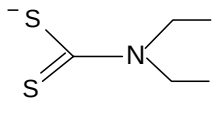
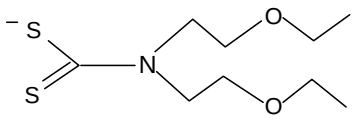
(a)



dedc



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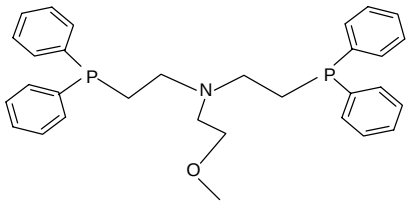
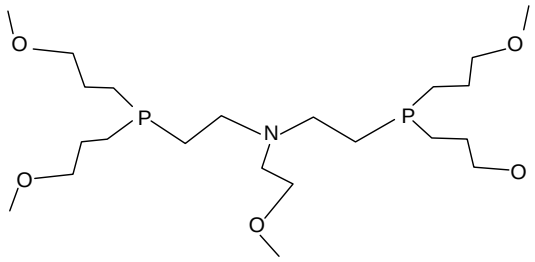
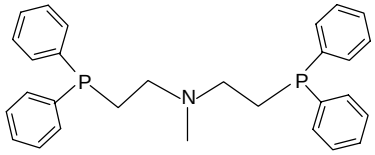


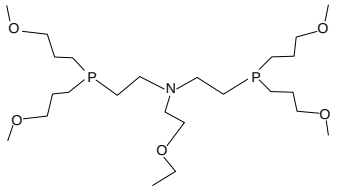
pnp2



pnp3



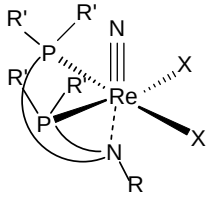
pnp24

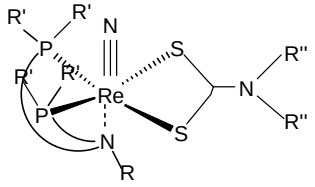


pnp5

(b)

[Re(N)Cl$_2$(PNP)] and [Re(N)(DTC)(PNP)]$^+$ complexes





PNP	X	Re complex
pnp24	Cl	[Re(N)Cl$_2$(pnp24) **(1)**
pnp2	Cl	[Re(N)Cl$_2$(pnp2)] **(2)**

PNP	DTC	Re complex
pnp24	dedc	[Re(N)(dedc) (pnp24)]$^+$ **(3)**
pnp2	dedc	[Re(N)(dedc) (pnp2)]$^+$ **(4)**
pnp3	dedc	[Re(N)(dedc) (pnp3)]$^+$ **(5)**
pnp5	dbodc	[Re(N)(dbodc)(pnp5)]$^+$ **(6)**

Fig. 1. (a) DTC and PNP ligands utilised in the present study. (b) Nitrido rhenium heterocomplexes characterised by ESI/MS and collisional experiments.

In the last decade, chemistry of ^{99m}Tc-radiopharmaceuticals [1,2] has been expanded through the introduction of an efficient method for the production of ^{99m}Tc-species containing a terminal $[^{99m}Tc(N)]^{2+}$ group at *nca* level [5]. However, studies focused on the inorganic chemistry of nitrido-Tc species are still rare compared, for example, to the plethora of investigation devoted to oxo-Tc compounds [6]. Recently, a systematic investigation on the coordination properties of the nitrido metal fragment $[Tc(N)(PXP)]^{2+}$, composed by a diphosphine ligand (PXP) coordinated to a $[Tc^{V}(N)]^{2+}$ core, has been undertaken by our group. This fragment constitutes a robust moiety showing a selective reactivity toward bidentate chelating ligands (BID) having π-donor atoms as coordinating sites to form heterocomplexes of the type $[Tc(N)(BID)(PXP)]^{0/+}$ [7].

Within this class of heterocomplexes, it has been reported by Boschi et al. that the compounds $[^{99m}Tc(N)(DTC)(PNP)]^{+}$ (where DTC is the monoanionic form of a dithiocarbamate ligand and PNP is a diphosphine incorporating a tertiary amine group) accumulate extensively in the myocardium of the rat [8]. In particular, one of these agents, $[^{99m}Tc(N)(pnp5)(dbodc)]^{+}$ (dbodc: diethoxyethyl-dithiocarbamate; pnp5: bis[(dimethoxypropylphosphino)ethyl]-ethoxyethylamine), has been selected for further biological studies because of its superior imaging properties exhibited in rats compared to commercial cardiac agents ^{99m}Tc-Sestamibi (Cardiolite®) and ^{99m}Tc-Tetrofosmin (Myoview®).

Taking advantage of the non-radioactive character of the natural occurring mixture of ^{185}Re/^{187}Re and of the lanthanide contraction, which ensures similar synthetic and structural chemistry between the second-row Tc and the third-row Re congeners, we have studied in detail the chemistry underlying the synthesis and characterisation of $[Re(N)(DTC)(PNP)]^{+}$-type compounds. We have established that the molecular structure of the prototype complex $[Re(N)(pnp2)(dedc)]^{+}$ **4** (pnp2: bis[(2-diphenylphosphino) ethyl]methoxy-ethylamine; dedc: diethyldithiocarbamate), determined by X-ray diffraction analysis [9], is best described as pseudo-octahedral, PNP diphosphine being facially coordinated with the tertiary-amine nitrogen weakly bound *trans* to the Re≡N group on the octahedron axis. The dithiocarbamate sulphurs face two *cis*-positioned phosphorus on the equatorial plane to complete the coordination sphere.

By replacement of rigid phenyl groups at the diphosphine phosphorus with dangling methoxypropyl fragments to mimic the agent exhibiting the best biological properties, it became impossible to grow crystals suitable for X-ray diffraction studies. Thus, we were forced to characterise alkyldiphosphine-containing compounds in the solution state by means of a combined mass spectrometry and multinuclear NMR investigation. These data confirmed the molecular structure of these complexes to be monomeric and, more important, to be identical to that shown by aryldiphosphine-containing complex **4**.

In this study, we report on ESI/MS characterisation of some nitrido rhenium heterocomplexes **1**–**6** containing a combination of heterodiphosphines (PNP) and dithiocarbamates (DTC): diethyldithiocarbamate (dedc) and diethoxyethyldithiocarbamate (dbodc) as DTC representatives, and bis[(diphenylphosphino)ethyl]methoxyethylamine (pnp2), bis[(diphenylphosphino)ethyl] methyl-amine (pnp24), bis[(dimethoxypropylphosphino)ethyl]methoxyethylamine (pnp3) and bis[(dimethoxypropylphosphino)ethyl]ethoxyethylamine (pnp5) as PNP representatives (see Fig. 1a). Neutral compounds **1** and **2** of general formula $[Re(N)Cl_2(PNP)]$ are intermediate species re-covered after treatment of the labile $[Re(N)Cl_2(PPh_3)_2]$ precursor with the relevant diphosphine (pnp2 or pnp24), whereas cationic complexes **3**–**6** are the resulting mixed heterocomplexes obtained after treatment of intermediate species with dithiocarbamate (see Fig. 1b).

2. Experiment

Pure neutral intermediate $[Re(N)Cl_2(PNP)]$ species and cationic $[Re(N)(DTC)(PNP)]^{+}$ complexes were prepared according to the procedure described previously [9].

ESI experiments were performed on an LCQ (ThermoFinnigan, San Jose, CA, USA) ion trap instrument. The 5×10^{-6} M solutions of the different compounds dissolved in dichloromethane (compounds **1**–**2**) or methanol (compounds **3**–**6**) were directly infused into the ion source pump at a flow rate of 8 μl/min by a syringe pump. The spray capillary voltage was set at 4 kV and the entrance capillary temperature was set at 270 °C. The nebulising gas was N_2. MS^n experiments were obtained by resonance activation of preselected species, and by varying the resonant excitation voltage in the range 0–2 V.

3. Results and discussion

Compounds **1** and **2** were prepared by ligand-exchange reactions from labile $[Re(N)Cl_2(PPh_3)_2]$ precursors in the presence of the relevant diphosphine in refluxing dichloromethane solutions [9]. They were intermediate complexes on the way to mixed nitrido heterocomplexes **3**–**6**.

The ESI mass spectrum of compound **1** is reported in Fig. 2. Worth noting is the absence of any molecular ion and practically the only ion present in the spectrum, at *m*/*z* 654, corresponds to the $[M-2Cl]^{\bullet+}$ radical cation. This behaviour parallels that already described in the case of ESI of some Pt complexes where, analogously, the molecular ion was not detected and the $[M-Cl]^{+}$ species was predominant [10]. It is to emphasise that those Pt complexes, under ionisation conditions either implying high internal energy deposition (e.g., electron ionisation) or privileging the formation of protonated species from sample solution (e.g., fast atom bombardment), did show the production of abundant $[M]^{\bullet+}$

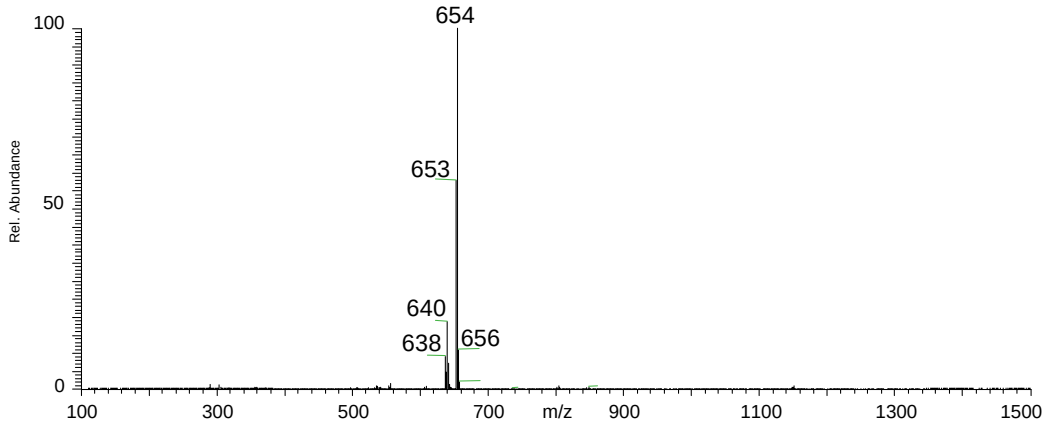


Fig. 2. ESI/MS spectrum of compound **1**.

and $[MH]^+$ ions, respectively [10]. This was considered an excellent proof that the $[M - Cl]^+$ formation is a process activated by ESI and it was rationalised by considering the fate of complexes like **1** inside the nebulised droplet. In the first stage, just after the droplet formation, due to the positive charge distribution on the droplet surface, it is reasonable to assume that the partial negative charge located on chlorine atoms promotes a radial orientation of the molecules. Once the dimension of the droplet decreases, either by thermally induced or reduced pressure solvent evaporation, an increasing charge density becomes present on the surface, leading to the cleavage of Re–Cl bonds, thus promoting the formation of the ion at *m*/*z* 654. In the present case, this process likely implies the losses of Cl^- and $Cl^\bullet$, the ion so formed bearing a single positive charge which could be reasonably justified by a change of the oxidation state of Re from 5+ to 4+.

The ion at *m*/*z* 654 exhibits the collisionally induced loss of a methyl radical and, consequently, a coordinative bond

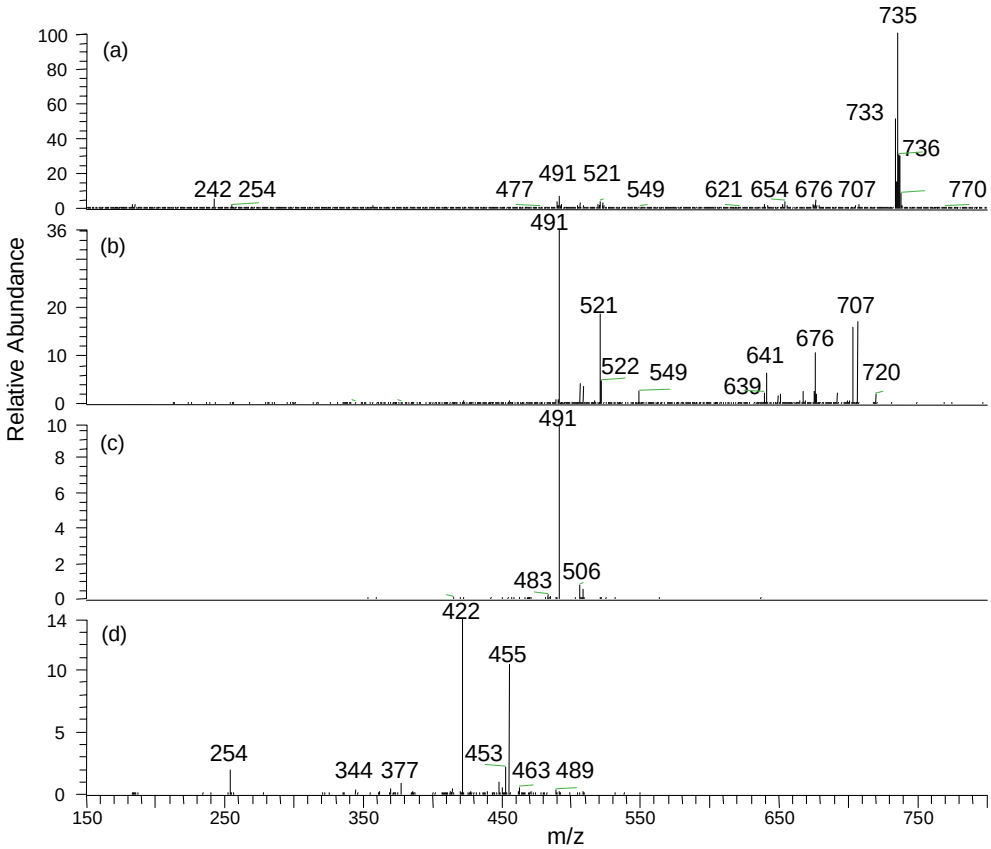
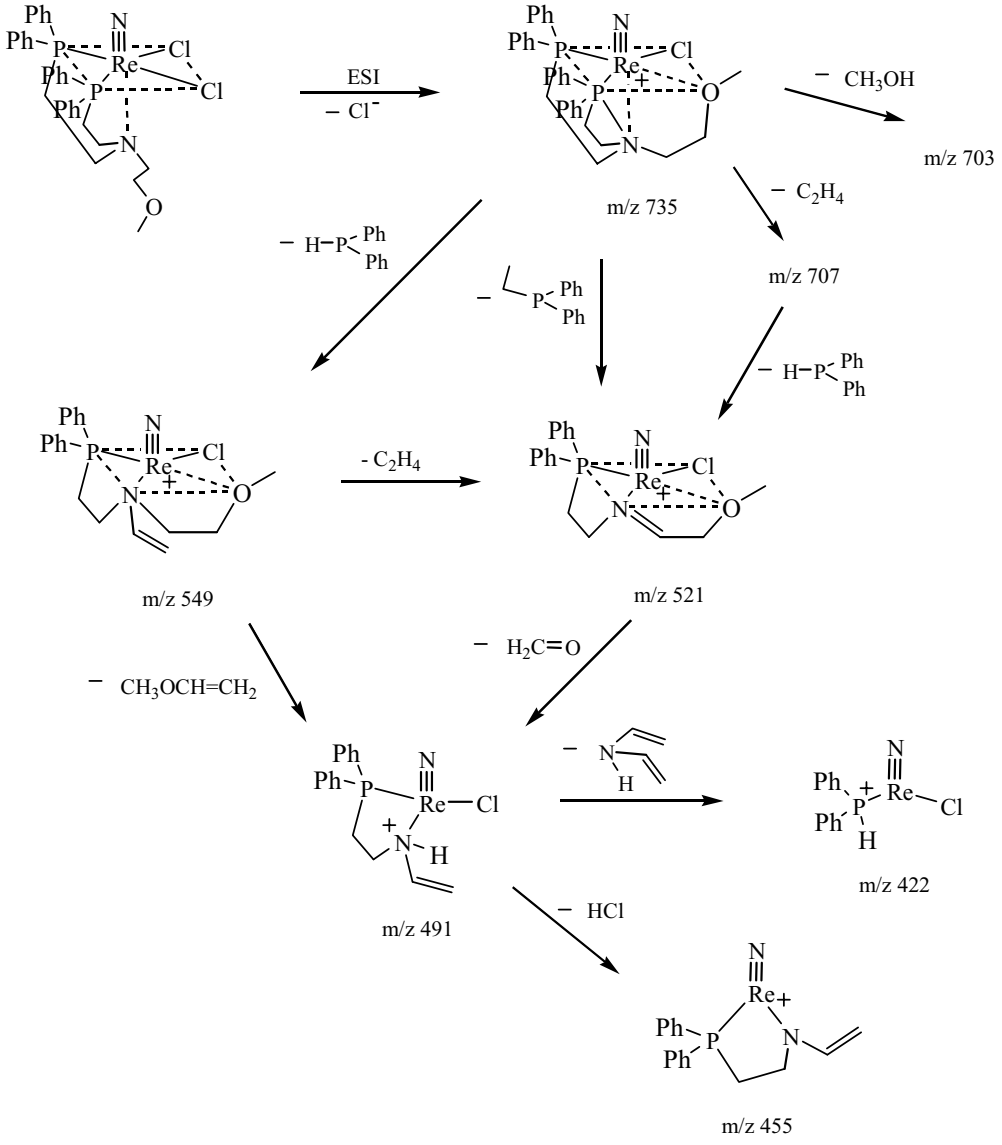


Fig. 3. (a) ESI/MS spectrum of compound **2**; (b) MS^2 spectrum of molecular ion (*m*/*z* 735); (c) MS^3 spectrum of product ion at *m*/*z* 521; (d) MS^3 spectrum of product ion at *m*/*z* 491.

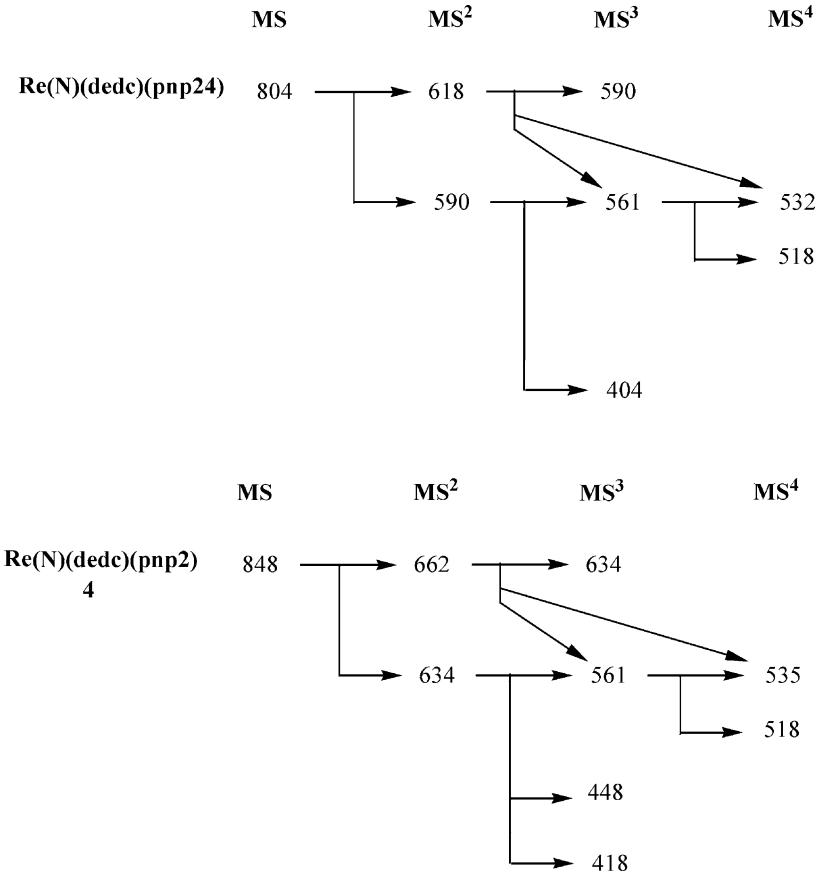
results substituted by a covalent one (Re–N), thereby restoring the original 5+ oxidation state of the metal. The abundance of the ion so generated, at *m*/*z* 639, is a good evidence of its stability and, consequently, of the privileged oxidation state 5+ of Re. In its turn, the ion at *m*/*z* 639 leads by collision to the product ion at *m*/*z* 555, corresponding to the contemporary loss of the aliphatic amine and of the nitride nitrogen. The resulting ion matches with a diphosphine rhenium adduct.

Compound **2** is isostructural with **1**, the only difference being the substituent at the amine moiety (a methoxyethyl group in **2** and a methyl group in **1**) in the diphosphine framework. Such a variation causes a different behaviour in ESI conditions. In this case, the $[M - Cl]^+$ ion, at *m*/*z* 735, becomes the only species detectable in the ESI spectrum, as outlined in Fig. 3a. Processes somehow different from those described for compound **1**, justified by the presence of the methoxyethyl pendant group, likely appear. Reasonably, after the first Cl^- loss induced by the positive charge density on the droplet surface, the oxygen atom of the amine pendant group interacts with the metal (see Scheme 1), leading again to a six-coordinate species in which the residual Re–Cl bond is strengthened, thus disactivating the second chlorine loss above described for compound **1**. The following process resembling the loss of the methyl radical just illustrated for **1**, i.e., the loss of the pendant methoxyethyl group, is still present, leading to the ion at *m*/*z* 676, but in this case the most favoured decomposition pathway leads to the ion at *m*/*z* 491, due to the subsequent loss of a diphosphine arm and of the pendant methoxyethyl group. The MS^n spectra reported in Fig. 3b–d and the related fragmentation pattern presented in Scheme 1 illustrates the different fragmentation behaviour of **2** with respect to **1**. For **2**, the additional rhenium–oxygen interaction (not possible in **1**) activates collisionally induced



Scheme 1.

Table 1
MS^n data obtained by resonant excitation of molecular ions *m/z* 804 (compound **3**) and *m/z* 848 (compound **4**)



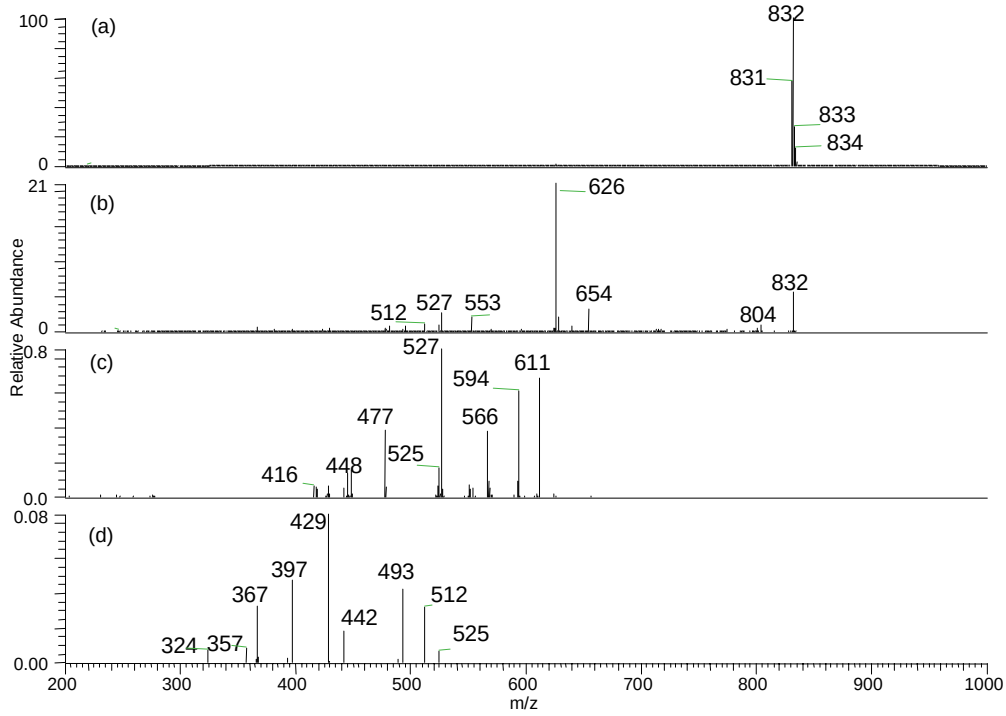
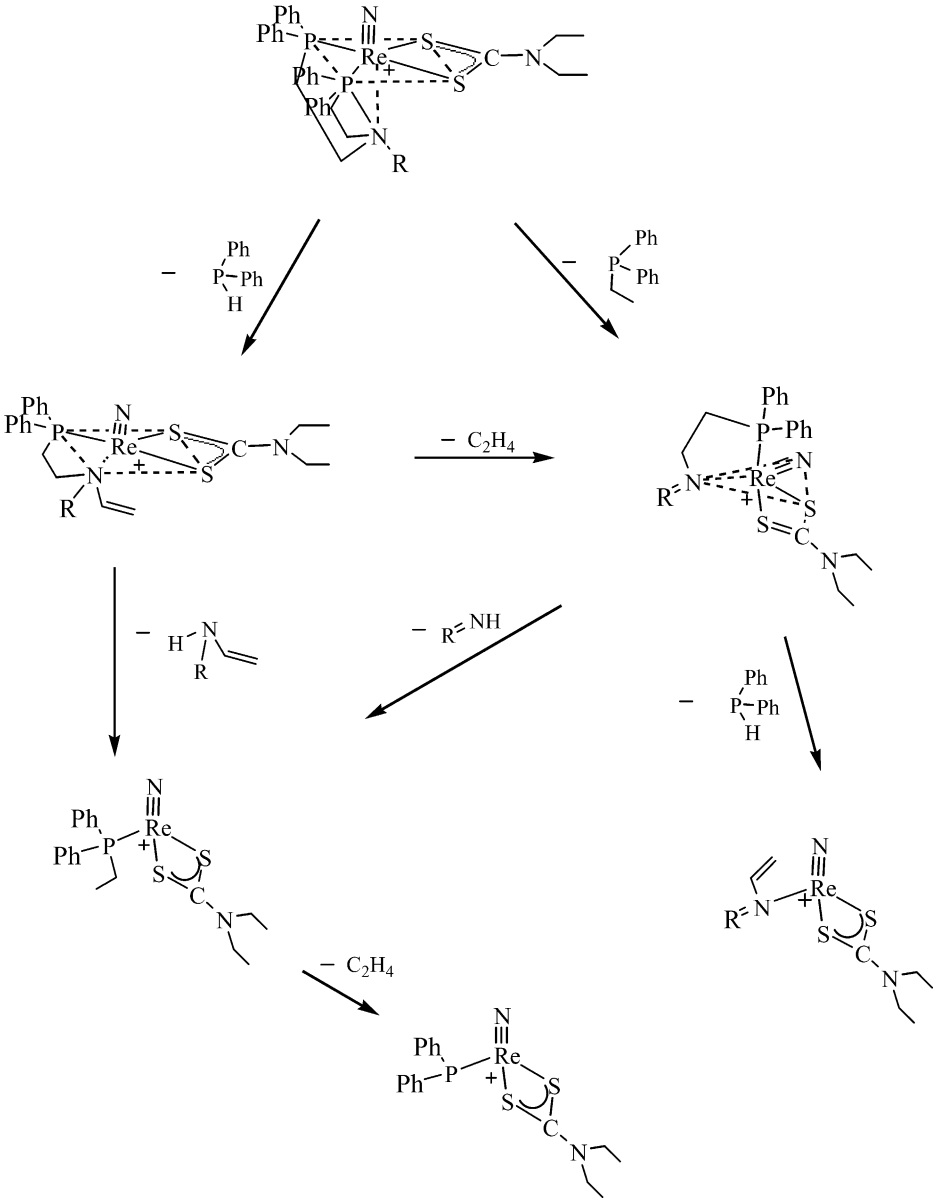


Fig. 4. (a) ESI/MS spectrum of compound **5**; (b) MS^2 spectrum of molecular ion (*m/z* 832); (c) MS^3 spectrum of product ion at *m/z* 626; (d) MS^4 spectrum of product ion at *m/z* 527.

fragmentation processes always implying the cleavage of the diphosphine ligand.

Intermediate compounds **1** and **2** treated with sodium salts of the appropriate dithiocarbamate (see Fig. 1) in dichloromethane/ethanol mixtures afforded asymmetrical mixed nitrido heterocomplexes **3** and **4**. A similar synthetic route was applied to obtain branched complexes **5** and **6**.

Compounds **3** and **4** show an identical behaviour in ESI conditions. The only ions detectable are the molecular cations at *m*/*z* 804 and *m*/*z* 848, respectively. Analogously, the collisionally induced fragmentation patterns of both complexes are similar (see Table 1). They are characterised by the loss of phosphorus-containing residues originating from the diphosphine ligand producing abundant peaks at *m*/*z* 618 and 590 and peaks at *m*/*z* 662 and 634 for complexes **3** and **4**, respectively. As detailed in Scheme 2, these two fragment ions contain a novel bidentate P,N-phosphinoamine along with the original dithiocarbamate and terminal metal-nitrido ligands in a five-coordinate array. This primary fragmentation is followed by two major routes, both involving crumbling of the native phosphinoamine chelate ligand. Thus, for **4** peaks at *m*/*z* 448 and 418 are consistent with the release of the second diphosphine arm and retention of the amine group, whereas, on the contrary, peaks at *m*/*z* 561 and 535 are indicative of amine loss with maintenance of the phosphine group. This alternative routes of fragmentation indicate that single Re–P and Re–N bonds are practically isoenergetic. In any case, the intact diethyldithiocarbamate ligand is retained in the rhenium coordination sphere, indi-

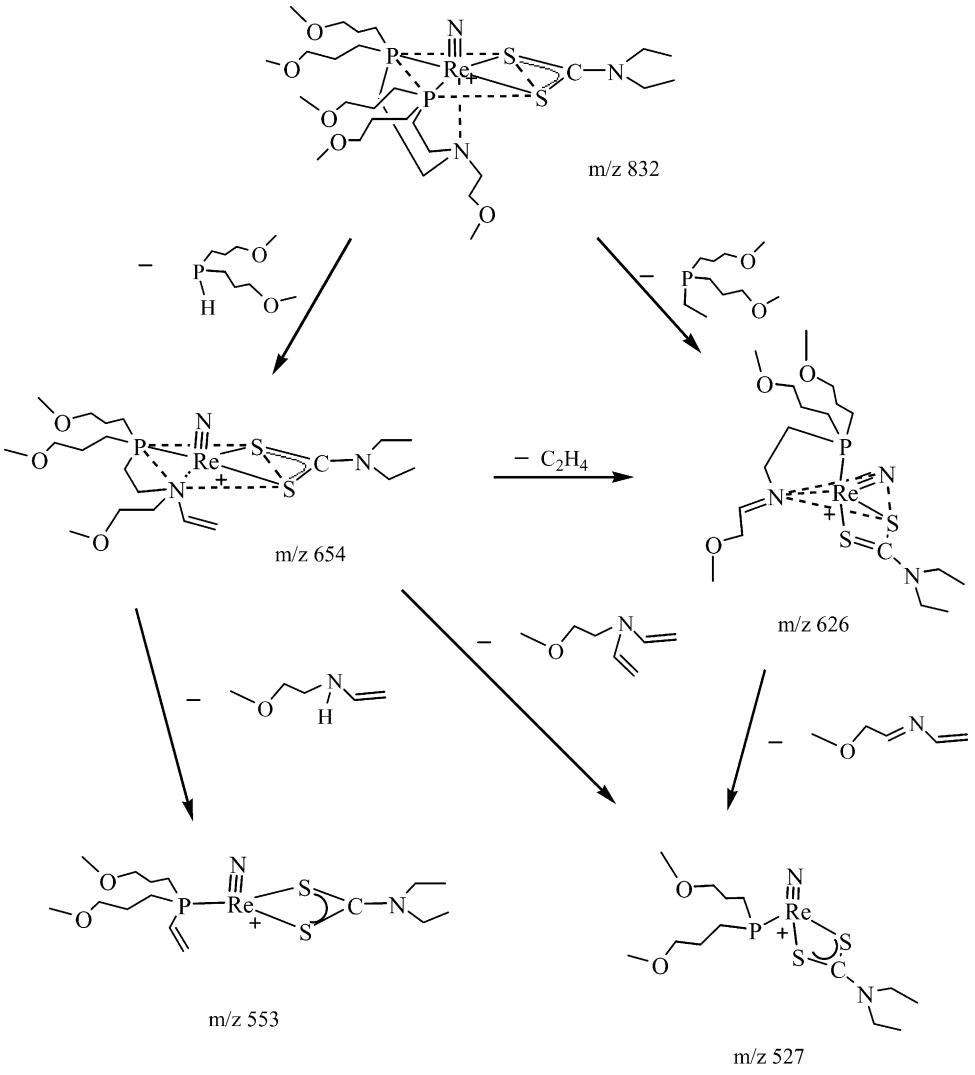


Scheme 2.

cating that the four-membered metal-dithiocarbamate ring is very stable and contains extremely robust Re–S bonds.

The ESI mass spectra of compounds **5** and **6** show the molecular cation at *m*/*z* 832 and 933, respectively, without any detectable fragmentation, giving further evidence of the high stability of the cations in the oxidative/reductive conditions typical of ESI experiments. However, as previously detected with compounds **1**–**4**, further MS^n spectra put in evidence the production of several fragment ions. The ESI/MS^n spectra of compound **5** are reported in Fig. 4, and the related fragmentation pattern is outlined in Scheme 3. The primary fragmentation is identical to that exhibited by compounds **3** and **4**, and corresponds to the loss of P-containing residues originating from pnp3 (compound **5**) and pnp5 (compound **6**), respectively, through cleavages of both P–C and N–C bonds. As can be seen from Fig. 4, the latter process is more favoured, suggesting a higher lability of the N–C bond. The ions so generated at *m*/*z* 654 and 626 undergo further fragmentation producing the abundant fragment at *m*/*z* 527. This process can be rationalised through the cleavage of the native P,N-phosphinoamine chelate ligand *via* release of the amine group only. It is important to note that this is the unique route of fragmentation operating at this stage, indicating that alkylphosphines form more stable bonds with rhenium than aryphosphines do in complex **4**, in which two alternative routes of fragmentation are operating. This behaviour is consistent with the general trend observed in phosphine-containing transition metal complexes, supporting the evidence that alkylphosphines usually form stronger metal–phosphorus bonds than arylphosphines. Again the diethyldithiocarbamate is retained intact in the metal coordination sphere.

Finally compound **6**, incorporating the branched diethoxyethyldithiocarbamate (dbodc) and pnp5, shows the unique molecular cation at *m*/*z* 933 in the full spectrum. Collisionally induced fragmentation evidences again the typical loss of one diphosphine arm generating the fragment ions at *m*/*z* 755 and 727, which adopt the standard five-coordinate arrangement composed by the terminal nitride group, the dithiocarbamate and the native bidentate



Scheme 3.

P,N-phosphinoamine ligand. The fragment ion at *m*/*z* 727 releases ethanol, likely originating from a dithiocarbamate pendant group, followed by cleavage of the C=N dithiocarbamate bond with production of the fragment ion at *m*/*z* 608 and eventually 566. In the latter ions it has to be noted that carbon disulfide is retained in the coordination sphere, confirming the tendency of this class of rhenium compounds to form quite stable metal–sulfur bonds.

The isostructural technetium analogue of the rhenium complex **6** was investigated in a previous contribution [11]. Comparison of the fragmentation profiles of these two compounds evidences similarity and differences. In ESI conditions both complexes show the unique molecular cation with no detectable fragmentation. Further collision experiments reveal that they both release one diphosphine arm, that is the common pathway exhibited by all these investigated heterocomplexes, giving the five-coordinate species including the terminal nitride group, the dithiocarbamate and the native P,N-phosphinoamine chelate ligand. The further loss of ethanol is common as well. At this point, the fragmentation patterns of the two compounds diverge. The technetium-containing ion releases the dithiocarbamate fragment leaving the native phosphineamine ligand intact, while the rhenium-containing ion shows cleavage of the C=N dithiocarbamate bond with retention of carbon disulfide in the metal coordination sphere, followed by cleavage of the phosphineamine chelate and release of the amine group. This different routes of fragmentation indicate that the terminal [Re≡N] group privileges metal–sulfur interactions, whereas the terminal [Tc≡N] group prefers metal–phosphorus and metal–nitrogen ones. Such diverse behaviour is a further difference encountered in the chemistry of the second-row technetium and third-row rhenium elements [12].

4. Conclusion

ESI/MS and collisional experiments have proven to be valuable tools for the characterisation of nitrido-Re heterocomplexes containing the $[Re(N)(PNP)]^{2+}$ synthon. Chloro-containing compounds **1**–**2** do not show the molecular ion peaks, $[M - Cl]^+$ and $[M - 2Cl]^+$ ions being the only species detected in the ESI spectra. Under the same conditions, dithiocarbamate-containing complexes **3**–**6** show only the molecular ion without detectable fragmentation. Collisional behaviour of these compounds is related to the charge of the overall molecule (neutral or cationic), and to the nature of the substituents incorporated in the diphosphine and/or dithiocarbamate ligands. While neutral $[Re(N)Cl_2(PNP)]$ compounds retain the [Re(N)(PNP)] synthon intact, cationic $[Re(N)(DTC)(PNP)]^+$ heterocomplexes release one diphosphine arm in the first fragmentation step producing a five-coordinate species containing a native bidentate phosphinoamine ligand along with the intact dithiocarbamate chelate. Branched dbodc incorporated in complex **6** undergoes further decomposition with loss of the secondary amine group and retention of carbon disulfide at rhenium, whereas dedc-complexes retain the metal-dithiocarbamate moiety intact. The competitive fragmentation of the native bidentate phosphinoamine ligand depends on the substituents at the residual coordinated phosphine. Less donating aryl-phosphines (complexes **3** and **4**) are released with retention of the near amine group, whereas more donating alkyl-phosphines (complexes **5** and **6**) are retained, and release of the amine group is observed.

Comparison of the collisional pathways of isostructural $[M(N)(dbodc)(pnp5)]^+$ heterocomplexes (M = Tc, Re **6**) show a similar primary decomposition (cleavage of one diphosphine arm) followed by different fragmentation processes. Rhenium appears to privilege metal–sulfur bonds releasing the phosphinoamine ligand with retention of the dithiocarbamate (or carbon disulfide) moiety. On the contrary, technetium seems to favour metal–phosphorus bonds releasing the dithiocarbamate ligand with retention of the phosphinoamine chelate.

Such different behaviour is a further difference encountered in the chemistry of the second-row technetium and third-row rhenium elements, in addition to the already observed differences in red-ox and substitution-kinetic behaviour. Since rhenium is frequently used as a technetium surrogate to study the behaviour of medical relevant ^{99m}Tc agents, ESI/MS^n data confirm that this correspondence should be used, at least, with some caution.

References

[1] S. Jurisson, J.D. Lydon, Chem. Rev. 99 (1999) 2205.
[2] S. Liu, D.S. Edwards, Chem. Rev. 99 (1999) 2235.
[3] Future of Nuclear Medicine, part 1: marketing research forecasts, J. Nucl. Med. 39 (2) (1998) 27N;
Future of Nuclear Medicine, part 2: assessment of the diagnostic radiopharmaceutical markets (2001–2020), J. Nucl. Med. 39 (3) (1998) 20N.
[4] P.J. Blower, S. Prakash, Perspect. Bioinorg. Chem. 4 (1999) 91.
[5] R. Pasqualini, V. Comazzi, E. Bellande, A. Duatti, A. Marchi, Int. J. Appl. Radiat. Isot. 43 (1992) 1329.
[6] (a) G. Bandoli, A. Dolmella, M. Porchia, F. Refosco, F. Tisato, Coord. Chem. Rev. 214 (2001) 43;
(b) F. Tisato, F. Refosco, G. Bandoli, Coord. Chem. Rev. 135/136 (1994) 325.
[7] C. Bolzati, A. Boschi, L. Uccelli, F. Tisato, F. Refosco, A. Cagnolini, A. Duatti, S. Prakash, G. Bandoli, A. Cittadini, J. Am. Chem. Soc. 124 (2002) 11468.
[8] A. Boschi, C. Bolzati, L. Uccelli, A. Duatti, E. Benini, F. Refosco, F. Tisato, A. Piffanelli, Nucl. Med. Commun. 23 (2002) 689.
[9] F. Tisato, F. Refosco, C. Bolzati, G. Bandoli, A. Boschi, L. Uccelli, E. Benini, A. Duatti, E. Marotta, in: M. Nicolini, U. Mazzi (Eds.), Technetium, Rhenium and Other Metals in Chemistry and Nuclear Medicine, vol. 6, SGEditoriali, Padova, 2002, p. 171.
[10] G. Banditelli, A.L. Bandini, G. Minghetti, R. Seraglia, P. Traldi, Rapid Commun. Mass Spectrom. 10 (1996) 1107.
[11] E. Marotta, F. Tisato, F. Refosco, C. Bolzati, M. Porchia, P. Traldi, Rapid Commun. Mass Spectrom. 17 (2003) 1225.
[12] E. Deutsch, K. Libson, J.-L. Vanderheyden, in: M. Nicolini, G. Bandoli, U. Mazzi (Eds.), Technetium and Rhenium in Chemistry and Nuclear Medicine, vol. 3, Raven Press, New York, 1989, p. 13.