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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS. XXIII *. THE IONS $[C_5H_5E^{IV}]^+$ IN THE GAS PHASE. SYNTHESIS AND STRUCTURE

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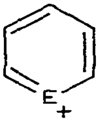
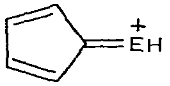
Summary

The ions $C_5H_5E^+$ (E = C, Si, Ge, Sn, Pb) were generated in the gas phase. Calculations of the atomization energies confirm their structure as nido-cluster. It is suggested that such ions could be synthesized under normal conditions for all the Group IVA elements, including carbon.

In the mass spectra of π-cyclopentadienyliron dicarbonyl complexes, π-$C_5H_5Fe(CO)_2ER_3$, containing an iron—Group IV element bond (E = Si, Ge, Sn, Pb), intense ions $C_5H_5E^+$ are present and these are often the most intense [1—6]. They are formed as a result of complex rearrangement from molecular or decarbonylated ions $C_5H_5FeER_3$ (R = alkyl or halide). This rearrangement involves the simultaneous participation of at least nine bonds and is characterized by very low activation energy [1,6]. The unusually high intensity of the $C_5H_5E^+$ ions indicates their high stability. Three possible structures of this ion may be suggested: elementaphenyl (A) 6-elementalfulvenyl, (B) and half-sandwich or nido-cluster (C).



(A)



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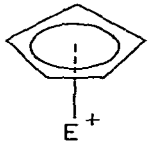

(C)

Previous calculations of atomization energies of these structures for $C_5H_5Ge^+$ by the statistical method [7] showed the nido-cluster to be the most stable [8].

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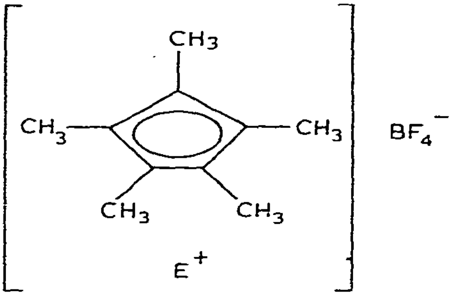
* For part XXII, see ref. 15.

Recently, Jutzi et al. synthesized nido-clusters of (pentamethylcyclopentadienyl)tin (I) and -germanium (II), the structures of which were confirmed by X-ray structural analysis [9,10].



(I, E = Sn;
II, E = Ge)

Using the statistical method [7] we have now calculated the energies of the ions of the type A, B and C for all elements of Group IVA, including carbon, and generated them in the gas phase.

Ions $C_5H_5E^+$ are present in the mass spectra obtained by simultaneous evaporation of cyclopentadienylthallium with EX_4 molecules (X = Cl for E = C, Si, Ge and Sn and X = C_6H_5 for E = Pb) at a pressure in the ionization chamber of 10^{-5}—10^{-4} mM Hg (see Table 1). Their formation may be explained by interaction of neutral molecule C_5H_5Tl with the ions EX_n^+ (n = 0—4), the most probable route being the reaction of C_5H_5Tl with EX_3^+ ions (see Table 1).

In order to estimate the stabilities of $C_5H_5E^+$ ions, the atomization energies of structures A, B and C were calculated for all Group IV elements (Table 2). The structural parameters used in the calculations are listed in Table 3. Variation of E—C bond lengths within 0.1 Å does not change the ratios of the atomization energies for the structures nor the nature of the stability variation when passing from carbon to lead. Calculation of the nido-cluster structure was carried out for a planar cyclopentadienyl ring with distances C—C 1.43 Å and C—H 1.08 Å. The structure of the 6-elementafulvenyl was calculated assuming a symmetrical five-membered ring with distances C(1)—C(2) 1.44 Å, C(2)—C(3)

TABLE 1

RELATIVE INTENSITIES OF $C_5H_5Tl^+$, EX_n^+ AND $C_5H_5E^+$ IONS AT SIMULTANEOUS EVAPORATION OF C_5H_5Tl AND EX_4

Ion	Element E				
	C	Si	Ge	Sn	Pb
$C_5H_5Tl^+$	31	56	38	6	4
EX_4	—	106	27	19	3
EX_3^+	100	82	100	100	59
EX_2^+	0.8	0.4	1.2	56	2
EX^+	—	—	1.6	65	43
E^+	—	—	—	—	100
$C_5H_5E^+$	0.05	<0.01	5.1	19	0.8

TABLE 2

ATOMIZATION ENERGIES (kcal/mol) OF $C_5H_5E^+$ IONS

Element	Structure		
	A	B	C
C	—1067	—1168	—1255
Si	—1007	—1128	—1173
Ge	—994	—1115	—1155
Sn	—998	—1121	—1150
Pb	—992	—1105	—1112

1.34 Å and C—H 1.08 Å [11]. Since upon replacement of a carbon atom by a hetero-atom in the benzene ring the configuration of the whole ion should change, atom coordinates in the elementaphenyl structure were determined for a closed hexagon having a maximum area at a C—C bond length of 1.4 Å and the C—E bond lengths listed in Table 3; the C—H bond length was taken as 1.08 Å. The atom coordinates in the silaphenyl ion calculated in this way are in good agreement with those obtained by Blustin [14] for the silabenzene molecule.

As follows from Table 2, the most stable $C_5H_5E^+$ ions are those with the nido-cluster structure; the stability increasing from lead to carbon. The conclusion that the cluster-ions, C, are most stable in the case of carbon is rather unexpected. We therefore calculated the total energies of the three structures A—C of $C_6H_5^+$ ions by the CNDO/2 method [12]. Results were in complete agreement with the statistical calculation, i.e. the most stable are $C_6H_5^+$ ions with the nido-cluster structure.

It therefore may be assumed that $C_6H_5^+$ ions in the mass spectrum of $C_5H_5Fe(CO)_2CH_3$ have the structure of cluster ions of type C and are formed by the the same type of route as $C_5H_5Ge^+$ ions [6]. Their weak intensity (~1%) compared with $C_5H_5Ge^+$ ions (100%) is explained by strengthening of Fe—CH_3 and C—H as compared with Fe—Ge and Ge—CH_3 bonds.

Thus, the results point to the existence of charged nido-clusters of type C for all elements of Group IV, including carbon. These ions are formed in gas phase as a result of ion-molecular reactions and it is likely that they could be synthesized under normal conditions. Of most interest is the carbon cluster which is an isomer of the phenyl cation.

TABLE 3

C—E DISTANCES (Å) USED IN CALCULATIONS OF ATOMIZATION ENERGIES

Structure	Element E				
	C	Si	Ge	Sn	Pb
A	1.4	1.8	1.9	2.05	2.15
B	1.3	1.7	1.85	1.93	2.05
C	1.53	1.92	2.0	2.16	2.29

Experimental

Mass spectra were obtained on a AEI MS-30 mass spectrometer at an ionization chamber temperature of 150°C and an ionization voltage of 12—15 V. The spectra were converted into the monoisotopic from by use of the AELITA program [13].

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