

LD FTMS Investigation of Rh(I) Complexes with Chiral 1,5-Bisnitrogen Ligands

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Received October 25, 1993.

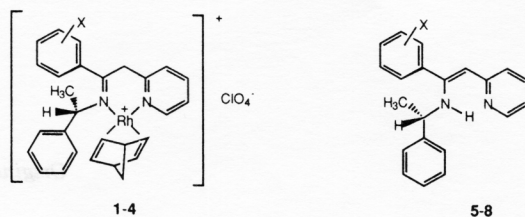
Laser Desorption/Ionization (LD/I) in combination with Fourier Transform Mass Spectrometry (FTMS) was applied to characterize and obtain molecular weight information on Rh(I) complexes with chiral 1,5-bisnitrogen ligands **1-4**.

INTRODUCTION

Conventional electron impact (EI) mass spectrometry has long been employed in the analysis and characterization of some organometallic molecules, but severe limitations emerged when it was applied to nonvolatile, thermolabile and high molecular weight compounds. Laser desorption/ionization (LD/I),¹ in combination with Fourier transform mass spectrometry (FTMS),²⁻⁴ has proven to be one of the most useful recent developments in the soft ionization techniques. The pulsed laser desorption technique consists of focusing the output of a high-power pulsed laser onto the surface of the sample to be analyzed and using mass spectrometry to analyze the generated ions. This has considerably increased the range of organometallic compounds that could be studied by mass spectrometry.

For determination of molecular weight information, LD compares well only with FAB (Fast Atom Bombardment) as a desorption method. However, there is a clear superiority of LD in that it does not require dissolution of the sample in a viscous matrix, with the possible problems of limited solubility and potential solvolysis associated with this preliminary step. Another obvious advantage is that LD, in contrast to FAB, can be conveniently coupled with FT mass spectrometry, providing a corresponding considerable increase in resolution and sensitivity.

The Rh(I) complexes **1-4** with *S*- α -methyl-[1-(substituted phenyl)-2-(2'-pyrido)-1-ethylidene] benzylamines **5-8** are interesting catalytic compounds.⁵ The role played by weak π -donor 1,5-bisnitrogen ligands is critical for the stabilizing and fine tuning of the reactivity of the metal centre in catalysis. This resulted in a shift of the C=C double bond in ligands (enamines) **5-8** to C=N (imines) in complexes **1-4**, as confirmed by the X-ray analysis of **2** and **6**.⁵



	X
1, 5	4'-CH ₃
2, 6	2'-C ₆ H ₅
3, 7	4'-Cl
4, 8	4'-Br

Here, we report the application of LD FTMS to characterize Rh(I) complexes **1–4** with chiral 1,5-bisnitrogen ligands **5–8**.

EXPERIMENTAL

The LDFT mass spectrometric system used consists of an Extrel FTMS 2001 DD instrument equipped with a 3 Tesla superconducting magnet, interfaced to a Quanta Ray DCR-11 pulsed Nd YAG laser. LD investigations of complexes **1–4** were performed at 1064 nm wavelengths. EI mass spectral analyses of ligands **5–8** were performed at 70 eV.

The Rh(I) complexes **1–4** were synthesized by reaction of Rh[norbornadiene]₂ perchlorate with the corresponding *S*- α -methyl-[1-(substituted phenyl)-2-(2'pyrido)-1-ethylidene] benzylamine.⁵ *S*- α -methyl-[1-(substituted phenyl)-2-(2'pyrido)-1-ethylidene] benzylamines **5–8** were prepared by condensation of the corresponding ketomethylpyridine and *S*-(-)-methylbenzylamine.⁵

RESULTS AND DISCUSSION

The LD mass spectra of the series of Rh(I) complexes **1–4** are shown in Figures 1 and 2.

The LD mass spectra of complexes **1** and **2** (X = 4'-CH₃, 2'-C₆H₅), Figure 1, are dominated by peaks due to molecular ions, which form the base peaks. The abundance of molecular ions decreases in the LD mass spectra of **3** and **4** (X = 4'-Cl, 4'-Br). It seems that the presence of halogen, as an electron-withdrawing substituent increases the tendency to Rh[norbornadiene] elimination from the molecular ions of **3** and **4**, and formation of the fragment ions of *m/z* 195. The peak due to norbornadiene elimination appears in the mass spectra of **2** (X = 2'-C₆H₅) at *m/z* 479. The other observed fragment species in the LD mass spectra of **1–4** are well related to the proposed structures of complexes and are in accordance with the mass spectra of the ligands.

The EI mass spectra of ligands **5–8** show prominent molecular ions and an almost uniform fragmentation of these molecules. The general fragmentation pattern of their molecular ions involves a loss of [C₆H₄NCH] and C₆H₄NCH₃, including the pyridine ring, as well as [C₆H₅CH₃CH] and [C₆H₅CH₃CH NH] which include the benzylamine part of the molecule, to give ions [M-91]⁺, [M-93]⁺, [M-105]⁺ and [M-120]⁺, respectively.

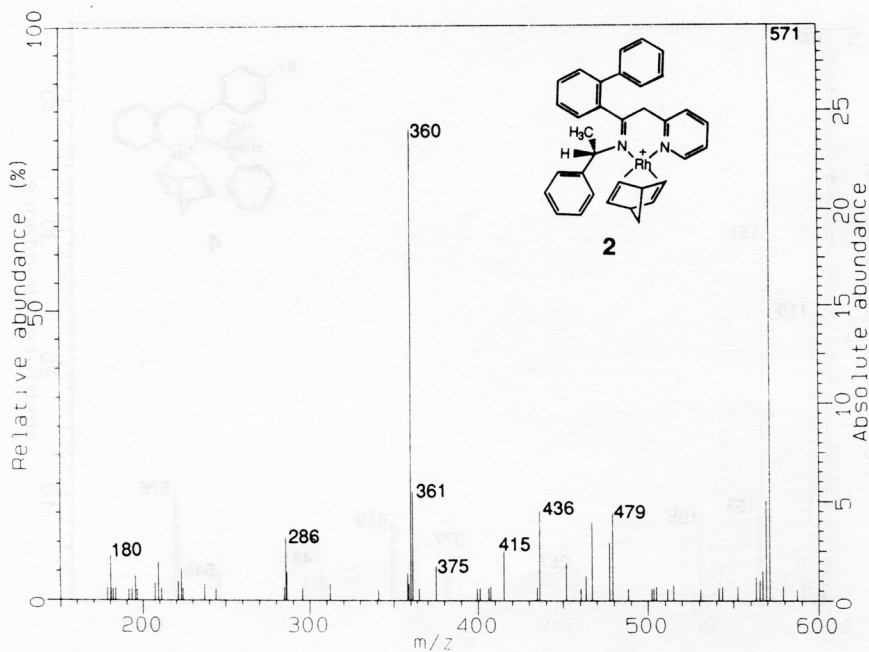
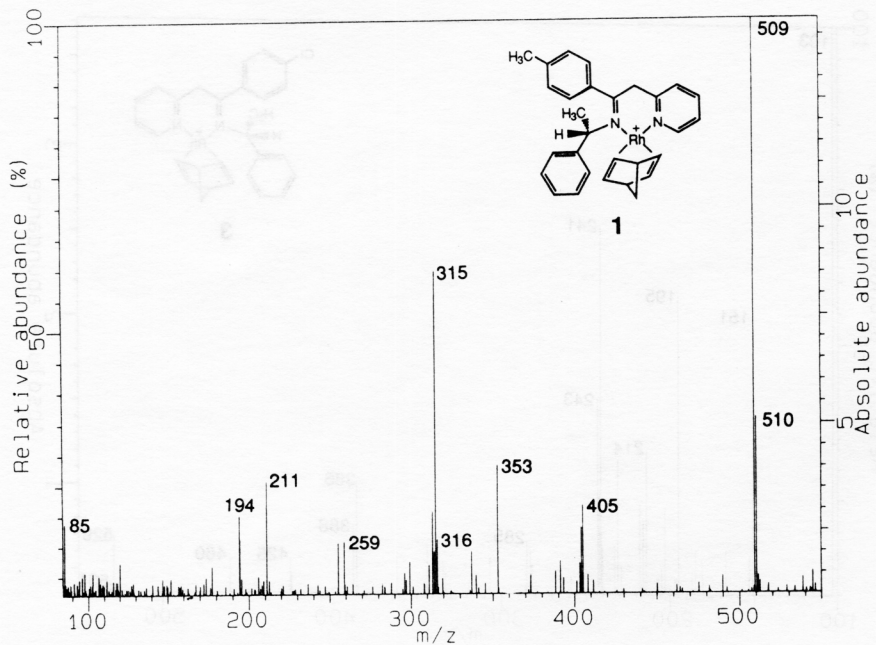
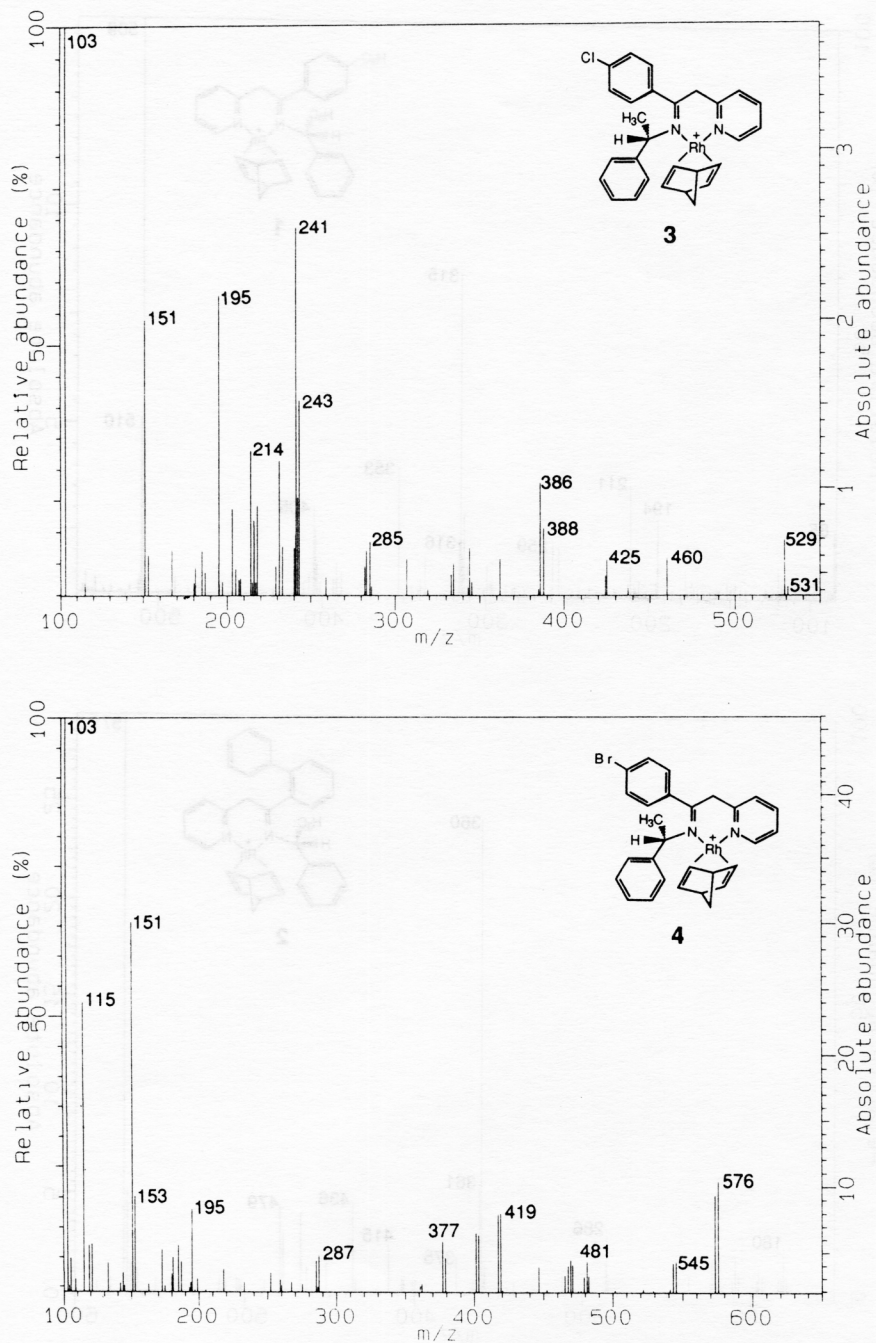


Figure 1. LD mass spectra of Rh(I) complexes **1** and **2**

Figure 2. LD mas spectra of Rh(I) complexes **3** and **4**

In conclusion it can be stated that the LD FTMS method can be successfully applied to studies of the stability and structure of large organometallic complex molecules.

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SAŽETAK

Istraživanje kompleksa Rh(I) s kiralnim 1,5-bisdušikovim ligandima s pomoću LD FTMS

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Karakterizacija i određivanje molekulskih težina Rh(I) kompleksa s kiralnim 1,5-bisdušikovim ligandima provedeno je primjenom laserske desorpcije/ionizacije (LD/I) u kombinaciji s Fourier-transformiranom spektrometrijom masa (FTMS).