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COMMENTS ON THE LOSS OF SMALL NEUTRAL FRAGMENTS OBSERVED IN THE MASS SPECTRA OF CARBONYL COMPLEXES CONTAINING ORGANIC RINGS

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Summary

The preference for loss of small stable molecules rather than of radicals in the fragmentation of complexed organic rings by electron impact is rationalized in terms of the activation energies of the possible fragmentation routes of the molecular ion

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Introduction

In the electron impact fragmentation of transition metal complexes containing organic rings, processes leading to the aromatization of the rings have been frequently observed [1]. These reactions, involving the loss of small neutral stable molecules are observed with low efficiency in the free ligands. On the other hand, peaks due to the loss of a hydrogen atom from the molecular ion are among the most intense in the mass spectra of the free ligands and are absent in the mass spectra of the complexes. It has been suggested [2], that in π-$C_6H_8Fe(CO)_3$ the elimination of carbon monoxide units to leave an electron deficient central metal, capable of an "extra" coordination, was the driving force for the aromatization of the organic ring. However, this proposal seems to be of rather limited applicability. Aromatization of the organic ring has been also observed with π-$OHC_{10}H_{11}Cr(CO)_3$ for which the aromatization of the ring to naphthalene after the loss of some CO groups does not increase the coordination number of the chromium atom. We describe below a case in which the CO losses occur without change of the coordination number of the metal atom bonded to the organic moiety and the processes leading to the aromatization still occur after the loss of two CO groups.

Results and discussion

The monoisotopic high mass region of the 50 eV mass spectrum of π-tetrahydronaphthalenenonacarbonyltetracobalt is shown in Fig. 1*. Peaks of the type $(P-n\ CO)^+$ become less intense with increasing n, while peaks of the type $P-(n\ CO + H_2)$ and $P-(n\ CO + 2H_2)$ predominate when $n \geqslant 4$, the base peak being (naphthalenetetracobalt)$^+$. In the mass spectrum of tetrahydronaphthalene the following ions are found (relative abundances in parentheses): *m/e* 132 (64.4), 131 (16.6), 130 (2.0), 128 (11.6)**.

The most interesting differences between the fragmentation of the complexed organic moiety and that of the free ligand are the absence of peaks due to the loss of atomic hydrogen and the increased importance of the peaks due to the loss of one and two hydrogen molecules. These last processes are the only observed fragmentation routes for the complexed ligand in the mass region investigated.

It is obvious that unsaturation of the cobalt atom cannot be invoked as the driving force for the aromatization of the organic ring We think that an

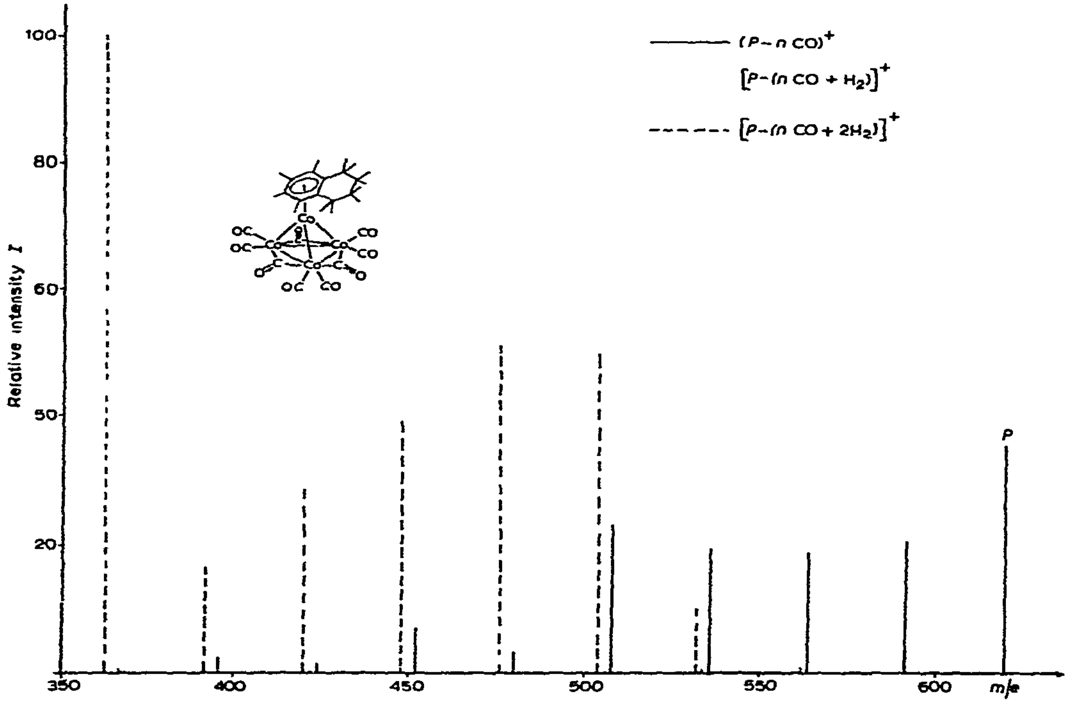

Fig 1 Monoisotopic mass spectrum of $C_{10}H_{12}Co_4(CO)_9$ (50 eV) The structure given here has been suggested in refs. 3 and 6.

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*The compound was prepared as previously described [3] For the mass spectrometric conditions see ref 4.

**Other ions of less importance for the present discussion are also observed For the more abundant ions see ref 5 explanation on energetic grounds is necessary in this case*. Approximate appearance potential (AP) measurements on free ligand show that the $(P{-}H_2)^+$ and $(P{-}2H_2)^+$ ions have almost identical appearance potentials, and that their APs are substantially lower ($\approx$ 3 eV) than that of $(P{-}H)^+$ ion. It was also found that the molecular ion requires about 1 eV to give the $(P{-}H_2)^+$ and $(P{-}2H_2)^+$ ions. Even though the activation energies for the loss of CO groups in carbonylic complexes cover a wide range, there are several examples, especially for substituted carbonyls, in which 1 eV is sufficient for the loss of two CO groups, and only a few cases are reported in which more than 1 eV is required for the loss of one CO group [8]. We can therefore infer that the loss of one (and perhaps two) CO group is a lower energy process than the fragmentation of the organic moiety and consequently only the less endothermic reactions, i e. reactions accompanied by the loss of small neutral molecules, can compete with the loss of CO groups. The high activation energy for the loss of a hydrogen atom precludes this process, since in the complex there are several other processes requiring lower energy.

Since the energetic factors should not drastically change in related complexes containing different organic rings or different transition metals, the above explanation should be of general applicability It is obvious that lowering of the activation energy for the loss of small neutral molecules can be achieved if the formation of new π bonds in the organic ring with a possible bonding interaction with the central metal results in increased stabilization of the electronic configuration of the transition metal, but a deficiency of the coordination number of the central metal cannot be considered to be responsible for the major differences found between the mass spectra of the free and complexed organic ligands.

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*For a general discussion on the importance of energetic factors in the fragmentations see for example ref 7