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Characterization of chromium–carbene complexes by high-performance liquid chromatography–mass spectrometry with particle beam interface

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Abstract

High-performance liquid chromatography (HPLC) coupled with mass spectrometric (MS) detection was used to separate and characterize a series of chromium–aminocarbene and alkoxy carbene complexes of the Fischer type, some of which were synthesized as new compounds. Chromium–carbene complexes are known to have interesting photochemical properties. The separation of all the compounds examined was performed under normal-phase conditions and a particle beam LC–MS interface was used. The acquisition of positive-ion and negative-ion chemical ionization mass spectra of the eluates was performed. The use of the LC–PB–MS system demonstrated the potential role of this technique in the elucidation of the structure of polar organometallic compounds, such as the carbene complexes of chromium examined.

Keywords: Liquid chromatography–mass spectrometry; Chromium–carbene complexes; Carbene complexes; Organometallic compounds

1. Introduction

The use of HPLC in the field of organotransition metal chemistry is now well consolidated, because HPLC has allowed rapid and efficient separations of a large number of organometallic compounds, including homo- and heterometallic clusters of different nuclearity. Some reviews [1,2] and recent papers [3–5] have described the state-of-the-art of HPLC in this area. On the other hand, the use of traditional detection systems such as spectrophotometric, fluorimetric

and amperometric methods gives scant information about the nature of the eluates and about the modifications which may occur in the chromatographic system. The interest in analyte identification and the opportunity of obtaining structural confirmation offered by mass spectrometry has generated considerable interest in developing an MS detector for HPLC.

The use of on-line coupled liquid chromatography–mass spectrometry (LC–MS) allows the separation of non-volatile and thermolabile compounds, not suitable for GC analysis, and provides structural information on the components of mixtures, even complex ones. Previous studies

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have demonstrated that the LC–particle beam MS (LC–PB–MS) system can be successfully used for the simultaneous separation and identification of some non-polar acetylenic derivatives of ruthenium–carbonyl [6] and of some iron–carbonyl dinuclear complexes [7].

Among organometallic compounds, Fischer-type carbene complexes have been the subject of much interesting and important work all over the world [8]. Their peculiar reactivity (both thermal and photochemical) makes them suitable substrates for access to important classes of organic compounds such as α -amino acids, β -lactams, quinones, γ -butyrolactones, cyclobutanones and many others. Chiral aminocarbene complexes have also been successfully employed in stereoselective organic synthesis [9–11]. In addition, since the pentacarbonylchromium unit is an electron-withdrawing group, Fischer-type carbene complexes can be specifically designed as “push–pull” organometallic compounds potentially useful in the field of non-linear optics. Complex IV is an example which was subjected,

together with some other carbene complex derivatives, to a preliminary study in the above field [12].

The aim of this study was to investigate the capability of LC–PB–MS to determine polar organometallic compounds, such as the chromium–carbene complexes reported in Fig. 1.

2. Experimental

2.1. Synthesis of and analytical and spectroscopic data for complexes I, II, IV and VI

^1H NMR spectroscopic measurements were made using Varian XL300 (300 MHz), XL200 (200 MHz) and WP 80 ST (80 MHz) instruments. All of the NMR spectra were taken in CDCl_3 and the samples were filtered through Millex-SR 0.5- μm filters (Waters–Millipore, Milford, MA, USA) before measurements were taken. IR spectra were recorded using Perkin-Elmer Model

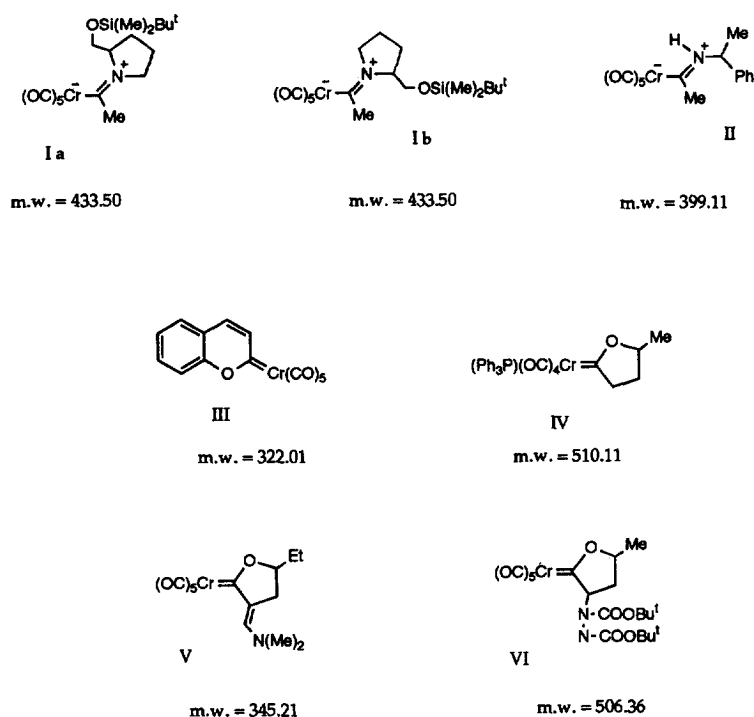


Fig. 1. Structures and molecular masses of the complexes.

298 and FT-IR 1725X1 spectrophotometers. All the reactions were carried out under an inert atmosphere (nitrogen or argon). Tetrahydrofuran (THF) and diethyl ether were freshly distilled over sodium wire with benzophenone under a nitrogen atmosphere just before use. All the chromatographic purifications were accomplished using silica gel (230–400 mesh). Pentacarbonyl- and triphenylphosphinotetracarbonyl(methoxymethylcarbene)chromium were prepared according to the literature [13,14]. All the reagents used were commercially available (Fluka, Merck). Complexes **III** and **V** are known compounds [15,16].

Complex I

Imidazole and *tert*-butyldimethylsilyl chloride were added to a solution of pentacarbonyl(methoxymethylcarbene)chromium and (*S*)-prolinol in THF. After 30 min at 30°C and then 30 min at room temperature, complex **I** was isolated, in 90% yield, as a 5:1 mixture of isomers **Ia** and **Ib**, after flash column chromatography [eluent hexane–dichloromethane (5:1)]. Isomers **Ia**: $[\alpha]_D = +275^\circ$ (CHCl_3 , $c = 0.0128$); IR (neat), $\nu(\text{CO } cis)$ 1972, 1979–1860 cm^{-1} ; $^1\text{H NMR}$, δ 0.05 [s, 6H, $\text{Si}(\text{CH}_3)_2$], 0.9 [s, 9H, $\text{Si}(\text{CH}_3)_3$], 2.0–2.25 (m, 4H, CH_2CH_2), 2.7 (s, 3H, $\text{Cr}=\text{C}-\text{CH}_3$), 3.5–3.7 (m, 2H, CH_2N), 3.80–3.85 (m, 2H, CH_2O), 4.65–4.70 (m, 1H, CHN); $^{13}\text{C NMR}$, δ 269.9 ($\text{Cr}=\text{C}$), 223.4 ($\text{CO } trans$), 219.2 ($\text{CO } cis$), 71.3, 65.3, 41.6, 25.9, 18.2, –5.6. Found, C 49.62, H 6.5, N 3.5%; $\text{C}_{18}\text{H}_{27}\text{CrNO}_6\text{Si}$ requires C 49.88, H 6.24, N 3.23%. Isomer **Ib**: $[\alpha]_D = +147^\circ$ (CHCl_3 , $c = 0.0163$).

Complex II

A solution of pentacarbonyl(methoxymethylcarbene)chromium and (+)- α -benzylmethylamine in diethyl ether was made to react at room temperature for 10 min; compound **II** was isolated in 90% yield by purification of the crude reaction mixture using flash column chromatography. IR (Nujol), $\nu(\text{NH})$ 3358 cm^{-1} , $\nu(\text{CO } carbonyls)$ 2045, 1972, 1945–1840 cm^{-1} . $^1\text{H NMR}$, δ 1.65 (d, 3H, CH_3CH), 2.6 (s, 3H, C_{carb} –

CH_3), 5.0 (m, 1H, CH), 7.2–7.5 (m, 5H, arom), 9.0 (broad s, 1H, NH).

Complex IV

Complex **IV** was synthesized in 50% yield from triphenylphosphinotetracarbonyl(methoxymethylcarbene)chromium and propylene oxide in diethyl ether, using the procedure described for analogous cyclic carbene complexes [17]. M.p. 93–94°C (*n*-pentane); IR (Nujol), $\nu(\text{CO } carbonyls)$ 2010, 1915, 1900, 1890 cm^{-1} ; $^1\text{H NMR}$, δ 0.7–1.1 [m, 2H, $\text{CH}_2\text{CH}(\text{CH}_3)$], 1.25 (d, 3H, CH_3), 3.1 (dd, 1H, CHHC_{carb}), 3.5 (dd, 1H, CHH), 4.65 [m, 1H, $\text{CH}(\text{CH}_3)$], 7.2–7.6 (m, 15H, PPh_3). Found, C 63.81, H 4.10%; $\text{C}_{27}\text{H}_{23}\text{CrO}_5\text{P}$ requires C 63.53, H 4.50%.

Complex VI

The carbanion generated from pentacarbonyl(3-methyl-2-oxacyclopentylidene)chromium and *n*-BuLi was made to react with di-*tert*-butyl azodicarboxylate in THF as solvent, for 2 h at –78°C. Complex **VI** was recovered in 70% yield after purification by flash column chromatography. M.p. 135°C (hexane); IR (Nujol), $\nu(\text{NH})$ 3386, $\nu(\text{CO } trans)$ 2064, $\nu(\text{CO } cis)$ 1995, 1968, 1940, 1013, 1756, 1706; $^1\text{H NMR}$, δ 1.5 [s, 18H, $\text{C}(\text{CH}_3)_3$], 1.8 (d, 3H, CH_3), 2.4 (m, 2H, CH_2), 5.0 (m, 2H, $\text{CH}-\text{CH}$), 6.0–7.0 (m, 1H, NH); $^{13}\text{C NMR}$, δ 28.0, 28.1, 31.3, 81.9, 82.7, 94.7, 155.8, 216.0, 223.0, 368.0. Found, C 47.91, H 4.97, N 5.13%; $\text{C}_{20}\text{H}_{26}\text{CrN}_2\text{O}_{10}$ requires C 47.43, H 5.14, N 5.53%.

2.2. Chromatography

The liquid chromatograph consisted of a Hewlett-Packard (Palo Alto, CA, USA) HP 1090 and a Rheodyne (Cotati, CA, USA) Model 7125 injector fitted with a 20- μl sample loop. A Hewlett-Packard HP 1050 Series variable-wavelength UV detector was used, monitoring the eluates at 254 nm. Separations were carried out on a stainless-steel column (25 cm \times 0.46 cm I.D.) filled with 5- μm LiChrosorb Si-60 or RP-18

(Merck, Darmstadt, Germany) at a flow-rate of 0.8 and 1.0 ml/min in the case of MS and UV detection, respectively. Under normal-phase conditions, a heptane–dichloromethane (80:20) isocratic mixture was used for the elution of **I** and **II**. For the separation of **III–VI** the following elution programme was used: heptane–dichloromethane (40:60), 1 min; dichloromethane from 60% to 100% in 3 min, with a linear gradient; dichloromethane 100%, held for 8 min. Various methanol–acetonitrile mixtures were employed for the elution of the compounds in reversed-phase chromatography.

Dichloromethane solutions of complexes **I–VI** (20 μ l) were injected; the amounts of metal injected were in the microgram range.

Preliminary investigations without the HPLC column [flow-injection analysis (FIA) mode] were carried out in order to optimize the transfer of the analytes through the interface.

Heptane and dichloromethane (HPLC grade) were purchased from Lab-Scan (Dublin, Ireland).

2.3. Mass spectrometry

A Hewlett-Packard HP 5989A mass spectrometer coupled with an HP 59980A particle beam LC–MS interface was used. Fragmentation was obtained using chemical ionization (CI); signals were acquired in both positive-ion (PCI) and negative-ion (NICI) full-scan modes. Methane was used as the CI reagent gas at ca. 1.1 Torr (1 Torr = 133.322 Pa); the ionization energy was 230 eV and the electron multiplier was set at 2350 V. The mass range scanned was 105–550 u for all the compounds examined. The source and the quadrupole temperatures were 250 and 100°C, respectively.

The desolvation chamber of the PB interface was held at 45°C; the nebulizer helium pressure was 45 psi (1 psi = 6894.76 Pa) and the capillary position was extended ca. 1 mm from the nebulizer tip in the nebulizer body.

Data acquisition was performed with an HP MS 59940A Chem Station (HP-UX series).

3. Results and discussion

All the pentacarbonylchromium–carbene complexes examined (**I–VI**) were efficiently separated using a silica column with heptane–dichloromethane mixtures.

The aminocarbene derivatives were separated under isocratic conditions, whereas the separation of the alkoxy carbene complexes required gradient elution. Under reversed-phase conditions the separations, which were carried out using methanol–acetonitrile mixtures as mobile phase, were unsatisfactory; in fact, all the compounds were eluted within about 1 min and the retention times appeared to be scarcely affected by the composition of the mobile phase. This behaviour suggests that the separation mechanism is influenced by steric features more than the polarity of the compounds.

The use of a flow-rate (0.8 ml/min) higher than those recommended (0.4–0.5 ml/min) for the optimum PB interface operating conditions caused only a moderate reduction in sensitivity.

Fig. 2 shows the isocratic separations of the first set of compounds (aminocarbenes **Ia**, **Ib** and **II**) obtained with UV detection at 254 nm and with MS detection under PICI conditions. A comparison between the UV trace and the total ion chromatogram (TIC) exhibits excellent chromatographic fidelity and just a slight peak broadening caused by the PB interface. In both instances elution was obtained by using heptane–dichloromethane (80:20, v/v). The slight shift observed in the retention times is due to the different flow-rate conditions. The chromatographic behaviour towards silica of the chromium–aminocarbene complexes examined depends on the steric hindrance around the nitrogen atom. In the case of **Ia** and **Ib**, the presence of a bulky cyclic substituent on the nitrogen atom gives rise to shorter retention times compared with **II**, which can interact more strongly with the stationary phase. Because of the same steric hindrance, the more shielded *E* stereoisomer (**Ib**) elutes after the *Z* derivative (**Ia**).

The PICI mass spectra of **Ib** and **II** are shown

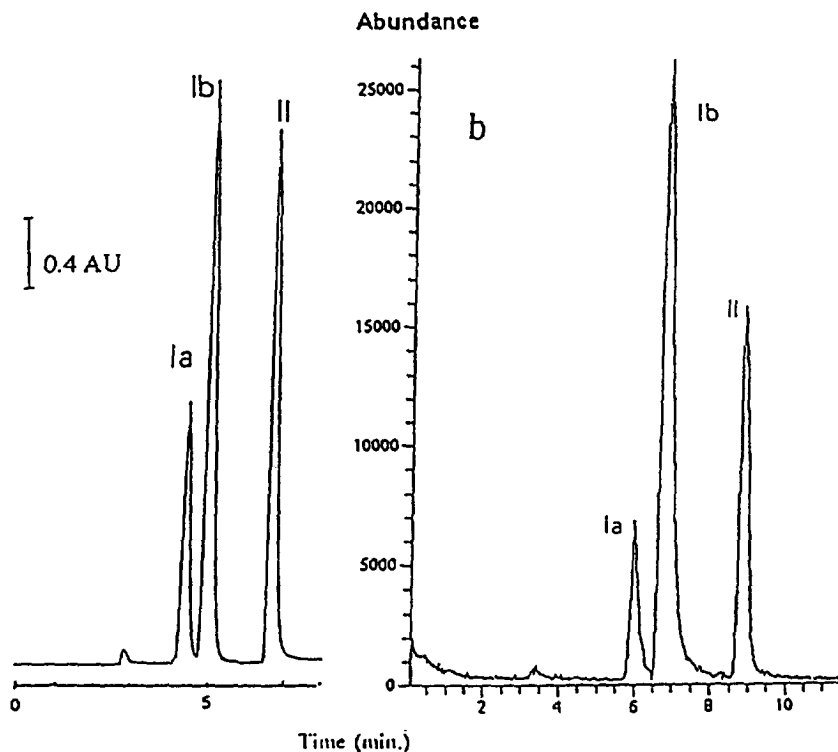


Fig. 2. Comparison of chromatograms of an aminocarbene mixture of **Ia**, **Ib** and **II** with (a) UV detection at 254 nm and (b) MS detection, TIC signal. Chromatographic conditions: column, LiChrosorb Si-60; mobile phase, heptane–dichloromethane (80:20); flow-rate, 1.0 ml/min for LC–UV, 0.8 ml/min for LC–MS. MS conditions: CI source, positive-ion signal; scan range, 105–550 u.

in Fig. 3. As expected, the *Z* and *E* stereoisomers of **I** have the same mass spectra. Because of the low stability of complex **I**, the molecular ion M^+ is visible at m/z 433 with very low abundance (ca. 1%) in the spectrum (Fig. 3a); on the other hand, the more stable compound **II** shows the molecular ion (m/z 339) together with the protonated form $[M + H]^+$ with abundances of 23% and 19%, respectively (Fig. 3b). Fragments due to the gradual loss of the carbonyl ligands (up to five) are present in the spectra at 28-u intervals. Compound **I** shows its main peak at m/z 242, corresponding to the fragment ion $[M - Cr(CO)_5]^+$; in the case of derivative **II** the release of three CO groups is favoured, even though the cleavage of the Cr–C bond and the loss of the $Cr(CO)_5$ moiety seem to be fairly easy (87%).

The results for the NICI mass spectra are

summarized in Table 1. It can be seen that there is no substantial difference between the PICI and NICI mass spectra: both give the same structural information about the compounds examined. The choice of the PICI operating mode was determined by the best response in terms of sensitivity, which was higher by one order of magnitude.

The second set of compounds analysed consisted of four chromium–alkoxycarbene complexes of the Fischer type. The normal-phase chromatographic separation obtained with LC–PB–MS is shown in Fig. 4.

Because of the greater polarity due to the presence of the oxygen atom, the elution of these compounds required a higher percentage of dichloromethane (from 60% to 100%) in the mobile phase. There are three important resonance structures (**A–C**) for heteroatom-substi-

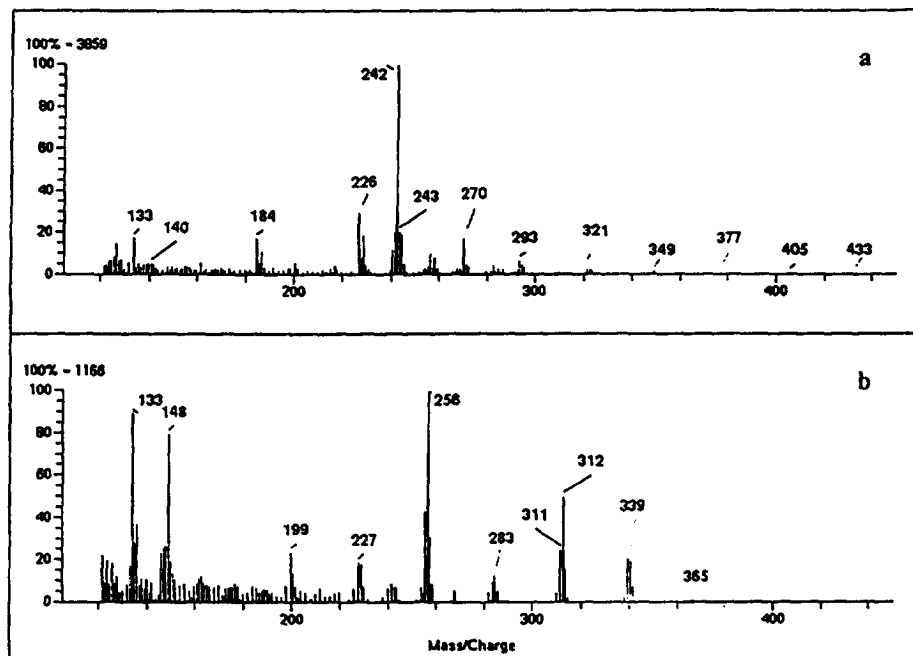


Fig. 3. LC-PB-PICI mass spectra of (a) **Ib** and (b) **II**. Conditions as in Fig. 2.

Table 1
NICI mass spectra of compounds **Ia**, **Ib** and **II**

Compound	<i>m/z</i>	Abundance (%)	Ion
Ia, Ib	405.05	1	$[M - CO]^-$
	377.05	1	$[M - 2CO]^-$
	348.95	1	$[M - 3CO]^-$
	344.05	9	$[M - 3CO - CH_3]^-$
	322.00	6	$[M - 4CO]^-$
	293.05	12	$[M - 5CO]^-$
	242.05	100	$[M - Cr(CO)_5]^-$
	226.15	17	$[M - Cr(CO)_5 - CH_3]^-$
184.15	9	$[M - Cr(CO)_5 - Bu^1]^-$	
II	338.95	6	$[M]^-$
	310.95	22	$[M - CO]^-$
	282.90	11	$[M - 2CO]^-$
	255.95	100	$[M - 3CO]^-$
	239.95	39	$[M - 3CO - CH_3]^-$
	228.00	34	$[M - 4CO]^-$
	199.00	21	$[M - 5CO]^-$
	148.10	61	$[M - Cr(CO)_5]^-$
	105.10	100	$[PhCHMe]^-$

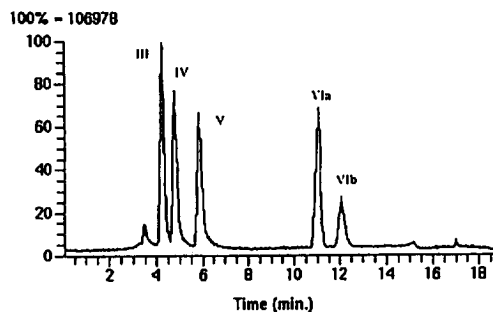


Fig. 4. Total-ion chromatogram of the alkoxy-carbene **III–VI** mixture. Elution programme: heptane–dichloromethane (40:60), 1 min; dichloromethane 60–100% in 3 min, with linear gradient; dichloromethane 100%, held for 8 min. Column, LiChrosorb Si-60; flow-rate, 0.8 ml/min. MS conditions as in Fig. 2.

tuted carbene complexes, the relative importance of which may differ in individual cases. These structures (see Fig. 5) may be useful in understanding the structure and reactivity of these compounds [18].

For the aminocarbene compounds, resonance structure **C**, in which the electron density is donated to the electron-deficient carbene carbon atom by the nitrogen atom, is noteworthy. In the case of alkoxy-substituted carbene complexes, the main role in the resonance is played by structure **A**, which shows the electron density mainly localized in the lone pair of the oxygen atom. Under the above-mentioned chromatographic conditions, the nature and the electron-donor properties of the organic ligand bonded on the $\text{Cr}(\text{CO})_5$ unit appear to be effective in determining the retention order of these structurally different species. First to elute is **III**; it seems to be different to the other three complexes, which contain a five-membered ring substituent.

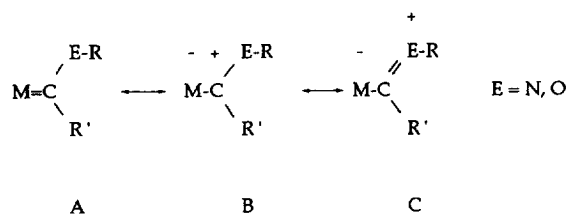
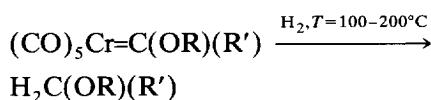


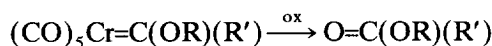
Fig. 5. Resonance structures of heteroatom-substituted carbene complexes.

The pentacarbonyl(2*H*-benzopyran-2-ylidene)chromium(0) compound **III** has a double bond incorporated in a six-membered ring; because of its structure, it could be considered as a precursor of coumarin derivatives, into which it could be transformed by oxidation. On the basis of X-ray analysis and resonance Raman spectroscopic studies [19], **III** can be considered as a complex with a pure metal–carbon double bond. Complexes **IV–VI** have a common pentacarbonyl(2-oxacyclopentylidene)chromium skeleton, variously substituted in positions 3 (Me, **IV** and **VI**; Et, **V**) and 5 [H, **IV**; $\text{CHN}(\text{Me})_2$, **V**; $\text{H}(\text{NCOOBu}^t)_2$, **VI**]. Compound **IV** shows the substitution of a carbonyl with a 15-group donor ligand, PPh_3 . The enamine complex **V** is an α,β -alkenylcarbene complex like **III**. Complex **VI** exists as two diastereoisomers (**a** and **b**), which were resolved by HPLC. Compounds **V** and **VI**, which contain a substituent in the 5-position with one or two nitrogen atoms, respectively, are retained longer by the stationary phase.

Fig. 6 shows the PICI and NICI mass spectra of complex **III**. The “coumarin-type” derivative **III** yields an intense molecular ion at m/z 322, in both the PICI (93%) and NICI (63%) modes; in the PICI mass spectrum the protonated molecular ion is also evident with a relatively high abundance (56%). Fragments due to the progressive loss of the five carbonyl ligands are visible in both the spectra. The peak at m/z 131 is attributable to the release of the carbene ligand from the metal complex, caused by the cleavage of the Cr–C double bond. In the mass spectra recorded under PICI conditions, two other interesting fragments are detected at m/z 133 (39%) and 147 (41%). They may be explained by considering that the carbene complexes have the capability of undergoing reductive and oxidative cleavage of the Cr=C bond:



in the absence of the catalyst and



where $\text{ox}=\text{Ce}^{4+}$, DMSO, O_2 . The oxidation,

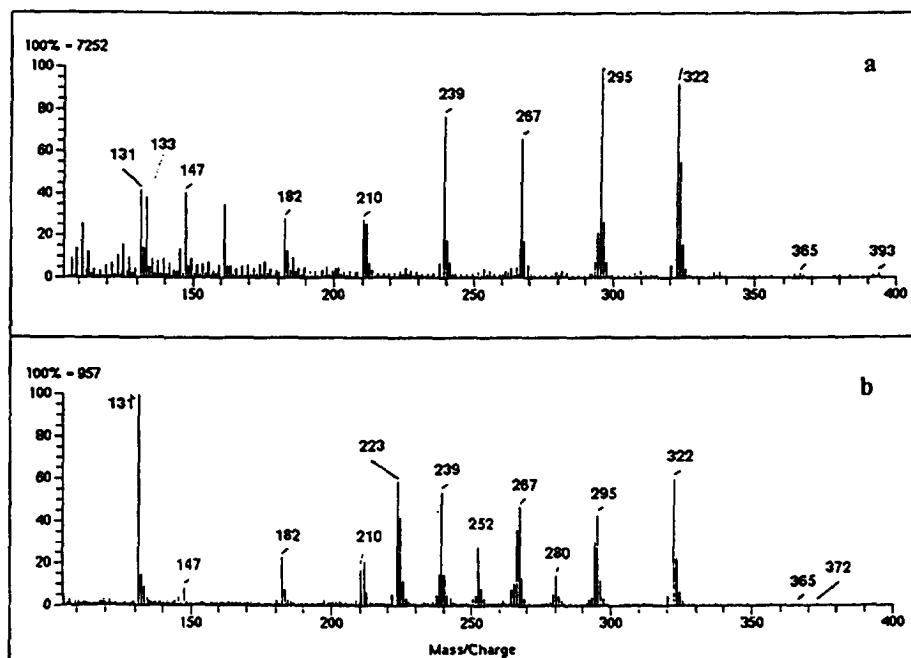


Fig. 6. CI mass spectra of **III**: (a) positive-ion signal; (b) negative-ion signal. Conditions as in Fig. 4.

which replaces the carbon–metal double bond of metal carbene complexes with a carbon–oxygen double bond, may occur in the presence of a variety of oxidizing agents, including pyridine N-oxide, dimethyl sulfoxide, cerium(IV) ion and oxygen [18]. In the MS source this kind of oxidative cleavage appears to be one of the most probable ways of fragmentation.

A similar mass spectrometric behaviour is shown by the α,β -alkenylcarbene complex **V**: the PICI and NICI mass spectra, shown in Fig. 7, exhibit a fragment ion at m/z 170, attributable to the oxidative cleavage of the compound examined. In this case the intensity of the peak is greater in NICI (32%) than in PICI (17%). In both spectra in Fig. 7 the parent ion at m/z 345 is visible with a similar abundance (ca. 35%), together with fragments due to the loss of the carbonyl ligands, the maximum abundance corresponding to the release of three CO groups (m/z 262, 100%). The intense signal at m/z 154 (PICI, 54%; NICI, 87%) derives from the loss of the $\text{Cr}(\text{CO})_5$ moiety. In the NICI mass spectrum an alternative fragmentation pathway can be

noticed, with signals at m/z 303, 275 and 247 corresponding to the $[\text{M} - n\text{CO} - \text{CH}_3]^-$ fragment ions with $n = 2, 3$ and 4, respectively.

The PICI mass spectra of the chromium–carbene complexes **IV** and **VI** appear to be simpler, as shown in Fig. 8a and b, respectively. Concerning the monosubstituted derivative with PPh_3 (**IV**), the main fragments at m/z 183 (100%) and 263 (45%) arise from the phosphinic ligand and are due to the ions $[\text{PPh}_2]^+$ and $[\text{PPh}_3 + \text{H}]^+$. By progressive decarbonylation, **IV** gives rise to four fragments in the 399–482 u range; the molecular ion, although scarcely visible, is present at m/z 510. An analogous behaviour is shown by **VI**, which shows M^+ at m/z 506 with low abundance, together with the five signals at m/z 478, 450, 422, 394 and 366 attributable to $[\text{M} - n\text{CO}]^+$ ions with $n = 1-5$. The mass spectrum in Fig. 8b is characterized by the fragment at 203 u, due to the simultaneous loss of the substituents in positions 3 and 5 and of two carbonyl ligands. The NICI mass spectra of chromium–carbene complexes **IV** and **VI** are unhelpful, since they show only fragments with

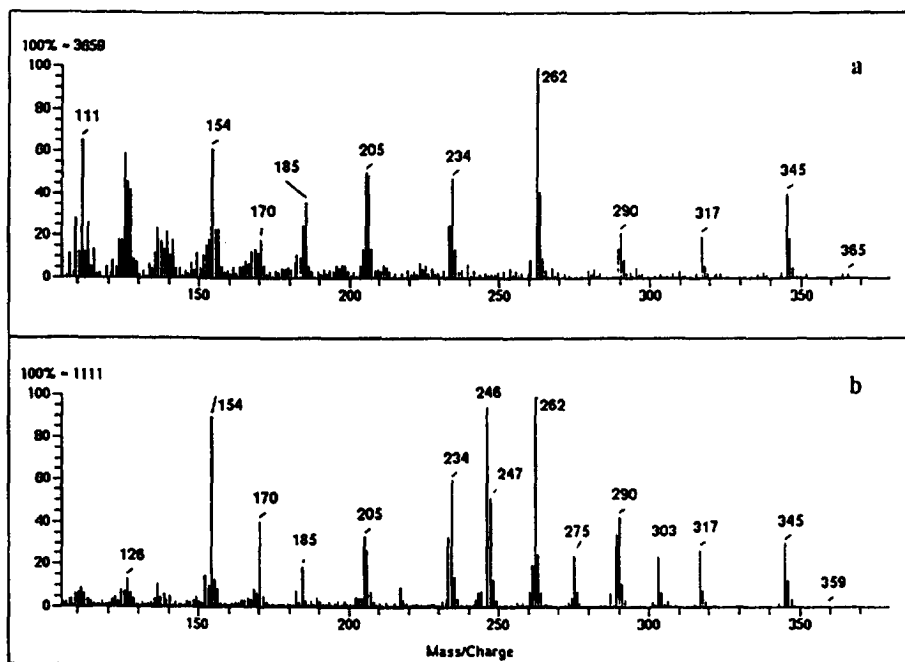


Fig. 7. LC-PB-Cl mass spectra of V: (a) positive-ion signal; (b) negative-ion signal. Conditions as in Fig. 4.

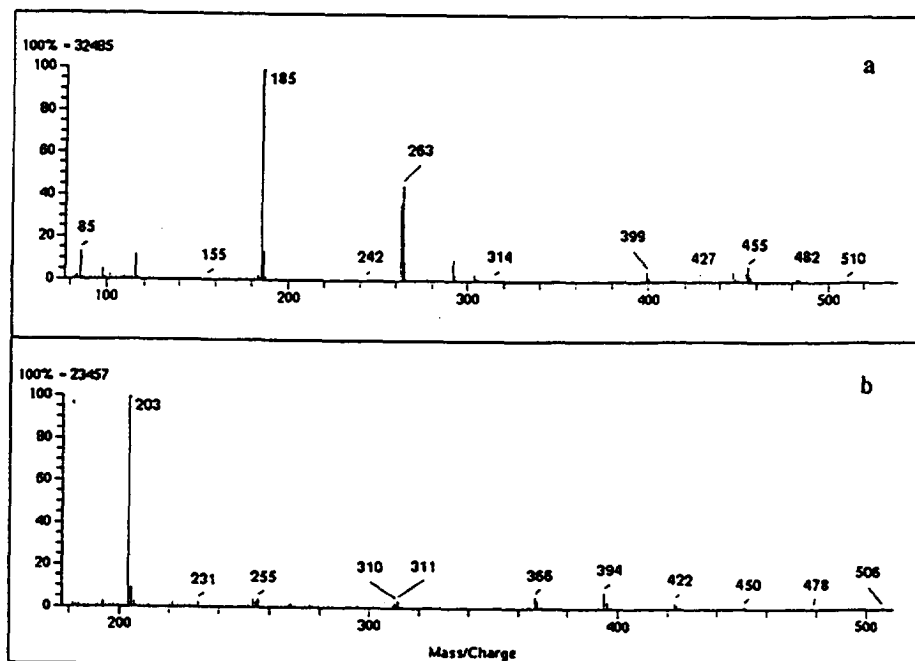


Fig. 8. PICl mass spectra of (a) IV and (b) VI corresponding to the separations reported in Fig. 4.

low mass values and do not give information about the molecular masses of these compounds.

In conclusion, this and preceding works demonstrate the potential role of coupled HPLC and MS techniques in metal carbonyl chemistry. In particular, these results show the applicability of the LC–PB–MS system in the elucidation of the stability and the structure of polar organometallic compounds, such as the chromium–carbene complexes examined.

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