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ANALYSIS OF TEN NOVEL RHENIUM COMPLEXES BY DESORPTION CHEMICAL IONIZATION MASS SPECTROMETRY *

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Summary

The desorption chemical ionization (DCI) mass spectrometry of ten rhenium compounds is compared to the desorption electron impact (DEI) mass spectrometry of the same compounds. Using 10% ammonia in nitrogen as the reagent gas, the DCI mass spectrometric (MS) technique provided $[M+H]^+$ ions for each rhenium compound. In most cases, the DEIMS method provided only fragment ions.

Introduction

While electron impact (EI) mass spectrometry (MS) has proven to be a useful method for the study of organometallic compounds [1–4], conventional EIMS techniques often fail to provide molecular weight information [1]. Field desorption (FD) MS has more recently been shown to be a valuable technique for providing molecular weight information for organometallic complexes [1,5,6]. Indeed, FDMS analysis of rhenium complexes has been reported [5]. Following the introduction of fast atom bombardment (FAB) ionization, mass spectrometry has become a major analytical tool for the study of organometallic compounds [6–9]. Because many mass spectrometric laboratories do not have FAB or FD capability, the ability to analyze thermally sensitive organometallic compounds by conventional mass spectrometry is still of considerable interest. Therefore, we have investigated the combined use of the

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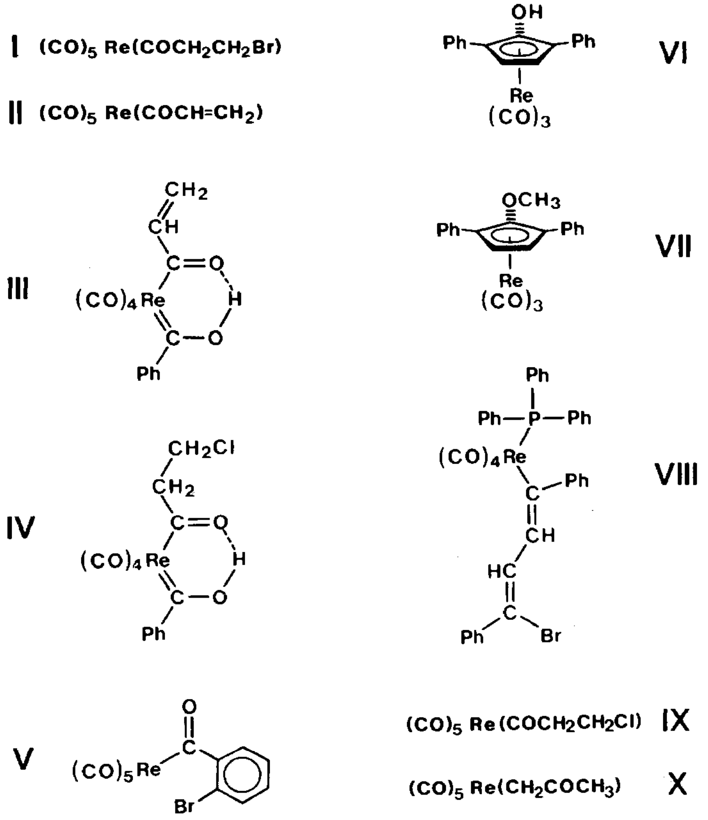

Fig. 1. Structures of the ten rhenium complexes investigated in this study.

desorption probe and chemical ionization (CI) as an alternate method for the MS analysis of certain classes of organometallic compounds. A description of desorption CIMS methodology and its historical development is provided by Cotter [10].

Organorhenium complexes are potentially useful in the study of stoichiometric and model catalytic processes due to their high stability. We are currently pursuing the synthesis and MS analysis of a variety of organorhenium compounds. Recently we have proposed a rhenabenzene intermediate in the reaction of (*E*,*E*)-1,4-dilithio-1,4-diphenylbutadiene with $PPh_3(CO)_4ReBr$ [11]. This reaction gives as products (after methylation or protonation) substituted cyclopentadienyl complexes VI and VII (Fig. 1). We are also pursuing the synthesis of rhenium acyl complexes [12] and Lukehart type rhena(acetylacetonate) complexes [12] containing functional groups, such as halogens, bonded to the acetylacetonate ligands. Such functionalized complexes may serve as useful intermediates in organic syntheses [13]. The convenient and accurate mass spectral identification of new organorhenium complexes is vital to these studies. In this report, the analysis of these newly synthesized compounds by desorption chemical ionization (DCI) mass spectrometry (MS) using 10% ammonia in nitrogen as the reagent gas is described. This study suggests that this technique may be applicable to organotransition metal complexes. For comparison, the compounds were also analyzed by desorption electron impact (DEI) MS. This paper presents the results of this study.

Experimental

Rhenium compounds

η^5-(1,3-diphenyl-2-hydroxycyclopentadienyl)tricarbonylrhenium (VI), η^5-(1,3-diphenyl-2-methoxycyclopentadienyl)tricarbonylrhenium (VII) and η^1-(4-bromo-1,4-diphenylbutadienyl)triphenylphosphinetetracarbonylrhenium (VIII) were synthesized as described elsewhere [11]. η^1-(3-bromopropionyl)pentacarbonylrhenium (I), η^1-(propenoyl)pentacarbonylrhenium (II), (2,2,2,2-tetracarbonyl-2-λ^6-rhena-4-penten-1,3-dionyl)benzene (III), (2,2,2,2-tetracarbonyl-2-λ^6-rhena-5-chloropentan-1,3-dionyl)benzene (IV), (2-bromobenzoyl)pentacarbonylrhenium (V), (3-chloropropionyl)pentacarbonylrhenium (IX) and pentacarbonylrhenium(propanone) (X) were prepared in a manner similar to that described elsewhere [12].

Mass spectrometry

Electron impact (EI) mass spectrometry (MS) was performed using a Finnigan 4023 quadrupole mass spectrometer. Samples were introduced into the MS via a Vacumetrics in-beam desorption probe. The MS source temperature was set at 270°C, with the electron energy set at 70 eV. For ammonia chemical ionization (NH_3CI)MS, the source temperature was set at 200°C, and the source pressure was adjusted to 0.25 torr (uncorrected reading) by flowing in 10% NH_3 in nitrogen gas. Samples were vaporized via the same Vacumetrics DCI probe equipped with a Pt wire tip and using a heating ramp of 50 mA s^{-1} for 60 s.

One sample was also analyzed by high resolution (HR) MS for additional confirmation using a Kratos MS50 operating at 7000 resolution. The MS50 was operated in the EI mode with a source temperature of 250°C. Measurements were made by peak matching to ions from PFTBA.

Results and discussion

Ammonia chemical ionization MS has been shown to be a useful technique for the analysis of certain types of compounds such as folic acid derivatives [14], substituted benzenes [15], steroids [16,17], and substituted anilines [18], glucuronides [19] and isofenphos [20]. DCIMS has been found to be a useful method for the analysis of thermally labile compounds [10]. Recently, DCIMS using ammonia as the reagent gas was found to be a valuable technique for the analysis of guanidino compounds [21]. Thus, this technique seemed to be a viable soft ionization method for the analysis of rhenium complexes.

Figure 1 displays the structures of the rhenium compounds that were investigated in this study. Figure 2 shows the mass spectra of V via the DCIMS technique (2a) and the DEIMS method (2b). The DCIMS results for V consisted of ions corresponding to $[M+H]^+$, $[M+NH_4]^+$, $[M+H-CO]^+$ and $[M+H-C_6H_5Br]^+$. The DEIMS data include a small M^+ peak followed by a series of fragment ions corresponding to loss of the CO ligands from the molecular ion, and also from the $[M-C_6H_4Br]^+$ ion at m/z 355. Therefore, the DCIMS results provide molecular ion information, but the DEIMS results provide complementary fragment ion information. Figure 3 compares the mass spectra of VI by EI (3a) and NH_3CI (3b) techniques. The NH_3CI results display a cluster at m/z 505 which corresponds to the $[M+H]^+$ ion. The cluster at m/z 522 corresponds to the $[M+NH_4]^+$ ion. The

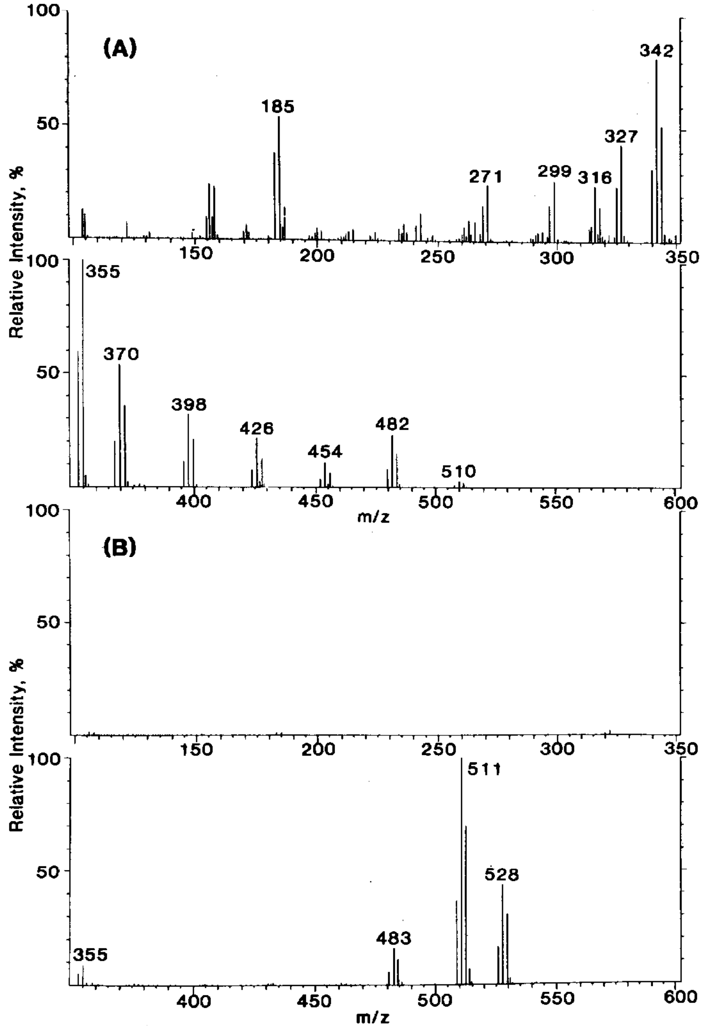

Fig. 2. EI mass spectrum (a) and NH_3CI mass spectrum (b) of V.

peaks at *m/z* 502 and 504 are thought to be due to $[M + NH_4 - H_2O]^+$ but could also be M^+ ions formed by a charge exchange mechanism due to the nitrogen in the CI gas. The EI results provide a molecular ion as the base peak at *m/z* 504. The *m/z* 476 peak can be assigned to $[M - CO]^+$ ion. Further fragmentation appears to be due to a combination of CO losses and losses due to rearrangement processes.

Table 1 lists the results obtained in the analysis of the ten rhenium compounds by DCIMS with ammonia as the reagent gas and compares these to the DEIMS results of the same compounds for the molecular ion region. As shown in Table 1, all the rhenium complexes produced $[M + H]^+$ ions when analyzed by the DCIMS technique using ammonia as the reagent gas. In addition, under these conditions, most of the compounds also displayed $[M + NH_4]^+$ ions. Two of the compounds (VI and VII) may have produced $[M + NH_4 - H_2O]^+$ ions under the DCIMS conditions; this reaction is reasonable for VI because it contains an OH function. Compound

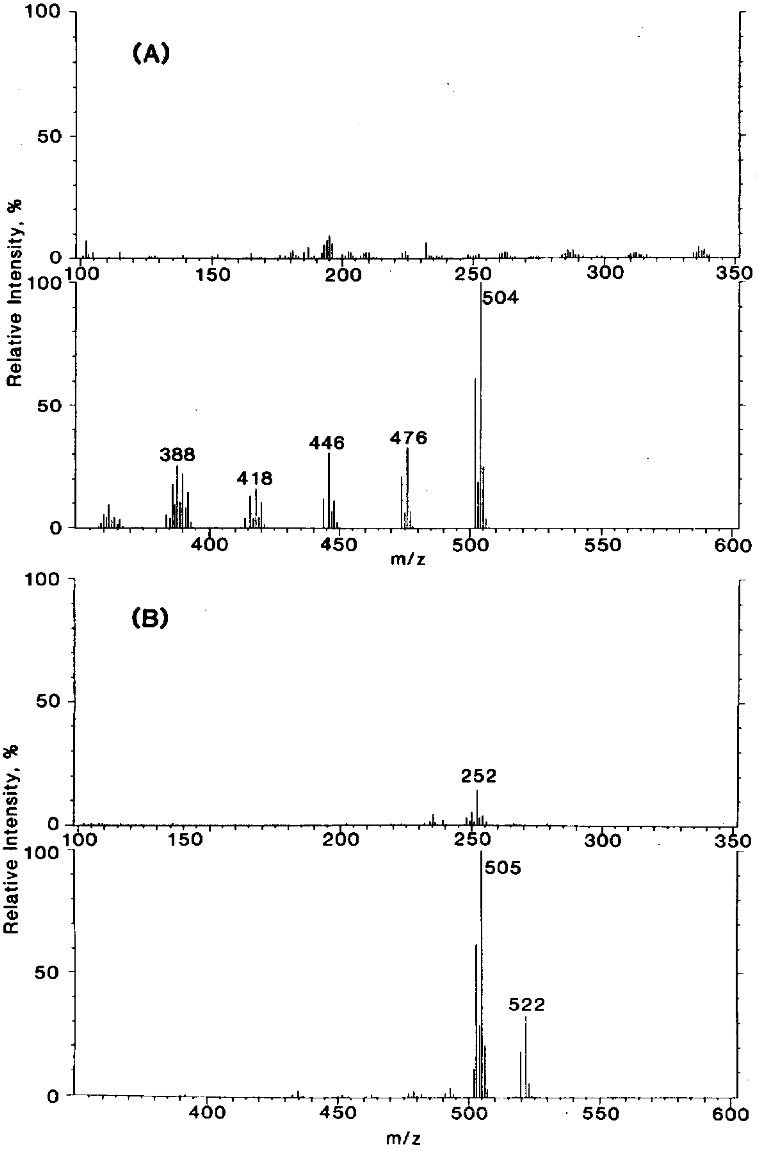

Fig. 3. EI mass spectrum (a) and NH_3CI mass spectrum (b) of VI.

VII, on the other hand, contains an OCH_3 function, presumably formation of the $[M + NH_4 - H_2O]^+$ for this compound would involve a rearrangement step. Alternately, these ions could be M^+ ions formed via charge exchange due to the nitrogen in the CI gas.

The DEIMS results for these compounds often lack molecular weight information. The one significant exception is VI which provided a base peak molecular ion under DEIMS conditions. Besides VI, only V and X gave a detectable M^+ ion under DEIMS conditions. The results in Table 1, therefore, demonstrate the utility of the DCIMS technique with ammonia as the reagent gas, for the analysis of rhenium complexes.

TABLE 1

PERCENT RELATIVE INTENSITIES OF IONS DETECTED IN THE MOLECULAR ION REGION FOR A SERIES OF RHENIUM COMPOUNDS ANALYZED BY DCIMS AND DEIMS[a,b]

Compound	MW[c]	DCIMS (NH_3)			DEIMS		
		$[M+H]^+$	$[M+NH_4]^+$	M^{+d}	M^+	$[M-H]^+$	$[M-CO]^+$
I	462	16	7	–	–	–	78[e]
II	382	100	10	–	–	–	–
III	460	14	2	–	–	0.6	2
IV	496	17	–	–	–	–	–
V	510	100	44	–	3	–	23
VI[f]	504	100	33	11	100	–	33
VII	518	100	17	8	–	–	–
VIII	844	3	–	–	–	–	–
IX	418	35	100	–	–	–	–
X	384	100	3	–	53	–	98

[a] The listed percent intensity is for the highest peak in the cluster. [b] "–" means not detected. [c] Calculated isotopic molecular weight. [d] Or $[M+NH_4-H_2O]^+$. [e] For $[M-2(CO)]^+$; $[M-CO]^+$ not detected.

[f] HRMS results: 502.033 daltons for the $[C_{20}H_{13}O_4{}^{185}Re]^+$ molecular ion, the calculated mass is 502.034, the difference = 1u, which is 2 ppm.

Thus, as shown by the data in Table 1 and Figs. 2 and 3, DCIMS using ammonia as the reagent gas has been found to be a useful technique for characterizing rhenium complexes. In addition, DEIMS can provide complementary fragment ion information on this type of compound. This ability to perform conventional mass spectrometry to obtain molecular weight information for rhenium complexes should prove to be a useful tool for organometallic chemistry. The DCIMS analysis of organotransition metal complexes containing metals other than rhenium is currently under investigation.

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