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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

IV*. π-CYCLOPENTADIENYLIRONDICARBONYLDICHLOROGERMANIUMS

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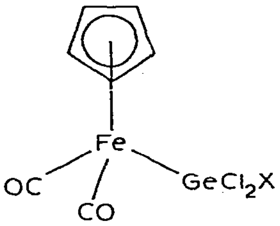
Summary

The mass spectra of $C_5H_5(CO)_2FeGeCl_2X$ (X = Cl, Me, Et, n-Pr or CH_2Ph) show very intensive rearrangement ions which are formed due to cyclopentadienyl ring migration from iron to the germanium atom or chlorine (substituent) migration from germanium to the iron atom.

In continuation to our investigations on the behaviour of π-complexes of transition metals under electron impact [1-3] the mass spectra of π-cyclopentadienylirondicarbonyldichlorogermaniums I-V have been examined. These com-



(I, X = Me ; II, X = Et ; III, X = n-Pr ; IV, X = Cl ; V, X = CH_2Ph)

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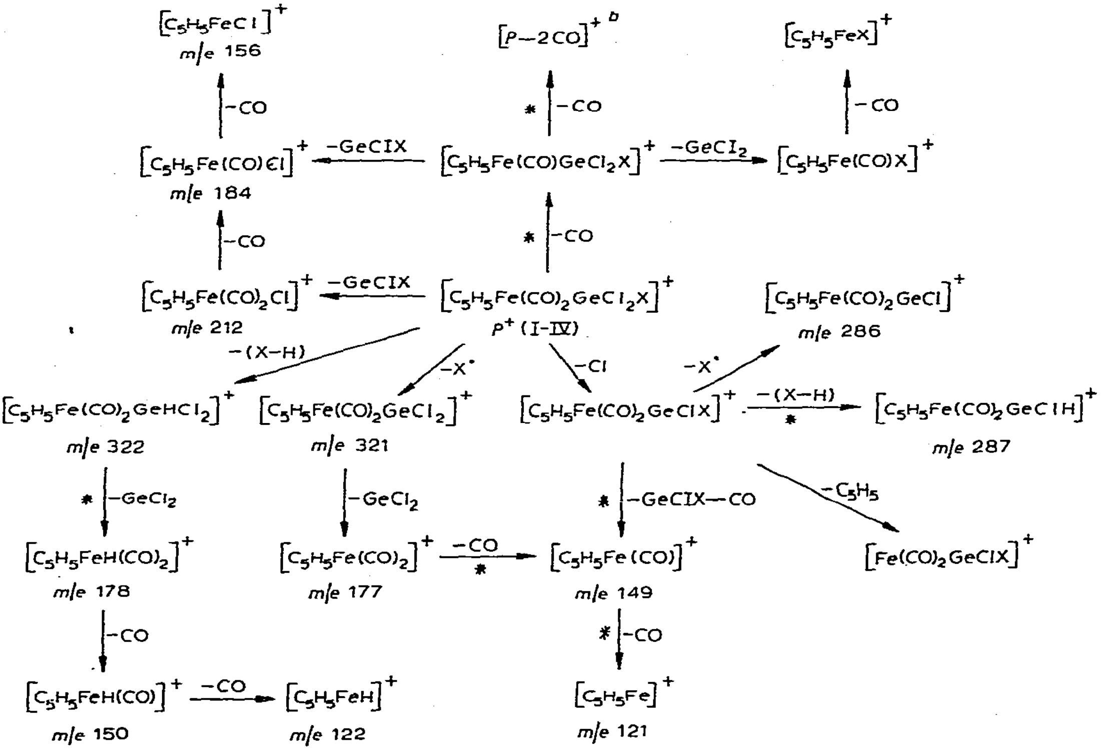
[*] For part III see ref. 1.

plexes contain iron and germanium atoms and are a convenient systems for comparative study of the properties of elements from different groups of the periodic table.

Molecular ions have low intensities in all the mass spectra of the substances under investigation. Complexes I-V decompose under electron impact by competitive pathways to yield $[P-CO]^+$, $[P-Cl]^+$ and $[P-X]^+$ ions which furthermore lose CO, Cl or X. All these processes give rise to the ions of common formula $[C_5H_5(CO)_l FeGeCl_m X_n]^+$, where l = 0-2, m = 1 or 2 and n = 0 or 1 (Scheme 1).

SCHEME 1[a]

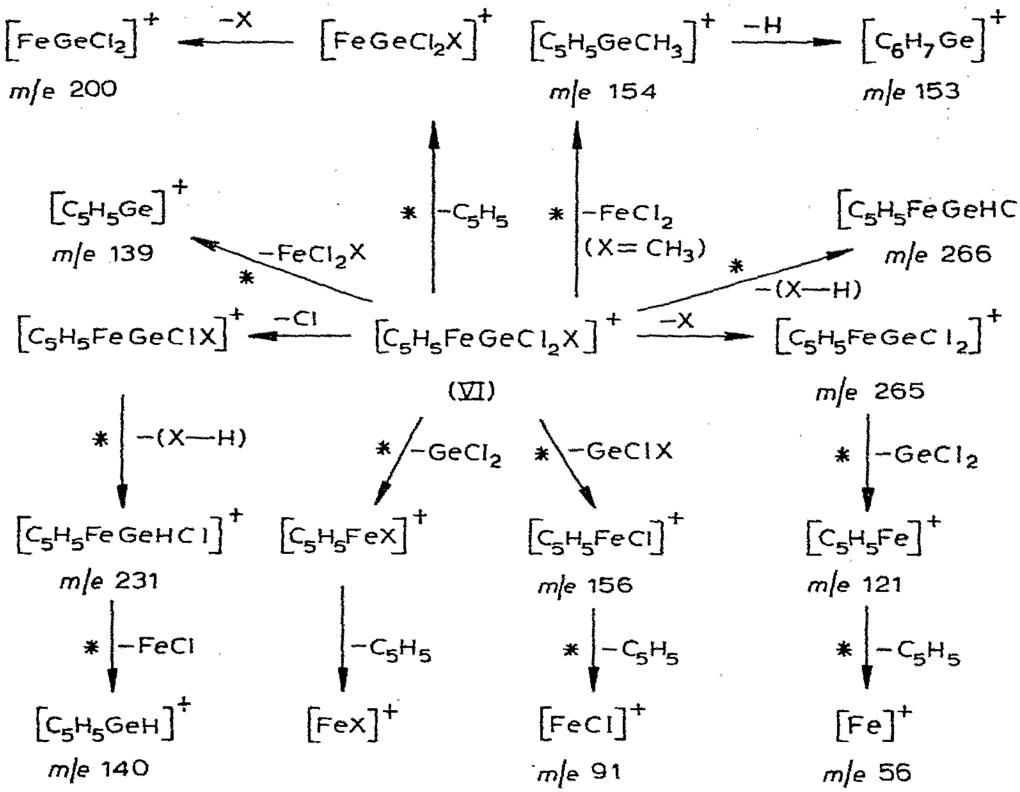


[a] The m/e values cited for the ions containing ^{35}Cl, ^{56}Fe and ^{74}Ge atoms; processes substantiated by the corresponding metastable peaks are labelled by asterices. [b] The probable decomposition pathways of $[P-2CO]^+$ ions are sited on Scheme 2.

The usual decomposition route of the bimetallic ions in complexes I-V is Fe—Ge bond cleavage. As a rule, the iron atom is a part of ion fragments and germanium atom is a part of neutral particle ($GeCl_2$ or GeClX). Scheme 1 shows the probable fragmentation paths involving the cleavage of the Fe—Ge bond in $[P-CO]^+$, $[P-Cl]^+$, $[P-X]^+$ and $[P-(X-H)]^+$ ions.

The full decarbonylation of the molecular ions I-V results in $[C_5H_5FeGeCl_2X]^+$ (VI) ions. These ions undergo the competitive loss of a cyclopentadienyl ring, chlorine atom or substituent X (Scheme 2). The major fragmentation

SCHEME 2



pathway of VI involves rearrangements, which can be divided into three main types:

(*a*). Hydrogen rearrangement consisting of migration of alkyl-hydrogen atom to the germanium atom; such rearrangements are usual for alkyl derivatives of Group IV elements [4,5] and the olefine molecule is lost in the process. As a result of this rearrangement in the mass spectra of II and III are $[C_5H_5FeGeHCl_2]^+$ ions which eliminate a chlorine atom.

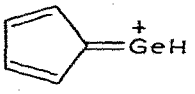
(*b*). Cyclopentadienyl ring migration to germanium atom resulting in $[C_5H_5Ge]^+$ and $[C_5H_5GeX]^+$ ions; the former has the most abundance in the mass spectra of complexes I-III.

(*c*). Chlorine atom or alkyl substituent X migration to the iron atom to afford $[C_5H_5FeCl]^+$ and $[C_5H_5FeX]^+$ ions; the former has 100% intensity in IV and the later has the highest abundance in the mass spectrum of V.

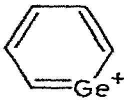
The one step formation of the $[C_5H_5FeX]^+$, $[C_5H_5FeCl]^+$ and $[C_5H_5Ge]^+$ ions from VI is confirmed by the presence of appropriate metastable peaks in the mass spectra. The $[C_5H_5FeCl]^+$ and $[C_5H_5FeX]^+$ ions are usual for mass spectra of π-complexes of the type $\pi\text{-}C_5H_5M(CO)_nX_m$ [6-8] (where M is transition metal). These are produced in the present case due to the cleavage of two bonds and the formation of one bond.

Generation of the $[C_5H_5Ge]^+$. Ions which can be described as the cleavage of five old and the formation of three (or four) new bonds appears to be unusual. Similar processes probably take place in a number of related compounds (π-$C_5H_5M(CO)_nEX_m$, M is a transition metal, E is a main Group IV element) under electron impact [9,10]. This reaction involves the simultaneous cleavage of five bonds and thus must possess a very low frequency coefficient (entropy factor). To realize a high rate constant for producing $[C_5H_5Ge]^+$ ions (which is confirmed by their high intensity) this process must be characterized by low activation energy.

The C_5H_5 migration to Ge atom is unprofitable because of the high frequency coefficient. This permits us to propose the structure of $[C_5H_5Ge]^+$ ions as VII or VIII.



(VII)



(VIII)

Experimental

The compounds I-V were synthesized as described previously [11]. Mass spectra were measured with an MX-1303 machine. The direct introduction system was maintained at 10° C, the ionisation chamber at 150° C, and the ionising voltage was 50 V.

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