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Mass spectrometry of rhenium complexes: a comparative study by using LDI-MS, MALDI-MS, PESI-MS and ESI-MS

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A group of rhenium (I) complexes including in their structure ligands such as CF_3SO_3-, CH_3CO_2-, CO, 2,2′-bipyridine, dipyridil [3,2-a:2′3′-c]phenazine, naphthalene-2-carboxylate, anthracene-9-carboxylate, pyrene-1-carboxylate and 1,10-phenanthroline have been studied for the first time by mass spectrometry. The probe electrospray ionization (PESI) is a technique based on electrospray ionization (ESI) that generates electrospray from the tip of a solid metal needle. In this work, mass spectra for organometallic complexes obtained by PESI were compared with those obtained by classical ESI and high flow rate electrospray ionization assisted by corona discharge (HF-ESI-CD), an ideal method to avoid decomposition of the complexes and to induce their oxidation to yield intact molecular cation radicals in gas state $[M]^{+\cdot}$ and to produce their reduction yielding the gas species $[M]^{-\cdot}$. It was found that both techniques showed in general the intact molecular ions of the organometallics studied and provided additional structure characteristic diagnostic fragments. As the rhenium complexes studied in the present work showed strong absorption in the UV–visible region, particularly at 355 nm, laser desorption ionization (LDI) mass spectrometry experiments could be conducted. Although intact molecular ions could be detected in a few cases, LDI mass spectra showed diagnostic fragments for characterization of the complexes structure. Furthermore, matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained. Nor-harmane, a compound with basic character, was used as matrix, and the intact molecular ions were detected in two examples, in negative ion mode as the $[M]^{-\cdot}$ species. Results obtained with 2-[(2E)-3-(4-*tert*-buthylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) as matrix are also described. LDI experiments provided more information about the rhenium complex structures than did the MALDI ones.

Supporting information may be found in the online version of this article.

Keywords: high flow rate electrospray corona discharge; nor-harmane; DCTB; polypyridil rhenium complex; trifluoromethanesulfoxy rhenium complex; acetoxy rhenium complex; arylcarboxy rhenium complex

INTRODUCTION

The interest in the study of organometallic compounds is due to their catalytic properties in synthetic reactions and their role in relevant biological processes. The transition metal complexes have been investigated, and many of them have shown that they might be utilized in electron transfer studies,[1] solar energy conversion[2–4] and catalysis.[5] Possible applications as luminescent sensors,[6–8] molecular materials for nonlinear optics[9,10] or optical switching[11] have also emerged. In particular, luminescent transition metal complexes of Re(I) and Ru(II) with polypyridil ligands have been recognized as good potential candidates for the development of pH sensing devices.[12] Moreover, there are potential biochemical and technological applications based on the formation of adducts between transition metal complexes of Re(I), Ru(II), Os(III), Rh(III) and Co(III) and biological macromolecules such as DNA.[13,14]

X-ray crystallography and nuclear magnetic resonance spectroscopy are techniques frequently used for characterization of these complexes. Mass spectrometry (MS) is an accurate and sensitive method to determine the molecular weight and the structure of compounds. It is based on the detection of the intact molecular ion as gas ionic species, which sometimes is quite hard to get from organometallic compounds.[15] Several ionization techniques have been attempted for the analysis of these complexes by MS.[15,16] However, most of those trials showed disadvantages. For instance, electron ionization (EI), a well-known "hard" ionization method, and fast atom bombardment, a quite "soft" one, both induce extensive fragmentation and often prevent the detection of the parent ions of the analyte.[15] Moreover,

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EI could not be used for thermolabile compounds. On the other hand, matrix-assisted laser desorption ionization (MALDI) is a "soft" ionization technique but often produces aggregates of analyte molecules ("clusters"), giving signals of high mass (higher than molecular ion mass), and few organometallic compounds have been studied by this method.[15–17]

Since the introduction of the electrospray ionization (ESI) technique, the use of MS in the field of organometallic chemistry has been significantly extended.[18,19] Because of the soft nature of ESI, an intact molecular ion is expected to be observed with very minor fragmentation. The ESI process requires the presence of the ions in the solution before desorption into the gas phase and subsequent mass analysis. Although this will be the situation easily reached for ionic compounds, neutral species need to be converted to a closely related ionic system for their characterization.

If in the organometallic structure a ligand that can be protonated is present, it is possible to observe the molecule (M) in its protonated form, $[M+H]^+$ in the ESI mass spectrum. $NaNO_3$ is another ionization agent that has been used successfully to produce $[M+Na]^+$ species.[15,20] Otherwise, *in situ* ionization techniques for organometallics are needed to be developed. One way to convert neutral organometallics to cationic or anionic species, thereby enabling mass spectrometric detection, is inducing their oxidation or reduction, respectively. Under certain conditions, the ESI metal capillary can act as an electrode for a redox reaction.[21,22] It has been shown that the ESI ion source is a constant or controlled-current device in which electrolysis can occur in a similar way to that carried out in a flow cell.[23] However, when this approach was used to observe the mass spectra for some neutral complexes of rhenium, a reaction with the solvent acetonitrile (interchange of CO ligand and acetonitrile) was observed.[24] In this communication, a few examples of rhenium compounds presented suffered from this reaction during the ESI process. Thus, the corresponding intact molecular ions could not be detected.

Probe electrospray ionization (PESI) is a recently developed ionization technique which uses a solid needle as sampling probe and ESI emitter instead of using a capillary.[25] A solid stainless needle or wire is adopted to repeatedly load a small amount of sample solution by stitching the needle tip into the biological tissues or solutions. Then, electrospray will be generated when a high voltage (i.e. 2–3 kV) is applied to the needle. Previous works have demonstrated that PESI source is suitable for direct analysis of many kinds of samples.[26–28]

Herein, we report for the first time the mass spectra of several organometallic complexes constituted with Re(I) and different sorts of ligands. We describe for the first time the application of PESI-MS for the analysis of organometallics. For comparison purposes, additional MS techniques such as ESI-MS, high flow rate electrospray ionization corona discharge assisted MS (HF-ESI-CD-MS), MALDI-MS and laser desorption ionization (LDI) MS were also used.

We focus our attention on many Re(I) complexes synthesized and studied from the photophysical and photochemical point of view.[14,29–31] These are seven neutral rhenium complexes whose structures are displayed in Fig. 1 [$L_1Re(CO)_3L_2$ with L_2 = 1,10-phenanthroline (1,10-phen), where $L_1 = CF_3SO_3^-$ (**1**); $L_1Re(CO)_3L_2$

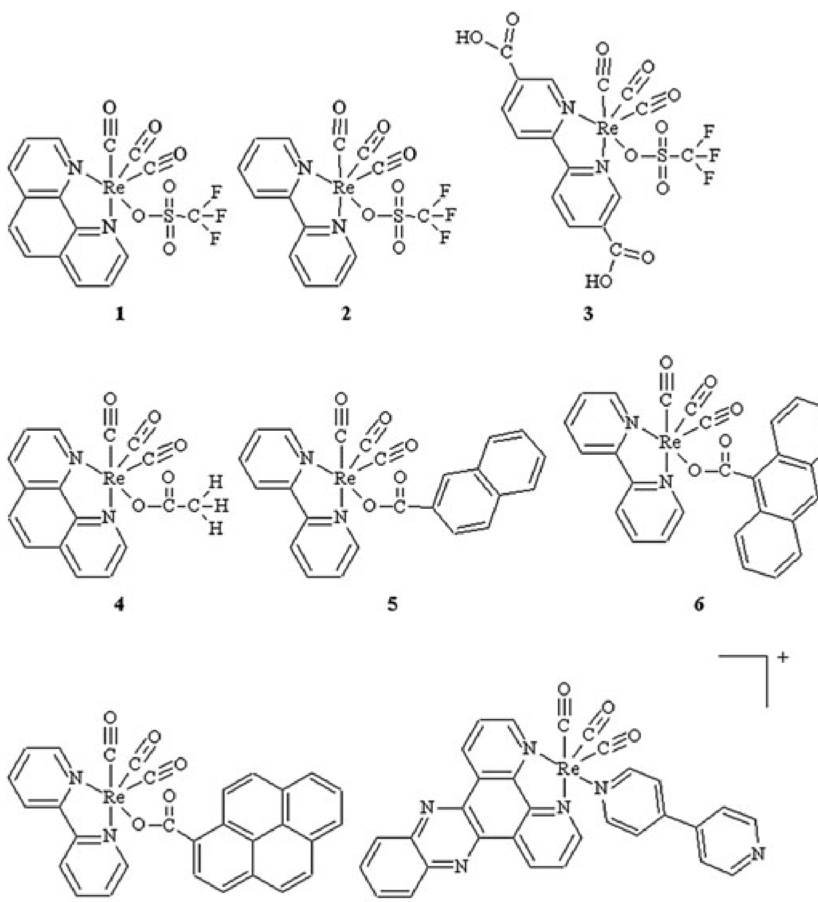

Figure 1. Structural representations for compounds **1–8**.

with $L_1 = CF_3SO_3^-$, where L_2 = 2,2′-bipy (**2**) or 5,5′-dicarboxy 2,2′-bipy (**3**) or $L_1 = CH_3CO_2^-$ (**4**); R-CO_2-Re(CO)$_3$(2,2′-bipy) with 2,2′-bipy = 2,2′-bipyridine, where R-CO_2^- = naphthalene-2-carboxylate (**5**), R-CO_2^- = anthracene-9-carboxylate (**6**) and R-CO_2^- = pyrene-1-carboxylate (**7**) a cationic complex **8** [(dppz)Re(CO)$_3$(4,4′-bipy)]$^+$ where dppz = dipyridil[3,2-a:2′3′-c]phenazine).

EXPERIMENTAL SECTION

The Re(I) complexes were prepared according to methods described elsewhere.[14,29–31] HPLC-grade methanol (Kanto Chemical Co Inc, Japan) and acetonitrile (J. T. Baker, United States), were used without further purification. 9H-Pirido[3,4-b]indole [nor-harmane(nHo)] and β-cyclodextrin (cyclomaltoheptaose) were purchased from Sigma-Aldrich Chemical Co., United States. 2-[(2E)-3-(4-*tert*-Buthylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) was purchased from Fluka Sigma-Aldrich, Switzerland. Water of very low conductivity (Milli Q grade) was used.

PESI-MS analysis

The PESI experimental procedures were similar to those described in our previous articles.[25,27,32] Briefly, the needle was moved up and down along a vertical axis using a custom-made linear actuator system. When the needle was at the bottom position, the tip of the needle was adjusted to touch the surface of the liquid sample. When the needle was moved up to the highest position, a high voltage of about 2–3 kV was applied to it. The distance of the needle stroke was 10 mm. As electrospray emitters, disposable acupuncture needles (Seirin, Shizuoka, Japan) with sub-micromere tip diameter were used throughout the PESI-MS experiments. The PESI mass spectra were obtained with an acquisition time of 1 s with 3 Hz of the probe motion.

The ions generated from the electrospray were sampled through the ion-sampling orifice with a diameter of 0.4 mm into the vacuum chamber and mass analyzed by a linear ion trap mass spectrometer (LTQ-Velos, Thermo Scientific, United States) equipped with collision-induced dissociation (CID) and pulse-Q collision-induced dissociation (PQD) modes.

Stock solutions of all complexes were prepared in methanol at a concentration 10^{-4} M. Dilutions were prepared from stock solutions. Each experiment was repeated at least three times to ensure reproducibility. Spectra were obtained and analyzed with the program Thermo Xcalibur Qual Browser.

ESI-MS analysis

ESI-MS analyses were performed using a linear ion trap mass spectrometer (LTQ-Velos, Thermo Scientific, United States) equipped with CID and PQD modes and was operated in the negative or positive ion mode. High flow electrospray with an assistance of corona discharge taking place at the tip of the electrospray capillary was used to avoid decomposition (interchange of ligands and solvent) of the rhenium complexes and to induce ionization of neutral analytes.[21,22] The source voltage applied was 8 kV, the source current was 15 μA, the sheath gas flow rate was 30 (a. u.), and the capillary temperature was 150 °C. Ion optics parameters: multipole 00 offset: –3.3 V, lens 0: –6.2 V; multipole 0 offset: ±6.3 V, lens 1: –9.2 V, gate lens: –91.9 V; multipole 1 offset: –6.6 V; and multipole RF amplitude: 602.3 (Vp-p). A syringe pump (Agilent, United States) with 2.3 mm in diameter was used to introduce the sample at a flow rate of 10 μl/min and methanol. Stock solutions of all complexes were prepared in methanol at a concentration 10^{-4} M. Diluted solutions were prepared from the stock solutions. Each experiment was repeated at least three times to ensure reproducibility. Spectra were obtained and analyzed with the program Thermo Xcalibur Qual Browser.

MALDI-TOF/TOF MS and LDI-TOF/TOF MS analysis

Rhenium complexes were analyzed by ultraviolet matrix assisted laser desorption ionization mass spectrometry (UV-MALDI MS) and by ultraviolet laser desorption ionization mass spectrometry (UV-LDI MS) performed on the Bruker Daltonics Ultraflex II TOF/TOF mass spectrometer (Leipzig, Germany). Mass spectra were acquired in linear positive and negative ion modes and with the LIFT device in the MS/MS mode. Stock solutions of complexes (10^{-4} M) were prepared in water. These solutions were then diluted 10- to 100- fold to a final concentration of 10^{-5} to 10^{-6} M. External mass calibration was made using β-cyclodextrin (MW 1134) with nHo as matrix in positive and negative ion mode. The matrix signal was used as an additional standard for calibration in both ionization modes. Sample solutions were spotted on an MTP 384 polished stainless steel target plate from Bruker Daltonics (Leipzig, Germany). For UV-MALDI MS, matrix solutions were prepared by dissolving nHo (1 mg/ml) in acetonitrile/water (1 : 1, v/v) solution and DCTB[17] (10 mg/ml) in dichloromethane. For UV-MALDI MS experiments, dry droplet sample preparation or sandwich method was used according to Nonami *et al.*[33], i.e. loading successively 0.5 μl of matrix solution, analyte solution and matrix solution after drying each layer at normal atmosphere and room temperature. The ratio of matrix to analyte was 3 : 1 (v/v), and the matrix and analyte solution loading sequence was (i) matrix, (ii) analyte, (iii) matrix and (iv) matrix. For UV-LDI MS experiments, two portions of analyte solution (0.5 μl × 2) were loaded on the probe and dried successively (two dry layers). Desorption/Ionization was obtained by using the frequency-tripled Nd:YAG laser (355 nm). The accelerating potential was 20 kV. Experiments were performed, first, using the full-range setting for laser firing position to select the optimal position for data collection and, second, fixing the laser firing position in the sample sweet spots. The laser power was adjusted to obtain high signal-to-noise ratio while ensuring minimal fragmentation of the parent ions, and each mass spectrum was generated by averaging 100 lasers pulses per spot. Spectra were obtained and analyzed with the programs FlexControl and FlexAnalysis, respectively.

UV absorption measurements

The spectra were recorded on a UV spectrophotometer. Measurements were made in quartz cells of 1 cm optical-path length at room temperature, as previously described.[14,29–31]

RESULTS AND DISCUSSION

LDI-MS and MALDI-MS experiments

Rhenium complexes used in this work show strong absorption in the UV–vis region, particularly at 355 nm.[14,29–31] This property allowed to desorb and ionize them using a UV laser, LDI, without needing the presence of a secondary molecule as photosensitizer or matrix in the sample (LDI-MS). However, for comparison purposes, we also recorded the mass spectra for all of them, adding a MALDI matrix in the sample (MALDI-MS). For the latter experiments, nHo and DCTB were chosen as matrixes. Although the former compound has been used efficiently for analysis of analytes with different chemical structures (i.e. oligosaccharides and proteins)[33] in the negative and in positive ion mode, here, we describe for the first time the use of nHo as matrix for the analysis of organometallic complexes. Previously, some rhenium complexes were analyzed by MALDI-MS using DCTB as matrix.[17]

As shown in Table 1, the results obtained by LDI-MS and MALDI-MS were quite disappointing. However, as Wyatt suggested in his recent article,[16] it is deeply satisfying to observe an intact, whole complex, but when fragments are observed, it should not be viewed as a failed analysis, as important and useful structural information can still be gleaned. Thus, with this phrase in mind, we analyzed the results here obtained.

For the neutral rhenium complexes **1, 2** and **3** with structure $L_1Re(CO)_3L_2$, where $L_1 = CF_3SO_3$, similar signal patterns were observed in LDI-MS experiments in the negative ion mode [Fig. 2 (a)–(c)]. Among these signals in all cases, a very strong signal was observed at *m/z* 148.78 and a minor signal at *m/z* 336.90 that correspond to the species $[CF_3SO_3]^-$ and $[CF_3SO_3\text{-}Re]^-$ [Fig. 2(a)–(c)]. The detection of the former as an abundant stable species agrees with the fact that the intact molecular ions of compounds **1**, **2** and **3** could not be detected by PESI-MS, ESI-MS and HF-ESI-CD-MS analysis in the positive ion mode (see the following discussion and Table 1). It is interesting to mention that the intact molecular ion of **3** could be detected as a very low intensity signal of the species $[M]^{-\cdot}$ at *m/z* 663.9 [Table 1, LDI column, (−) mode; Fig. 2(c) and Fig. 1S(a)]. Together with this signal, three expected fragments at *m/z* 635.90 (M-CO), 619.90 ($M\text{-}CO_2H$) and 581.90 ($M\text{-}CO_2F_2H$) were detected [Fig. 1S(a)].

Table 1. Results obtained by mass spectrometry using different ionization methods: comparative analysis of rhenium complexes in positive (+) and negative (−) ion mode[a]

Compound	PESI	ESI[b]	LDI		MALDI		
					nHo	DCTB	DCTB
	+	+	+	−	−	+	−
1	$[M\text{-}CF_3SO_3 + H]^+$ c	$[M\text{-}CF_3SO_3]^+$ c	$[M + H]^+$	c	c	c	c
2	$[M\text{-}CF_3SO_3 + H]^+$ c	$[M\text{-}CF_3SO_3]^+$ c	$[M\text{-}CF_3SO_3]^+$ c	c	c	c	c
3	$[M\text{-}CF_3SO_3 + H]^+$ c	$[M\text{-}CF_3SO_3]^{+c}$	$[M\text{-}CF_3SO_3]^+$ c	$[M]^{-\cdot}$	$[M]^{-\cdot}$	c	c
4	$[M + Na]^+$	$[M]^{+\cdot}$	c	$[M]^{-\cdot}$	$[M]^{-\cdot}$	c	c
5	c	$[M]^{+\cdot}$	c	$[M]^{-\cdot}$	c	c	$[M]^{-\cdot}$
6	$[M + H]^+$ $[M + Na]^+$	$[M]^{+\cdot}$	c	[M-(2,2′-bipy)]$^{-c,d}$	c	c	c
7	$[M + H]^+$ $[M + Na]^+$	$[M]^{+\cdot}$	c	[M-(2,2′-bipy)]$^{-c,d}$	c	c	$[M]^{-\cdot}$
8	$[M]^+$	$[M]^+$	[M-(4,4′-bipy)]$^+$ c	c	c	$[M]^{+\cdot}$	c

[a] $[M]^+$, $[M]^{+\cdot}$, $[M + H]^+$, $[M + Na]^+$, $[M]^-$ and $[M]^{-\cdot}$ indicate the structure of the intact molecular ion (M) detected. $[M\text{-}CF_3SO_3 + H]^+$, where CF_3SO_3 is the common ligand in **1**, **2** and **3**; [M-(4,4′-bipy)]$^+$, where 4,4′-bipy is one of the ligands in **8**; and [M-(2,2′-bipy)]$^-$, where 2,2′-bipy is the common ligand in **6** and **7**, indicate the characteristic main fragment detected, although the intact molecular ion was not observed.

[b] Results were obtained in conditions of high flow rate electrospray ionization assisted by corona discharge experiments.

[c] Intact molecular ion was not detected.

[d] Additional diagnostic signals formed by fragmentation of dimeric clusters (M2) were also observed (see the Results section).

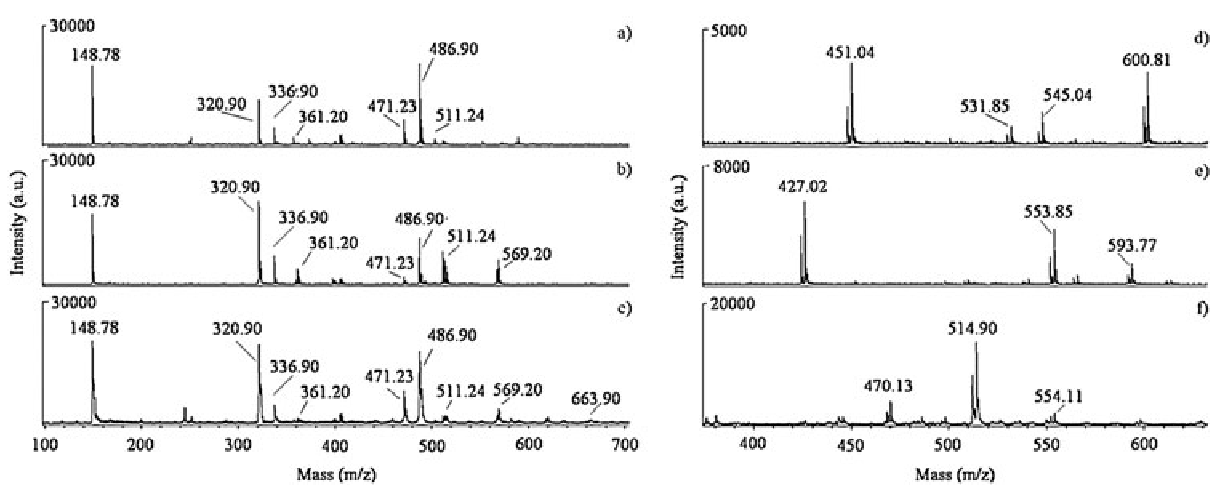

Figure 2. LDI mass spectra of $L_1Re(CO)_3L_2$, where $L_1 = CF_3SO_3^-$ and L_2 = 1,10-phen (MW = 599.9) compound **1** (a and d), L_2 = 2,2′-bipy (MW = 575.9) compound **2** (b and e) and L_2 = 5,5′-dicarboxy 2,2′-bipy (MW = 663.9) compound **3** (c and f). Negative ion mode: (a)–(c). Positive ion mode: (d)–(f).

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As LDI is not a soft desorption ionization method, additional signals related with clusters and its fragmentations were observed. The photochemical decomposition of the complexes and their clusters in LDI experiments would account for the common complex behavior observed for **1**, **2** and **3**.

It is interesting to note that when DCTB was used as matrix in MALDI experiments, the intact molecular ions of **1**, **2** and **3** were not detected. On the contrary, with nHo as matrix, the intact $[M]^{-\cdot}$ species for compound **3** [Fig. 1, $(CF_3SO_3)Re(CO)_3$(5,5′-dicarboxy 2,2′-bipy), compound **3**] at *m/z* 663.9 could be detected in the negative ion mode [Table 1, MALDI, nHo and DCTB columns; Fig. 1S(a)–(b)]. This signal was observed in LDI and in MALDI experiments with nHo. In both cases, the intensity of the signal was very low, and similar fragmentation patterns were observed. The presence of the carboxylic groups as substituents in the 2,2-bipyridine structure would account for the special anion stability observed.

After the volatilization/ionization of the neutral complex, if the loss of the CF_3SO_3 as anion moiety occurs, then the complementary fragment may keep a positive charge, and this is the reason the species M-(CF_3SO_3) was not observed in the negative ion mode. However, when LDI-MS experiments were performed in the positive ion mode, the characteristic structural diagnostic fragments $[M\text{-}CF_3SO_3]^+$ were observed for the three compounds [Fig. 2(d)–(f); Table 1, LDI column, (+) mode]. In the LDI mass spectra of compound **1** together with the intact molecular ion as $[M+H^+]$ (*m/z* 600.81) [Fig. 2(d)], two additional signals were detected at *m/z* 451.04 and 545.04 corresponding to the species $[M\text{-}CF_3SO_3]^+$ and $[M\text{-}2(CO)+H]^+$, respectively. In the LDI mass spectra of **2**, the structure diagnostic fragment $[M\text{-}CF_3SO_3]^+$ was observed at *m/z* 427.02, and for complex **3**, this fragment was observed at *m/z* 514.09 [Table 1, LDI column, (+) mode; Fig. 2(e)–(f)]. Characteristic signal from the three complexes was not observed when nHo was used as matrix in MALDI-MS experiments in the positive ion mode as well as when DCTB was used in the positive and negative ion mode (results not shown).

MALDI mass spectrum of compound **4**, obtained in the negative ion mode using nHo as matrix, is shown in Fig. 3(a). The intact molecular ion was observed as the species $[M]^{-\cdot}$ at *m/z* 510.4. Besides, the fragments $[M\text{-}CH_3CO_2]^-$ at *m/z* 451.5 and $[CH_3CO_2]^-$ at *m/z* 59.4 were observed. On the contrary, using DCTB, the signal corresponding to the intact molecular ion $[M]^{-\cdot}$ was difficult to detect, showing these experiments' very low reproducibility. When LDI mass spectrum was recorded in the negative ion mode, the intact molecular ion was also detected as a high-intensity signal [Fig. 3(b)].

The LDI mass spectra for complexes **5, 6** and **7** with general structure R-CO_2-$Re(CO)_3$(2,2′-bipy) [Fig. 1, 5, R-CO_2 = naphthalene-2-carboxylate; **6**, anthracene-9-carboxylate; and **7**, pyrene-1-carboxylate] were measured in both the positive and negative ion mode. The intact molecular ion was not detected in the former; however, it was possible to observe the common species $[M\text{-}(R\text{-}CO_2)]^+$ at *m/z* 427.10 in each spectrum as well as the characteristic fragment $[2M\text{-}(R\text{-}CO_2\text{-}4H)]^+$ yielded by the corresponding dimeric cluster 2 M. These peaks were located at *m/z* 1021.26, 1071.12 and 1095.21, respectively (Fig. 2S).

Negative-ion LDI mass spectra for this complexes were obtained (Fig. 3S). The intact molecular ion as $[M]^{-\cdot}$ at *m/z* 598.40 was only detected for compound **5** [Table 1, LDI column, (−) mode; Fig. 3S(a)] together with several fragments. After the ionization/volatilization of these rhenium complexes, two different fragmentation processes took place. On one hand, the covalent bond between the rhenium and the carboxylic group was broken. Thus, the stable aromatic carboxylate anions were detected (**5**, *m/z* 170.91, naphthalene-2-carboxylate; **6**, *m/z* 221.28, anthracene-9-carboxylate; **7**, *m/z* 245.16 pyrene-1-carboxylate). On the other hand, the stable diagnostic fragment anions [M-(2,2′-bipy)]$^-$ were also observed (Table 1, LDI column, (−) mode). Those signals were located at *m/z* 442.04, 492.04 and 516.04 for complex **5, 6** and **7**, respectively [Fig. 3S(a)–(c)]. Other intense signals at *m/z* 613.40, 713.57 and 761.29 were also observed and could be rationalized as the species $[(R\text{-}CO_2)_2\text{-}Re(CO)_3]^-$ produced by fragmentation of the corresponding dimeric clusters with the formula $[R\text{-}CO_2\text{-}Re(CO)_3(2,2'\text{-bipy})]_2$ [Fig. 3S(a)–(c); Scheme 1]. No characteristic signals from the three complexes were observed when nHo was used as matrix in MALDI-MS experiments conducted in the positive and negative ion mode. On the contrary, those performed with DCTB as matrix showed for complex **5** and **7** the intact molecular ion as $[M]^{-\cdot}$ in the negative ion mode at *m/z* = 598.02 and 672.02, respectively [Table 1, MALDI, nHo and DCTB columns; Fig. 4S(a)–(b)].

For the cationic complex **8** {Fig. 1, $[(dppz)Re(CO)_3(4,4'\text{-bipy})]^+$}, the intact molecular ion was not detected in the positive ion mode when LDI and MALDI experiments with nHo as matrix were conducted. The most intense signal observed was located at *m/z*

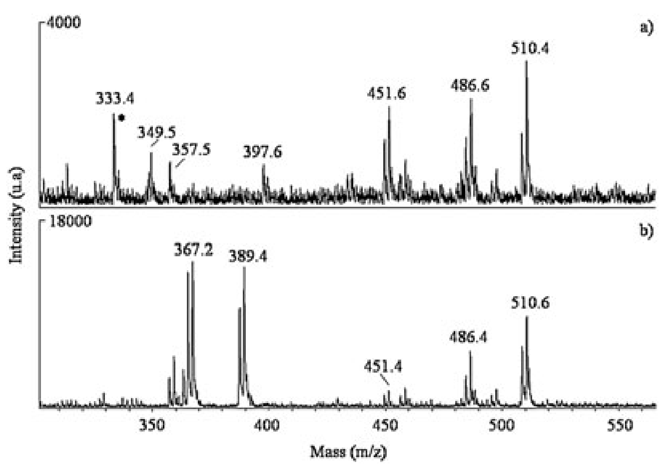
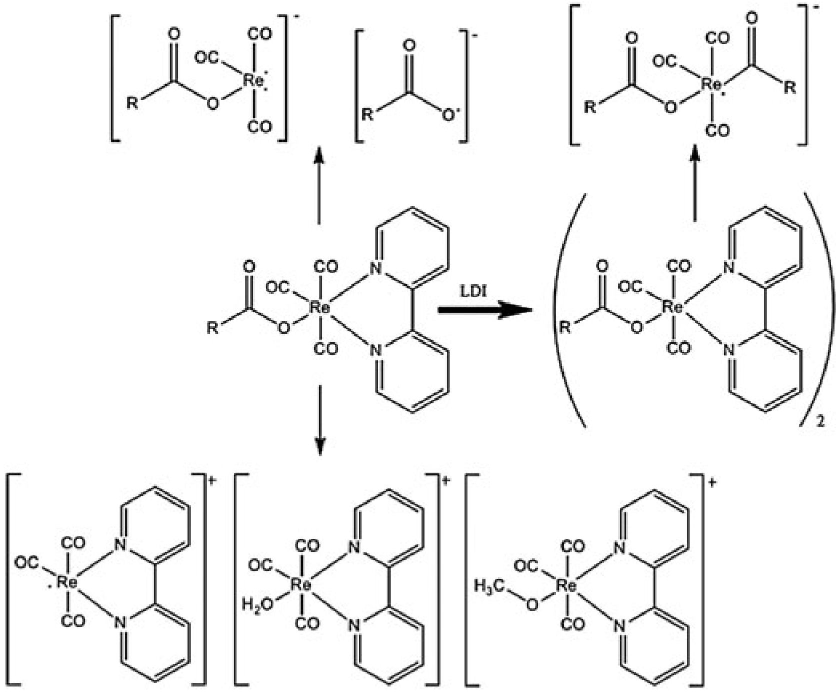


Figure 3. Negative ion mass spectra of compound **4**, $(CH_3CO_2)Re(CO)_3$(1,10-phen). (a) MALDI mass spectrum acquired with nHo as MALDI matrix and (b) LDI mass spectrum. Asterisk denotes clusters of nHo.



Scheme 1. Fragmentation scheme of compound **5**, R–CO_2^- = naphthalene-2-carboxylate; compound **6**, anthracene-9-carboxylate; and compound **7**, pyrene-1-carboxylate in positive and negative ion mode.

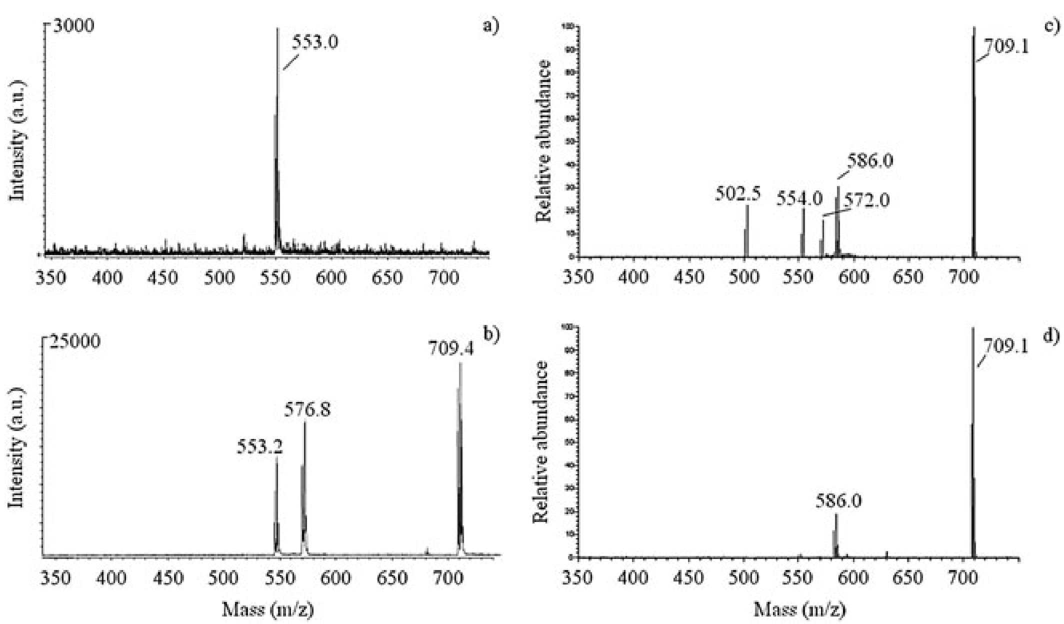


Figure 4. Positive ion mass spectra of complex **8**, $[(dppz)Re(CO)_3(4,4'\text{-bipy})]^+$ (MW = 709.09). (a) LDI mass spectrum, (b) MALDI mass spectrum acquired with DCTB as MALDI matrix, (c) PESI mass spectrum and (d) ESI mass spectrum. **[8]** = 10^{-6} M. Capillary temperature = 150 °C, voltage = 2 kV, current = 0.10 μA, gas flow rate = 30.

553.0 corresponding to the fragment $[M\text{-}(4,4'\text{-bipy})]^+$. This fragment was also observed as an important protonated fragment $[M\text{-}(4,4'\text{-bipy}) + H]^+$ at *m/z* 554.0 in the mass spectra obtained by PESI-MS [see LDI and PESI-MS results in Fig. 4(a) and (c)]. The intact molecular ion as the cation radical $[M]^{+\cdot}$ was detected by MALDI MS when DCTB was used as matrix [Table 1, MALDI, nHo and DCTB columns; Fig. 4(b)]. As expected, no signal was observed in the negative ion mode.

PESI-MS experiments

Although MALDI-MS is a soft ionization technique as was described earlier for most of the organometallic compounds here studied, it was not possible to detect the intact molecular ion, and only fragments produced for the loss of one or more ligands and/or the ligands themselves were detected. The obvious reason was that the analytes studied absorb part of the laser

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photons when the analyte–matrix sample was shot, and as consequence, it is almost impossible to find a proper matrix. As is shown in Table 1 using at least two different MALDI matrixes, more information could be obtained. Thus, we decided to perform PESI-MS experiments to analyze if this newer ionization method is soft enough to produce intact molecular ions, thus providing information about molecular mass of the analytes under study.

PESI-MS experiments were performed with the rhenium complexes in methanol solution using disposable acupuncture needles as electrospray emitters. For the neutral rhenium complexes **1, 2** and **3** [Fig. 1, $L_1Re(CO)_3L_2$, where $L_1 = CF_3SO_3$], a similar fragmentation pattern was observed in PESI-MS experiments [Fig. 5(a)–(c)]. In the positive ion mode, three main signals were observed for those compounds assigned to the fragments $[(M\text{-}CF_3SO_3) + H]^+$, a structure diagnostic peak (Table 1, PESI column) and the species formed by the interchange of ligand with the solvent $[(M\text{-}CF_3SO_3) + H_2O + H]^+$ and $[(M\text{-}CF_3SO_3) + CH_3O + H]^+$ at *m/z* 452.2, 470.4 and 484.0 [Fig. 5(a), compound **1**]; 428.0, 446.0 and 460.0 [Fig. 5(b), compound **2**]; and 515.9, 533.9 and 547.9 [Fig. 5 (c), compound **3**]. The intact molecular ion could not be detected in any case (Table 1, PESI column, compounds **1–3**).

On the contrary, the organometallic complex **4** with structure $L_1Re(CO)_3L_2$, where $L_1 = CH_3CO_2$ and L_2 = phenanthroline (Fig. 1), showed the intact molecular ion as $[M + Na]^+$ at *m/z* 533.0 [Table 1, PESI column; Fig. 5S(a)] together with the signal of ions formed by a similar fragmentation pattern as those described earlier for compounds **1**, **2** and **3**. Thus, the signals of the species $[(M\text{-}CH_3CO_2) + H]^{+\cdot}$ and the species formed by interchange of ligand with the solvent $[(M\text{-}CH_3CO_2) + H_2O + H]^+$ and $[(M\text{-}CH_3CO_2) + CH_3O + H]^+$ at *m/z* 451.61, 470.44 and 484.63 were observed [Fig. 5S(a)]. The different behavior shown by compound **4** and compounds **1**, **2** and **3** could be explained, taking into account that the covalent bond between Re(I) and the ligand CF_3SO_3, (CF_3SO_3–Re), present in these complexes, is weaker than the CH_3CO_2-Re covalent bond present in complex **4**.

Figure 5 shows the positive-ion PESI mass spectra for complexes **5, 6** and **7** [Fig. 1; R-CO_2-$Re(CO)_3$(2,2′-bipy), where R-CO_2^- = naphthalene-2-carboxylate, anthracene-9-carboxylate and pyrene-1-carboxylate, respectively]. In this experiment, it was possible to detect the intact molecular ion for compounds **6** and **7** as the $[M + H]^+$ and $[M + Na]^+$ species at *m/z* 649.1 and 671.1 [Table 1, PESI column; Fig.5(e), compound **6**] and at *m/z* 673.1 and 695.1 [Fig. 5(f), compound **7**; Table 1, PESI column]. Thus, the ligands anthracene-9-carboxylate and pyrene-1-carboxylate remain in the structure, and the intact molecular ion could be detected. In the positive ion mode, compound **5** showed three signals that were also observed for **6** and **7** [Fig. 5 (d)–(f), signals at *m/z* = 428.0, 445.0 and 459.0]. These peaks were assigned to the fragments $[M\text{-}(R\text{-}CO_2) + H]^+$ first, to the species formed by interchange of ligand (R-CO_2) with the solvent $[M\text{-}(R\text{-}CO_2) + H_2O]^+$ second and $[M\text{-}(R\text{-}CO_2) + CH_3O]^+$ third [Fig. 5(d)–(f) and Scheme 1]. Unfortunately, compound **5** did not show the intact molecular ion or a characteristic diagnostic fragment containing the naphthalene-2-carboxylate moiety for its molecular mass assignment [Fig. 5(d)].

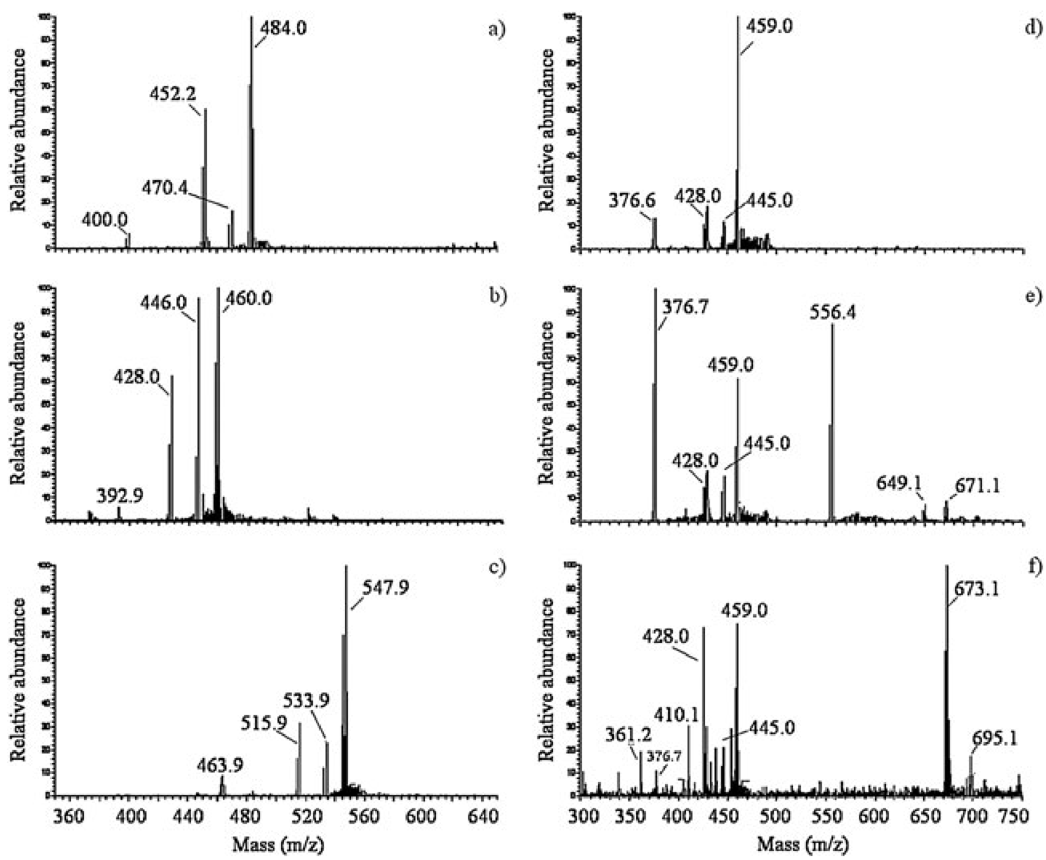

Figure 5. Positive ion PESI mass spectra of complex $L_1Re(CO)_3L_2$, where $L_1 = CF_3SO_3^-$ and (a) compound **1**, L_2 = 1,10-phen (MW = 599.9); (b) compound **2**, L_2 = 2,2′-bipy (MW = 575.9); (c) compound **3**, L_2 = 5,5′-dicarboxy 2,2′-bipy (MW = 663.9); and complex R–CO_2–$Re(CO)_3$(2,2′-bipy), where (d) compound **5**, R–CO_2^- = naphthalene-2-carboxylate (MW = 598.0); (e) compound **6**, anthracene-9-carboxylate (MW = 648.0); and (f) compound **7**, pyrene-1-carboxylate (MW = 672.0).

For the cationic organometallic species **8** {Fig. 1, [(dppz)Re(CO)$_3$ (4,4′-bipy)]$^+$}, the intact molecular ion as [M]$^+$ was detected in the positive ion mode as shown in Fig. 4(c). Together with this signal at *m/z* 709.1, the peaks corresponding to the fragment [M-(4,4′-bipy) + H]$^+$ at *m/z* 554.0 and to the species formed by interchange of ligand with the solvent [M-(4,4′-bipy) + H_2O + H]$^+$ and [M-(4,4′-bipy) + CH_3O + H]$^+$ at *m/z* 572.0 and 586.0, respectively, were observed. Once again, PESI showed to be a proper "softer" ionization technique for the analysis of organometallics. As it was discussed previously, LDI experiments did not show the intact molecular ion, and only clusters and fragments were detected (Table 1, compound **8**, PESI and LDI columns).

ESI-MS experiments

High flow rate electrospray ionization assisted by corona discharge (HF-ESI-CD) taking place at the tip of the electrospray capillary was used to avoid decomposition of the rhenium complexes and to induce specifically one electron exchange (oxidation or reduction). The organometallic complexes were analyzed in the positive and negative ion mode. Intact molecular ions were not detected in the latter (Table 1, ESI column). Nevertheless, for the neutral rhenium complexes **1, 2** and **3** [Fig. 1, L_1Re (CO)$_3$ L_2, where $L_1 = CF_3SO_3$], the intact molecular ion could not be detected in the positive ion mode either. In this ion mode, a fragmentation pattern and interchange of ligand by solvent similar to those described earlier for PESI-MS experiments were observed (Fig. 6S). The only difference is that in PESI experiments, these species were charged because of protonation (Table 1, PESI column, compounds **1**, **2** and **3**), whereas during the HF-ESI-CD experiments, these species were formed from a molecular radical cation [M]$^{+\cdot}$, and protonation did not occur (Table 1, ESI column, compounds **1**, **2** and **3**).

Using ESI-MS as HF-ESI-CD-MS was possible to detect the intact molecular ion of compound **4** [Fig. 1, ($CH_3CO_2^-$)Re (CO)$_3$(1,10-phen)] as the species [M]$^{+\cdot}$ at *m/z* 510.82 in the positive ion mode [Fig. 5S(b)]. Two peaks assigned to the fragment species [M-CH_3CO_2]$^+$ and its corresponding oxidized species [M-CH_3CO_2 + O_2]$^+$ located at *m/z* 451.61 and 482.90, respectively, were also observed [Fig. 5S(b)].

Positive-ion HF-ESI-CD-MS analysis of complexes **5, 6** and **7** [Fig. 1, R-CO_2-Re(CO)$_3$(2,2′-bipy)] showed the intact molecular ion as [M]$^{+\cdot}$ for each analyte [Fig. 7S(a)–(c); Table 1, compounds **5**, **6** and **7**, ESI column]. The characteristic fragmentation yielding the species [M-(R-CO_2)]$^+$ at *m/z* 427.01 was also observed for the three complexes, but the earlier mentioned interchange of ligand by solvent detected in the PESI-MS analysis here did not take place.

Finally, the positive-ion ESI mass spectrum of the cationic organometallic complex **8** {Fig. 1, [(dppz)Re(CO)$_3$(4,4′-bipy)]$^+$} is shown in Fig. 4(d). The signal at *m/z* 709.1 corresponds to the intact molecular ion [M]$^+$ (Table 1, compound **8**, ESI column). The presence of a signal at *m/z* 157.0, assigned to the species [bipy]$^+$, shows that some fragmentation also occurred even using a quite soft ionization method as ESI.

CONCLUSIONS

We demonstrated in this work for the first time that PESI, a recently developed ionization technique, is useful for the study of rhenium complexes. The mass spectra obtained give information about molecular weights and the structures of the compounds studied, because intact molecular ions and characteristic fragments were observed. The experiments were performed with rhenium complexes in methanol solution using disposable acupuncture needles as electrospray emitters. The intact molecular ion of the cationic compound **8** was observed as [M]$^+$, and as [M + H]$^+$ and/or [M + Na]$^+$ species in the case of the neutral compounds **4**, **6** and **7** complexes with R-CO_2- as ligand; R = CH_3 or R = Ar with Ar: aromatic). In the case of complexes with the ligand CF_3-SO_3- (compounds **1**, **2** and **3)**, intact molecular ions were not detected, showing that the oxidation is taking place at the tip of the stainless needle, and the fragmentation and release of the CF_3-SO_3- ligands occur in the ionization chamber.

In the case of compound **5**, an ArCO_2–rhenium complex (Fig. 1), the get proper PESI experimental conditions, in a reproducible way, the intact molecular ion could not be found, although it was observed in some experiments at random.

In ESI experiments, the intact molecular ion of compound **8** [Fig. 1, [(dppz)Re(CO)$_3$(4,4′-bipy)]$^+$], the only cationic complex studied, was easily detected even when conventional parameters for ESI measurements were applied. On the other hand, the neutral complexes studied could not be detected under these experimental conditions. HF-ESI-CD was necessary to detect intact molecular ions in the positive ion mode for compounds **5**, **6** and **7** with structure R-CO_2-Re(CO)$_3$(2,2′-bipy), where R-CO_2^- = naphthalene-2-carboxylate, anthracene-9-carboxylate and pyrene-1-carboxylate and compound **4** with structure CH_3CO_2-Re (CO)$_3$ (1,10-phen). The oxidation of those compounds took place at the tip of the electrospray capillary, producing the intact gas molecular ion as the ionic radical species [M]$^{+\cdot}$ detected (Table 1). For the family of rhenium complexes with the group CF_3SO_3- as ligand (compounds **1**, **2** and **3**, Fig. 1 and Table 1), instead of the group CH_3CO_2- (compound **4**, Fig. 1 and Table 1), the intact molecular ions could not be detected even when HF-ESI-CD was applied. The weaker character of the covalent bond between the CF_3SO_3- ligand and Re(I) would account for this fact.

In general, more efficient fragmentation or decomposition of the analytes was observed when laser desorption ionization methods (LDI and MALDI) were used compared with the ESI methods (PESI, ESI and HF-ESI-CD). However, LDI-MS and MALDI-MS allowed to observe intact molecular ions for organometallic complexes with the structure (CF_3SO_3)Re(CO)$_3$(2,2′-bipy) and (CF_3SO_3)Re(CO)$_3$(5,5′-dicarboxy 2,2′-bipy), whereas by PESI-MS and ESI-MS only fragments, some of which exhibited structural diagnostic characteristic fragments, were observed (Fig. 1 and Table 1, compounds **1** and **3**).

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Supporting Information

Supporting information may be found in the online version of this article.

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