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Positive and Negative Ion Mass Spectrometry of Carbonylrhodium(I) Derivatives of 3,5-Dimethyl- and 3,5-Bis(trifluoromethyl)pyrazole

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The mass spectrometric behaviour of some carbonylrhodium(I) derivatives of 3,5-dimethyl- and 3,5-bis(trifluoromethyl)pyrazole (pz′H and pz″H respectively) has been studied in detail by means of different ionization techniques (Electron Impact and Field Desorption), by recording the positive and negative ion mass spectra and by using linked scan methods for metastables. The species trans-$(Ph_3P)_2(OC)Rh(pz''\text{-}N)$ which showed an unexpected behaviour has been investigated by means of collisional activation experiments.

Introduction

A series of transition metal derivatives having pyrazoles or pyrazolato anions as ligands has been reported previously by some of us. The series includes gold(I) [1], platinum(II) and palladium(II) derivatives [2], as well as some carbonylrhodium(I) complexes with 3,5-dimethyl- and 3,5-bis(trifluoromethyl)pyrazole [3]. In any case the coordination behaviour of the pyrazolato** anion (*e.g.* monodentate, pz-N, or exobidentate, μ-pz-N,N′) was shown to be affected, *inter alia*, by the nature of the substituents on the heterocyclic ring. Thus, in the case of rhodium, both binuclear complexes, $[(L)(OC)Rh(\mu\text{-pz-N,N}')]_2$ (pz′: L = CO, II, L = Ph_3P, IV; pz″: L = CO, III, L = Ph_3P, V), and mononuclear species, *trans*-$(Ph_3P)_2(OC)Rh(pz''\text{-N})$, VI, and *cis*-$(OC)_2RhCl(pz'H)$, I, were obtained and investigated by spectroscopic methods (IR and ^1H, ^{31}P, ^{19}F, ^{13}C NMR). In some cases the rhodium derivatives were so volatile that purification by vacuum sublimation was possible. The availability of such a series of highly volatile compounds with ligands differently substituted and a monoisotopic metal center (^{103}Rh), makes these rhodium(I) pyrazolates ideal candidates for mass spectrometric investigations.

In recent years, the application of mass spectrometry in the field of coordination compounds has gained increasing importance: however only in a very limited number of cases has this technique been applied to pyrazolato complexes [4], even if the thermal stability of these molecules, the large range of available pyrazoles and the isolation of their derivatives with a lot of elements of the periodic system [5], should encourage comparative studies. On the other hand, rhodium complexes have been widely investigated by mass spectrometry. Thus the ionization energies (I.E.) of some substituted acetylacetonates [6, 7] as well as of other dicarbonyl-β-diketonates were employed as a guide to the interpretation of mass spectral features, an approach which has been reviewed by Westmore [8] quite recently. Many other papers have reported mass spectrometric fragmentation of different types of rhodium complexes [9].

In the present work the mass spectral behaviour of the carbonyl rhodium(I) derivatives I–VI (see Table I) is described in detail and discussed with the aid of positive and negative ion Electron Impact mass spectra, Field Desorption mass spectra and linked scans [10] for metastable data.

Experimental

All mass spectra were obtained using a VG ZAB-2F instrument. Electron Impact (EI) mass spectra were obtained at 70 eV (200 μA) with a source temperature of 130–150 °C; samples were introduced

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**Throughout this paper, a generic pyrazole is indicated as pzH, 3,5-dimethyl- and 3,5-bis(trifluoromethyl)pyrazole as pz′H and pz″H, respectively.

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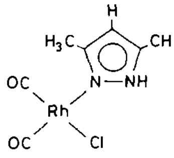
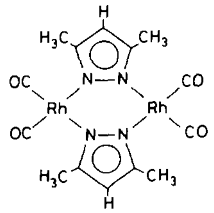
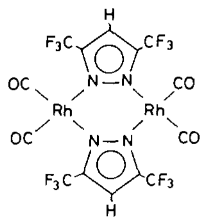
TABLE I.


(I)

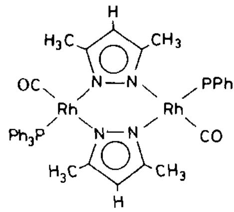
$(OC)_2(pz'H)RhCl$


(II)

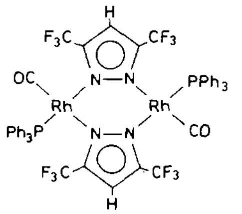
$[(OC)_2Rh(pz')]_2$


(III)

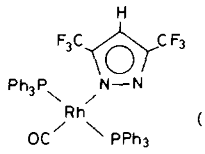
$[(OC)_2Rh(pz'')]_2$


(IV)

$[(OC)(Ph_3P)Rh(pz')]_2$


(V)

$[(OC)(Ph_3P)Rh(pz'')]_2$


(VI)

$(Ph_3P)_2(OC)Rh(pz'')$

via direct inlet system. Negative ions mass spectra were obtained in EI conditions*.

Field Desorption (FD) mass spectra were obtained with an extraction voltage of 11 KV and with an emitter current of 20–25 mA.

Collisional Activation (CA) experiments were performed using 8 keV ions colliding with air in the collision gas cell of the second field free region.

Compounds I–VI were obtained as reported previously [3].

Results and Discussion

Compound I

Complex I, *cis*-$(OC)_2(pz'H)RhCl$, is unique among the rhodium derivatives investigated in this work owing to the presence of a neutral pyrazole. The fragmentation pattern of $M^{+\cdot}$, reported in scheme 1a, has been obtained by means of linked scans. From the molecular ion, m/z 290 (25%), a step by step loss of CO leads to the ions at m/z 262 and 234. The latter, through an HCl elimination, gives rise to the base peak, $[pz'Rh]^{+\cdot}$. Further fragmentations to pz′ and $Rh^{\cdot}$ are observed. The negative ion mass spectrum is more simple, showing an important primary pathway (–pz′H), which leads to the base peak, and minor sequential loss of CO (scheme 1b). The FD spectrum shows only an intense peak at m/z 290, corresponding to the molecular ion.

Compounds II and III

The complexes II and III have been described as tetracarbonyldi(μ-pyrazolato)dirhodium(I) derivatives: the dimeric nature of these species is now confirmed by the presence of the molecular ions at m/z 508 and 724 respectively, either in positive and negative ion or in FD mass spectra. The fragmentation pattern of the $M^{+\cdot}$ ions is shown in the schemes 2a, II, and 3a, III. In both cases a gradual loss of CO is observed to give, at last, the base peaks $[Rh_2pz'_2]^{+\cdot}$, m/z 396, and $[Rh_2pz''_2]^{+\cdot}$, m/z 612. Such a pattern, which is typical of carbonylrhodium(I) derivatives, is accompanied by other primary decomposition processes, which are different in the two cases. Thus, in the case of compound II, the loss of $(OC)_2Rh_2$ and $(OC)_3Rh_2$ unities, processes which are supported also by linked scan data, gives rise to organic ions at m/z 246 and 218: the latter is likely to be the well known carbonyl derivative $OC{-}[\overline{-N{-}C(CH_3){=}CH{-}C(CH_3){=}N}]_2$ [11]. In the case of complex III, the other primary process starts with a $F^{\cdot}$ loss and is followed by the usual elimination of CO. The fragmentation of the base peaks, $[Rh_2pz'_2]^{+\cdot}$ and $[Rh_2pz''_2]^{+\cdot}$, displays more remarkable differences. Indeed in the case of $[Rh_2pz''_2]^{+\cdot}$, the first step concerns the cleavage of a rhodium–nitrogen bond, followed by loss of Rhpz″ and $F^{\cdot}$, while in the other case, the dinuclear unity is retained but the heterocyclic ring is broken. The loss of the $C_3H_5^{\cdot}$ radicals, to give ions at m/z 355 and 314, suggests that the heterocyclic ligand undergoes a ring contraction, perhaps to a diazirinic derivative, which might act as bridging ligand. The negative ions mass spectra (scheme 2b and 3b), in both cases, are more simple and show a sequential loss of CO to give the binuclear ions $[Rh_2pz_2]^{-\cdot}$ at m/z 396 and 612 respectively. In addition, complex III displays another interesting primary decomposition which leads to the ion at m/z 490 ($C_{10}H_2F_{11}N_4Rh$): the same species is observed also in the positive mass spectrum and is indicative of a complex rearrangement of the molecular ion.

Compounds IV and V

The complexes IV and V, which were described as dimeric species analogous to II and III, where a carbonyl on each rhodium atom has been substituted by a Ph_3P ligand, show a more complicated behaviour

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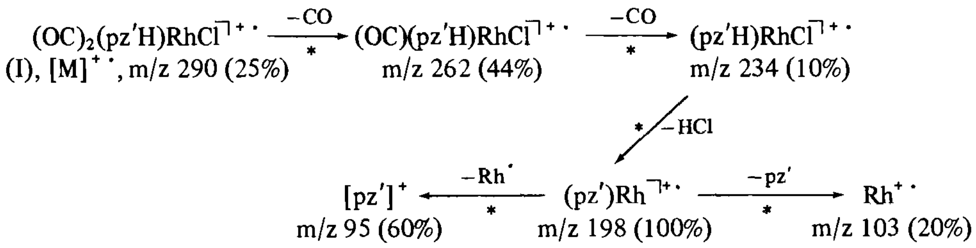
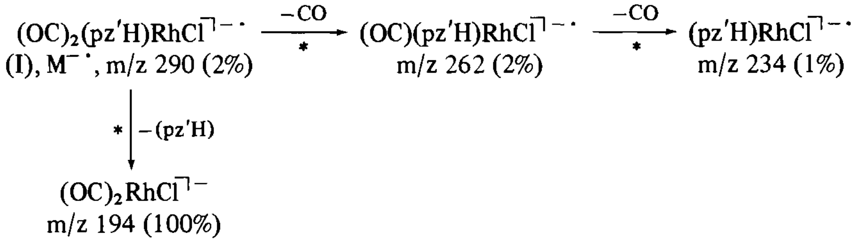
*The positive and negative ion mass spectra of compounds I–IV can be obtained from P. Traldi.

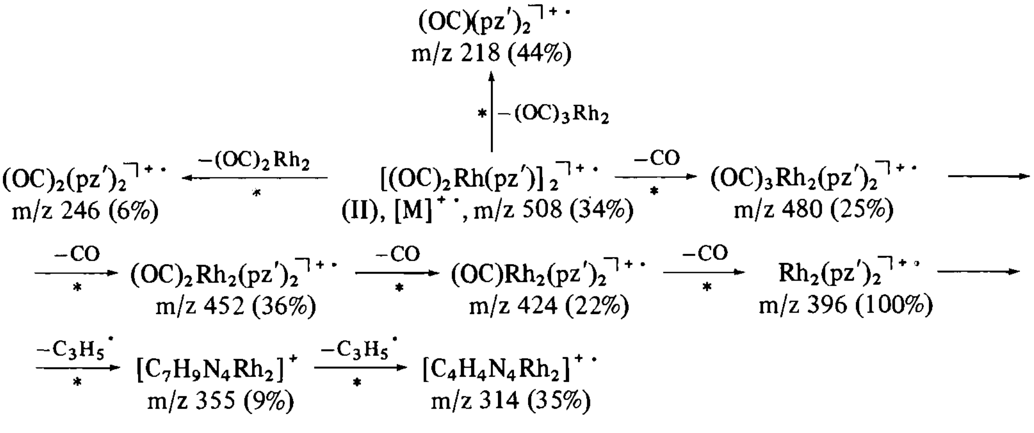


Scheme 1a.

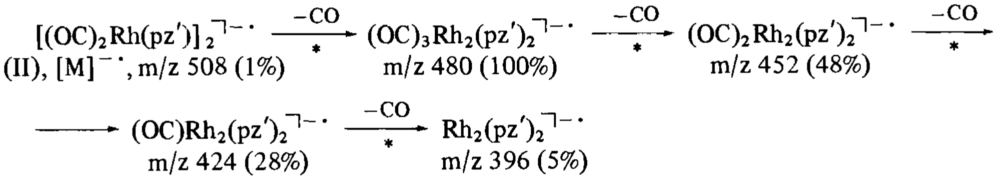


Scheme 1b.

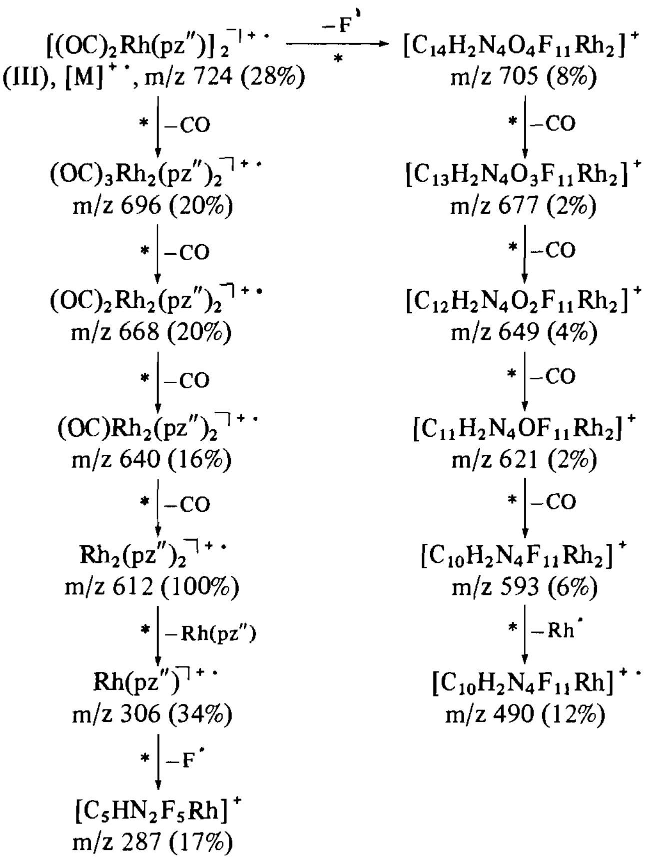
under electron impact. Also in these cases the dimeric nature of the species is confirmed by the expected molecular ions (m/z 976 and 1192 resp.) which, however, in the case of complex IV is observed only in the FD spectrum. Indeed in the positive ions spectrum of compound IV the molecular ion is not observed under any experimental condition: the highest mass species is in any case the $[M-H_2]^{+\cdot}$ ion m/z 974 (5%) (scheme 4a). From these a decomposition process, which involves the loss of two C_6H_4 groups, leads to the species at m/z 822. Such a pattern suggests a change in the oxidation state of the rhodium atoms through the formation first of an orthometallated, m/z 974, and later of a phosphide species, m/z 822. In agreement another path affords the ion $[Ph_3P\text{-}H]^{+\cdot}$. However a different formulation cannot be excluded and an unambiguous explanation of the fragmentation mechanism cannot be given



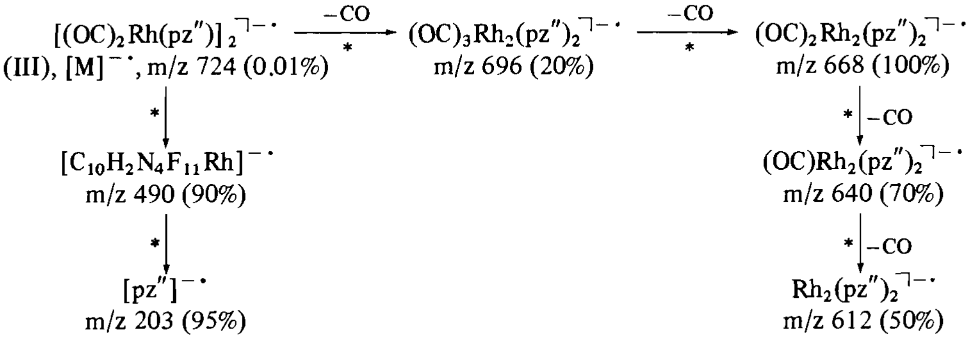
Scheme 2a.



Scheme 2b.



Scheme 3a.

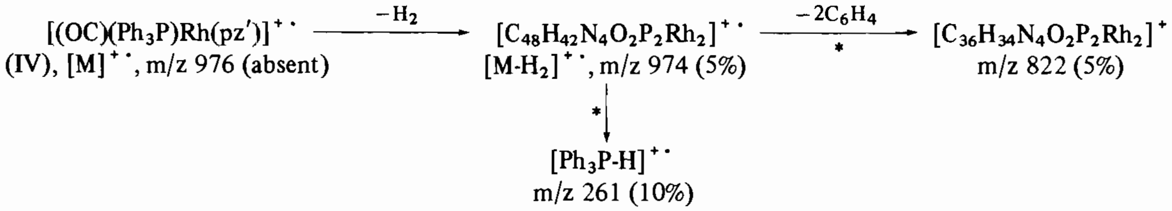


Scheme 3b.

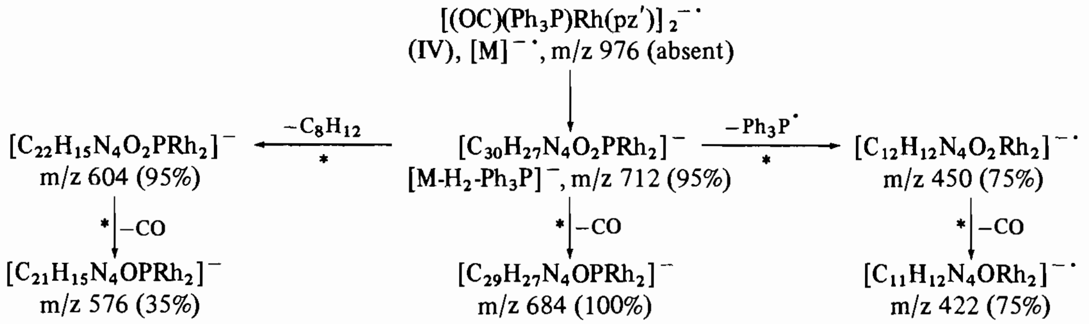
in the absence of studies on labelled species, which are not available to us at present.

In the negative ion mass spectrum, the highest mass ion is observed at m/z 712 and corresponds to a loss $Ph_3P^{\cdot}$ and H_2. From these ions there originate either a loss of triphenylphosphine and CO or a process ($-C_8H_{12}$) which involves the pyrazole ring. This process leads to a species, m/z 604, which might contain a diazirinic moiety, as observed in the case of II. In the positive ion spectrum of compound V, the molecular ion at m/z 1192 is very intense (73%): the fragmentation pattern displays a sequential loss of $Ph_3P^{\cdot}$ and pyrazolato groups while other primary processes give rise to $[Ph_3P]^+$ and $[pz'']^{+\cdot}$ ions (scheme 5a).

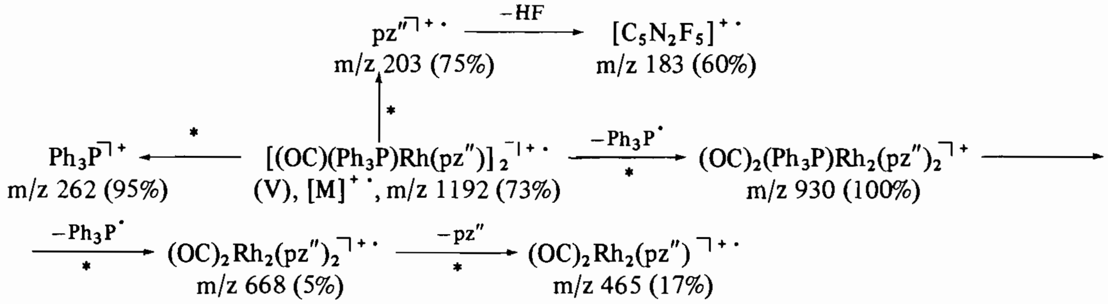
The negative ion mass spectrum of the same compound (Fig. 1) appears to be more complicated: the ion of higher mass (m/z 1164) is due to the decarbonylated species, from which the more abundant species, m/z 902, is obtained by loss of $Ph_3P^{\cdot}$, with a fragmentation pattern (Scheme 5b) showing a competitive loss of triphenylphosphine and carbon monoxide. A different primary process gives, probably through a hydrido intermediate



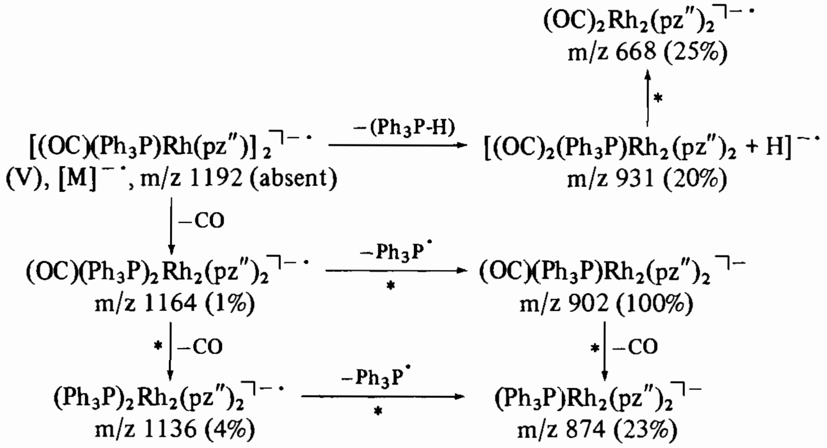
Scheme 4a.



Scheme 4b.



Scheme 5a.



Scheme 5b.

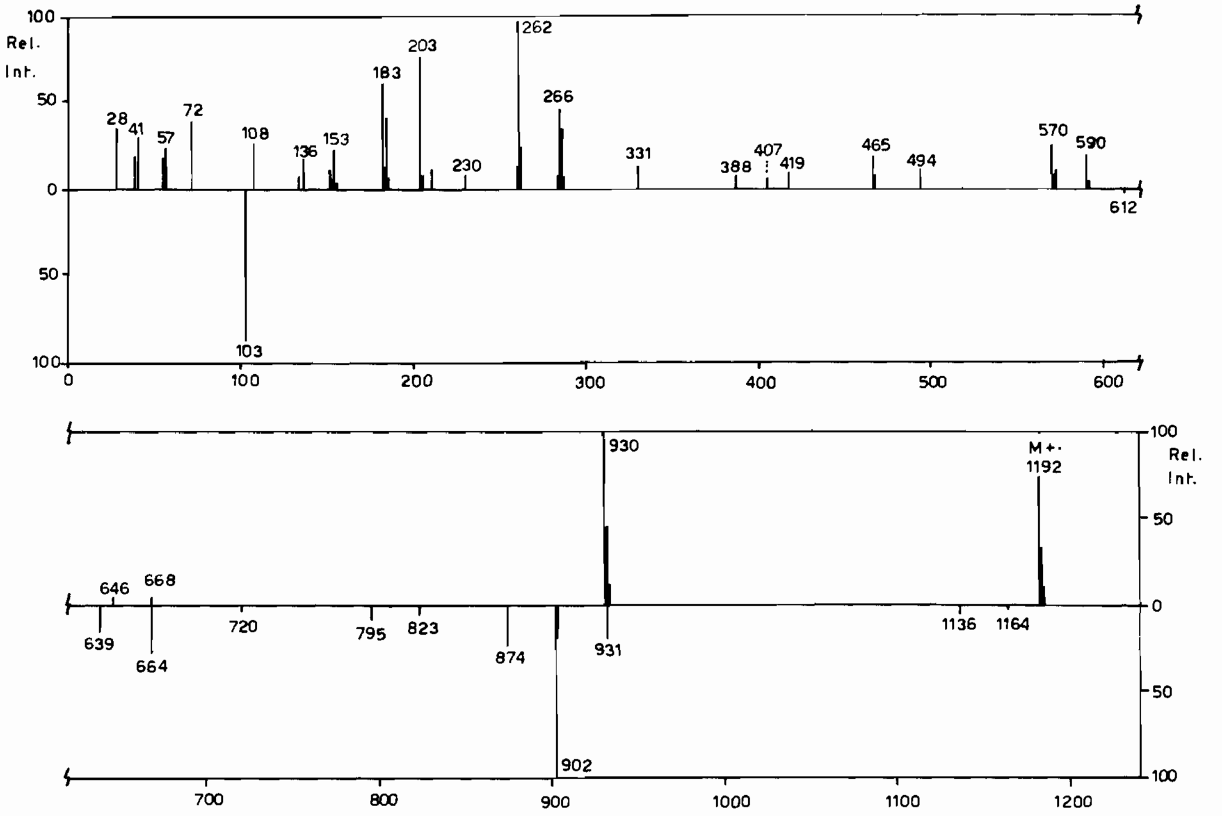


Fig. 1. Positive (up) and negative (down) ion mass spectra of $[(Ph_3P)(OC)Rh(\mu\text{-}pz''\text{-}N,N')]_2$ (compound V).

(m/z 931), the species $[(OC)_2Rh_2(pz'')_2]^{-\bullet}$, observed also in the positive ion spectrum.

Compound VI

The monomeric derivative, *trans*-$(Ph_3P)_2(OC)Rh(pz''\text{-}N)$ (compound VI), shows a very different behaviour: actually the molecular ion, expected at m/z 858, is not observed either in the EI spectra or by the FD technique. On the other side a peak is observed at m/z 1192 which corresponds to the dinuclear species $[(Ph_3P)(OC)Rh(pz'')]_2$. The rearrangement of the molecule, which is likely to be due to a thermal effect, implies the loss of a phosphine:

$$2(Ph_3P)_2(OC)Rh(pz''\text{-}N) \xrightarrow{\Delta} [(Ph_3P)(OC)Rh(\mu\text{-}pz''\text{-}N,N')]_2 + Ph_3P$$

and a different coordination of the pyrazolato anion, in agreement with the well known tendency of these ligands to act as exobidentate rather than as monodentate ligands. According to a preliminary mass spectral investigation of the complex *trans*-$(Ph_3P)_2(OC)Ir(pz''\text{-}N)$ [12], this type of rearrangement seems to be independent of the metallic center. It is noteworthy that the dimerization of complexes of this type by thermal effect is not unprecedented: indeed the complex $(Ph_3P)_2(SC)Rh(pz'\text{-}N)$ has been found to be stable only below −50 °C. At higher temperatures, dimerization occurs with elimination of Ph_3P [13]. The easy loss of phosphine in these types of complexes, as observed also in the fragmentation pattern of compounds IV and V, may be due, *inter alia*, to steric factors.

As a consequence of the observed dimerization, the fragmentation pattern of the ions at m/z 1192 of the complex VI (Fig. 2) is reminiscent of that of compound V. To clarify the structural identity of the species at m/z 1192, in the two cases (compounds V and VI), collisional activation (CA) experiments were carried out in the conditions described in the experimental section: the corresponding spectra are reported in Fig. 3 and 4 respectively.

On the basis of the remarkable differences observed a different structure can be assigned to the two ions having the same elemental composition. Such differences may be explained in terms of *cis–trans* isomers: the existence of two isomers was ascertained in the case of the analogous derivative IV, for which both the *cis* isomer and a mixture of the *cis* and *trans* isomers were obtained. In the case of compound V only the *trans* derivative was isolated, which

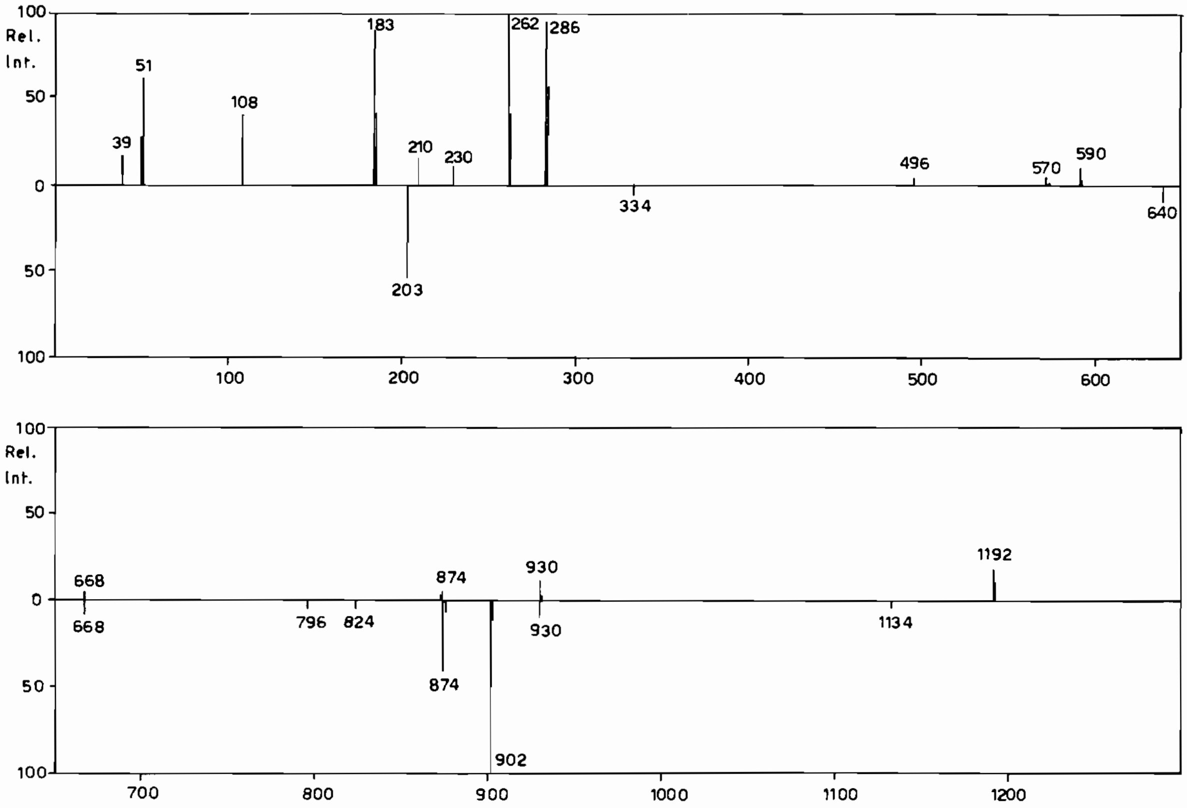


Fig. 2. Positive (up) and negative (down) ion mass spectra of *trans*-$(Ph_3P)_2(OC)Rh(pz''\text{-}N)$ (compound VI).

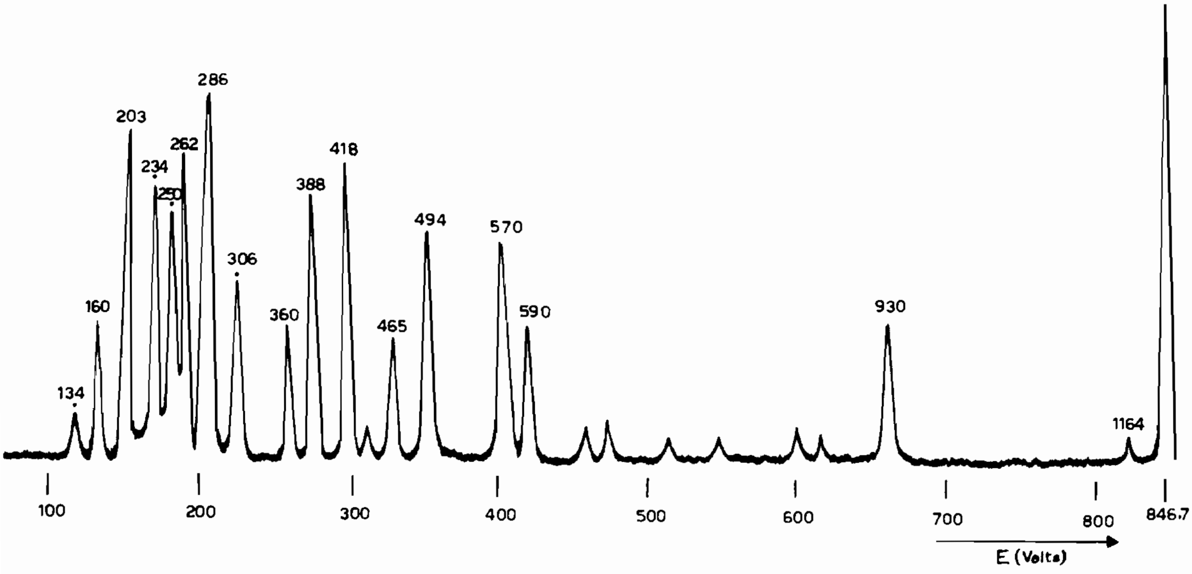


Fig. 3. CA spectrum of $[(Ph_3P)(OC)Rh(\mu\text{-}pz''\text{-}N,N')]_2$.

should correspond to the molecular ion. Thus the ions obtained from compound VI are likely to be the *cis* isomer or perhaps a mixture of the *cis* and *trans* isomers: in any case an unambiguous structural assignement is not possible since the *cis* species has not been hitherto isolated.

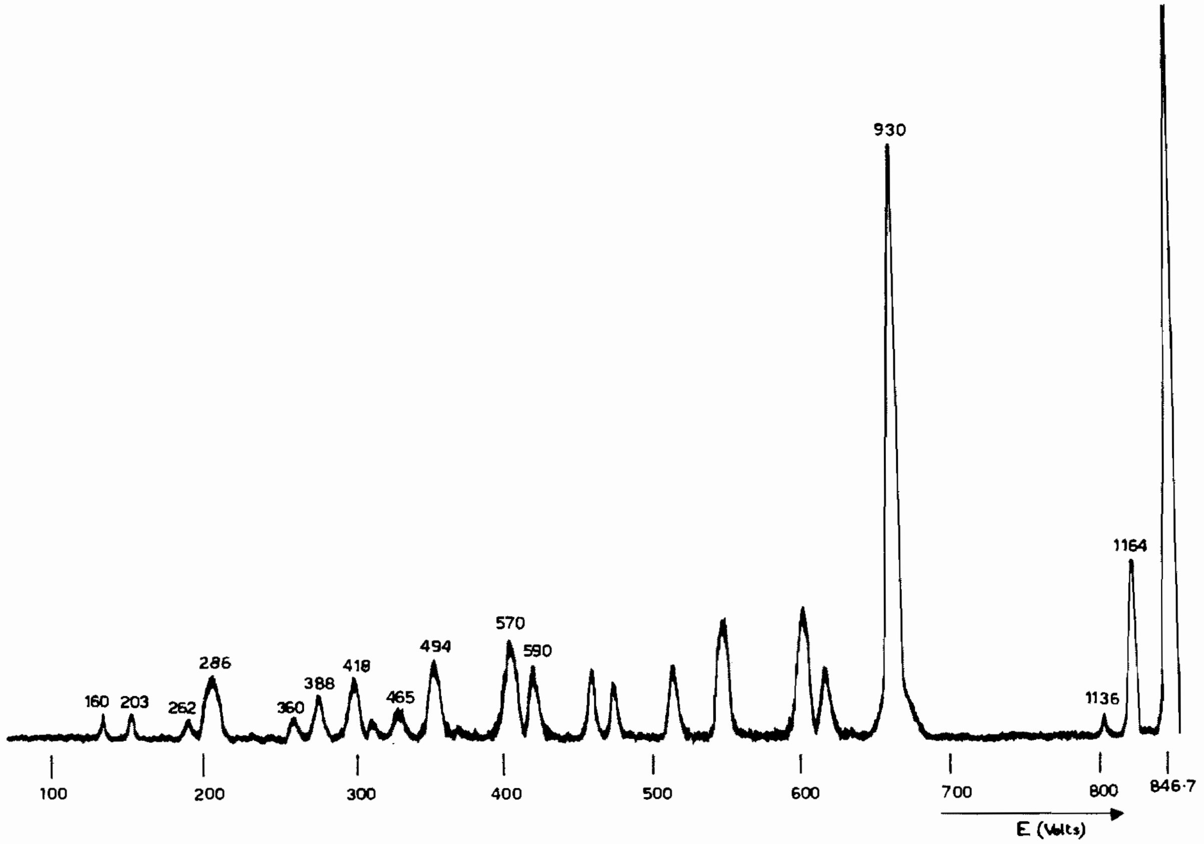


Fig. 4. CA spectrum of $(Ph_3P)_2(OC)Rh(pz''\text{-}N)$.

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