Structure and Mechanisms of Formation of $C_6H_6Fe^+$ Ions Produced by Electron Impact on η^5-$C_5H_5Fe(CO)_2CH_3$

Dag Ekeberg, Georg Hvistendahl, Yngve Stenstrøm* and Einar Uggerud

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo 3, Norway

Ekeberg, D., Hvistendahl, G., Stenstrøm, Y. and Uggerud, E., 1992. Structure and Mechanisms of Formation of $C_6H_6Fe^+$ Ions Produced by Electron Impact on η^5-$C_5H_5Fe(CO)_2CH_3$. – Acta Chem. Scand. 46: 92–96.

Collisional activation (CA) mass spectrometry has been employed to show that $C_6H_6Fe^+$ ions formed upon electron impact of dicarbonyl-(η^5-2,4-cyclopentadienyl)-methyliron consist of a 1:1 mixture of fulvene–iron and benzene–iron structures. Analysis of daughter-ion spectra of the deuterium-labelled analogue shows that there exist two independent fragmentation routes leading to the different ion structures. These routes differ in the sequence in which the CO ligands and H_2 are lost from the molecular ion.

$C_6H_6Fe^+$ ions are produced in the gas phase as the result of loss of H_2 and two CO ligands from energized $C_5H_5Fe(CO)_2CH_3^+$ ions. The structure of $C_6H_6Fe^+$ was for several years assumed to be a complex between Fe^+ and benzene,[1] but in 1981 Müller and Lüdemann[2] raised the question of whether the structure of the C_6H_6 moiety is fulvene rather than benzene.

Nekrasov et al.[3] have studied the formation of $C_6H_6Fe^+$, undertaking deuterium-labelling experiments. Analysis of the electron ionization (EI) mass spectrum of $C_5H_5Fe(CO)_2CH_3$ (1, Scheme 1) led these workers to conclude that the extent of dehydrogenation increases with coordination unsaturation of the metal atom. This conclusion was based on the fact that there is an increase in the ratio $S = [C_6H_6Fe(CO)_n^+]/[C_5H_5Fe(CO)_nCH_3^+]$ with a decreasing number of carbonyl group ($S = 0$ for $n = 2$, $S = 0.06$ for $n = 1$ and $S = 1.9$ for $n = 0$). In addition, the EI spectrum of $C_5H_5Fe(CO)_2CD_3$ showed that HD loss in the predominant process with partial scrambling of H/D. The scrambling was found to increase with increased coordination unsaturation of the metal atom.

It is well known that molecular ions produced by 70 eV EI have a broad energy distribution and that a majority of the fragment ions are formed via high-energy processes.[4] In order to gain information about the chemically more relevant low-energy processes it was necessary to perform experiments with ions which have energies close to the critical energy of each of the reactions under investigation. Equally important is high reaction specificity. Both requirements were achieved by studying the decomposition of long-lived metastable ions.[5]

The purpose of the study described in this paper was to determine the molecular structure of the $C_6H_6Fe^+$ ions and the reaction mechanism by which the ions are formed from $C_5H_5Fe(CO)_2CH_3$. By a systematic investigation of the fragmentation of metastable ions we wished to obtain reliable information about (a) in which sequence H_2 and the two CO ligands actually are lost and (b) the detailed mechanism of the loss of H_2. The latter point is closely related to the molecular structure of $C_6H_6Fe^+$. Information about this structure will be obtained by comparison of the
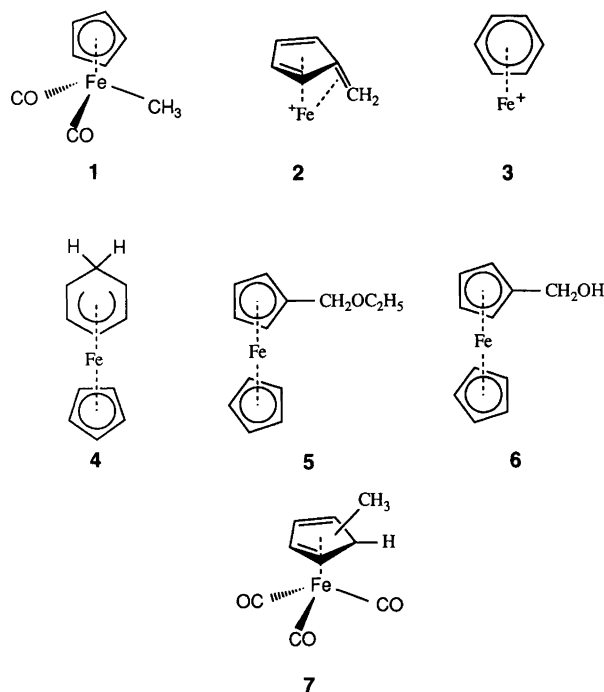
Scheme 1.

collisional activation mass spectrum of the ion of unknown structure and corresponding reference ions with known structures.

Experimental

All spectra were recorded using a double focusing mass spectrometer of EB geometry (model 7070F VG Analytical Ltd. Manchester, UK). The samples were introduced to the ion source via a temperature-regulated direct insertion probe.

Daughter-ion spectra were recorded by linked scanning of the electric and magnetic sectors keeping the ratio B/E constant.[6] Collisionally induced decomposition (CID) was achieved using He as the collision gas. Before the CID spectrum was taken, the He pressure in the collision cell was increased until the primary ion beam was attenuated by 80%.

The synthesis of $C_5H_5Fe(CO)_2CH_3$ was performed using standard methodology as previously described for acyl compounds.[7] Addition of CH_3I or CD_3I to a suspension of $C_5H_5Fe(CO)_2^-K^+$ in THF followed by evaporation and flash chromatography (silica gel 230–400 mesh, hexane) gave the σ complexes in 66 and 68% yields, respectively. The purity of the two methyl compounds were ascertained by ^1H NMR spectroscopy. The degree of deuteriation was confirmed to be >99% corresponding to the deuteriation of the starting CD_3I, both by ^1H NMR and MS. Ferrocenyl-methanol (6) was made according to the literature.[8] Ethoxymethylferrocene (5) was made using the literature[9] procedure except that 95% EtOH was used and the compound was purified by flash chromatography (silica gel 230–400 mesh, ethyl acetate–hexane 5:95 v/v) to give (5) in 85% yield. The spectroscopic data were in accordance with the literature.[10] Compound 4 was made according to Wilkinson's procedure;[11] the spectroscopic data were consistent with those previously reported.[12] Compound 7 was made using a modification of the procedure for preparation of η^4-cyclopentadienetricarbonyl iron.[13] Freshly prepared methylcyclopentadiene and $Fe_2(CO)_9$ were refluxed in diethyl ether overnight. Evaporation and flash chromatography (silica gel 230–400 mesh, ethyl acetate–hexane 5:95 v/v) gave 7 in 67% yield as a mixture of regioisomers as seen from the complex NMR spectra. Experimental details will be published in due course.

Results and discussion

The EI mass spectrum of η^5-$C_5H_5Fe(CO)_2CH_3$ (1) is reproduced in Fig. 1(a). The molecular ion, M^+, was found at m/z 192. Loss of one and two CO ligands gave rise to peaks at m/z 164 and m/z 136, respectively. The base peak at m/z 121 corresponds to loss of both CO ligands together with the methyl group. The peak at m/z 177 corresponds to loss of the methyl group from M^+, and further loss of CO gives rise to a peak at m/z 149. The $C_6H_6Fe^+$ ion at m/z 134 is
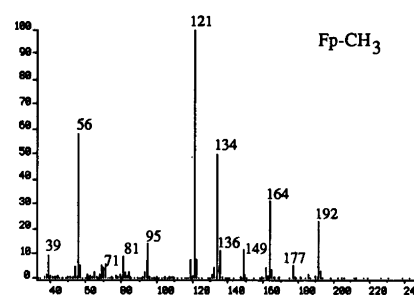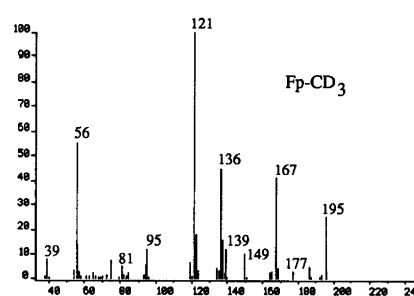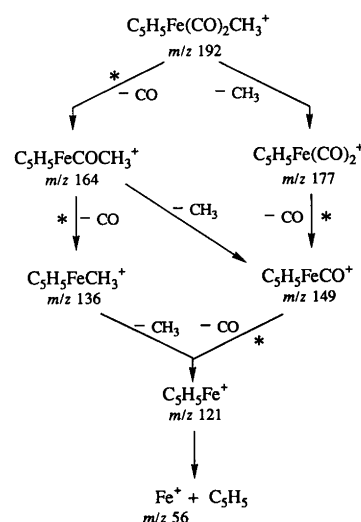

Fig. 1. EI mass spectra of dicarbonyl (η^5-2,4-cyclopentadienyl)-methyl iron (1) and its trideuteriomethyl analogue.

formed from the molecular ion upon loss of both CO ligands and H_2. The peak at m/z 56 corresponds to the naked iron ion. The fragmentation processes are summarized in Scheme 2. Fig. 1(b) shows the mass spectrum of the corresponding trideuteriomethyl analogue.

Scheme 2.

The first step in establishing the reaction mechanism was to determine in which order the two CO ligands and H_2 are lost.
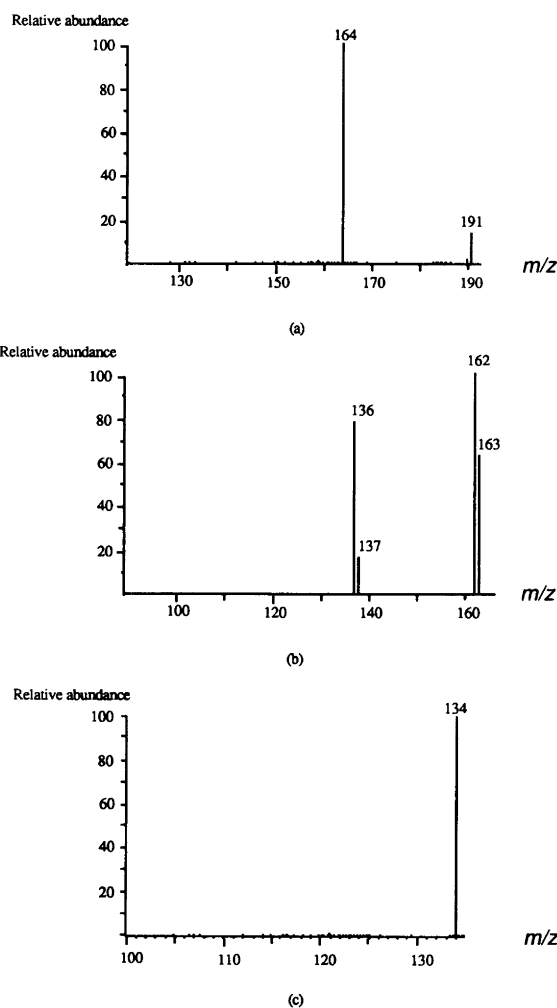
Fig. 2. Daughter-ion spectrum of the metastable ions
$C_5H_5Fe(CO)_2CH_3^+$ (*m/z* 192) (a), $C_5H_5Fe(CO)CH_3^+$ (*m/z* 164) (b) and $C_5H_5FeCH_3^+$ (*m/z* 136) (c).

containing one CH_3 and one C_5H_5 group: (a) loss of both hydrogen atoms fromt he cyclopentadienyl ligand; (b) loss of one hydrogen atom from the cyclopentadiene ligand and one from the methyl group; (c) loss of both hydrogen atoms from the methyl group. These mechanisms can only be distinguished by deuterium labelling.

The daughter-ion spectrum of metastable $C_5H_5Fe(CO)_2$-CD_3^+ ions (*m/z* 195) is shown in Fig. 3(a). The only process observed was loss of CO and formation of $C_5H_5Fe(CO)$-CD_3^+ (*m/z* 167). The major process observed in the daughter-ion spectrum of metastable $C_5H_5Fe(CO)CD_3^+$ ions [Fig. 3(b)] was loss of HD. Only a minor peak corresponding to loss of H_2 is observed. The other major peak observed corresponds to loss of CO. Fig. 3(c) shows the daughter-ion spectrum of metastable $C_5H_5Fe(CO)CD_3^+$ ions (*m/z* 139). This spectrum shows that loss of H_2, HD and D_2 occur in the ratio (0.42 : 0.47 : 0.11) which is close to the theoretical distribution obtained if we assume complete randomization of the eight hydrogens (0.36 : 0.54 : 0.10).[5]

The important conclusions to be drawn from the isotope-labelling experiments are that loss of H_2 from
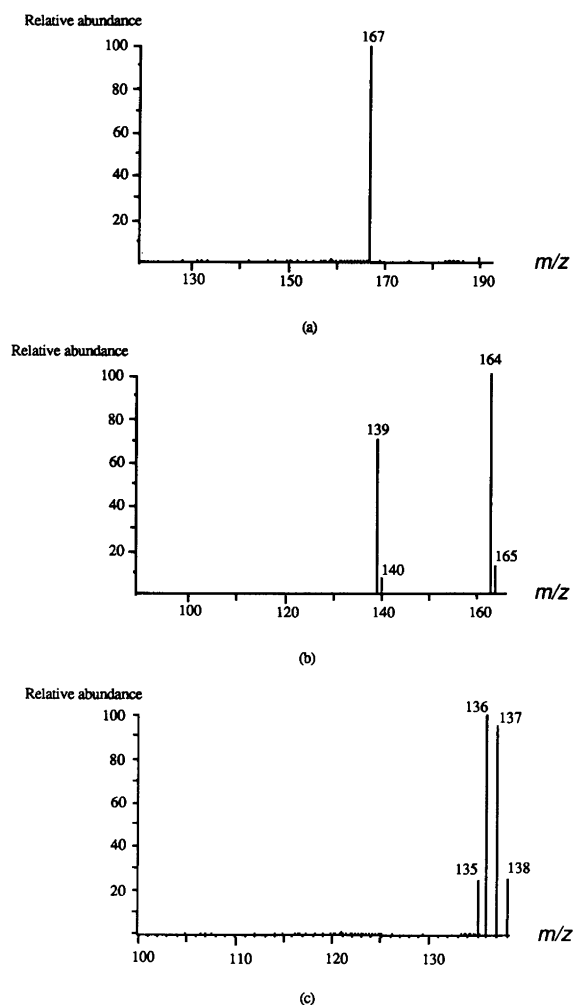
The daughter-ion spectrum of metastable $C_5H_5Fe(CO)_2$-CH_3^+ ions is shown in Fig. 2(a). The major process observed was CO loss which gave $C_5H_5Fe(CO)CH_3^+$ (*m/z* 164). Loss of CH_2O, or more probably CO + H_2, is much less abundant, only 2 % relative to loss of CO. No loss of CH_3 was observed. Metastable $C_5H_5Fe(CO)CH_3^+$ ions (*m/z* 164) lose both CO and H_2 [Fig. 2(b)]. The two reactions are almost equally abundant, indicating that the two competing reactions have nearly identical critical energies. The daughter-ion spectrum of metastable $C_5H_5FeCH_3^+$ ions (*m/z* 136), the result of two successive CO losses, is shown in Fig. 2(c). Only one peak corresponding to the loss of H_2 is observed.

From these data we conclude that there are two parallel routes for the formation of $C_6H_6Fe^+$ from $C_5H_5Fe(CO)_2CH_3^+$. One route is the following sequence of losses: −CO, −H_2, −CO, and the other route corresponds to the sequence: −CO, −CO and −H_2.

There are in principle three distinct mechanisms for the specific elimination of a hydrogen molecule from an ion

Fig. 3. Daughter-ion spectrum of the metastable ions
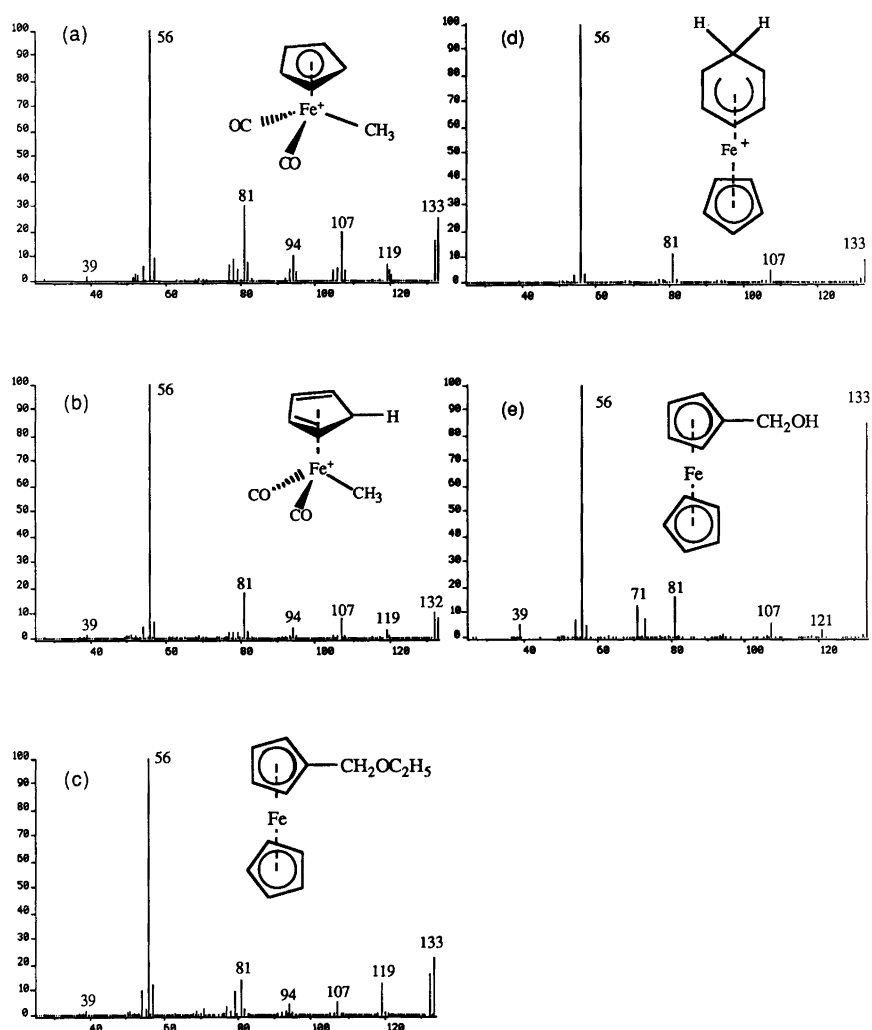$C_5H_5Fe(CO)_2CD_3^+$ (*m/z* 195) (a), $C_5H_5Fe(CO)CD_3^+$ (*m/z* 167) (b) and $C_5H_5FeCD_3^+$ (*m/z* 139) (c).

Fig. 4. Collisional activation mass spectra of C₆H₆Fe⁺ (m/z 134) ions from different neutral precursors.

C₅H₅Fe(CO)CH₃⁺ occurs largerly via mechanism (b) (one hydrogen is lost from the methyl group and one from the cyclopentadienyl ring). H₂ loss from C₅H₅FeCH₃⁺ probably occurs via a different mechanism which involves full randomization of the hydrogens, probably by migration of the methyl group to the cyclopentadienyl ring.

The second part of the investigation concerns the structure of the C₆H₆Fe⁺ ion (m/z 134). Although several structures may be formulated, we considered only the two most probable, the fulvene–iron complex (2) and the benzene–iron complex (3). These reference ions were generated via independent routes.

Benzene–iron ions (3) were produced by electron impact of C₅H₅FeC₆H₇ (4) via loss of H and C₅H₅. Fig. 4(d) shows the CA spectrum of (3). The spectrum is clearly structure indicative. Loss of benzene is the dominant fragmentation reaction, while loss of H and subsequent losses of acetylene give rise to the peaks at m/z 133, 107 and 81.

The reference spectrum of what is believed to be the fulvene–iron ion 2 can be formed in two different ways.

The most direct approach was to use [η⁵-C₅H₄CH₂X)Fe-(η⁵-C₅H₅) X = OH (6), OC₂H₅ (5)], the idea being that successive losses of C₅H₅ and X would lead C₅H₄CH₂Fe⁺ upon EI of the mother compound. This would most likely be successful for X = OC₂H₅, which is a better leaving group than OH.

The other approach started with η⁴-CH₃C₅H₅Fe(CO)₃ (7). Electron impact of this compound resulted in successive elimination of three CO ligands and H₂. The weakness of this approach is that 7 exists in three isomeric forms, which may complicate the reactions leading to the desired C₆H₆Fe⁺ isomer. However, this argument is less relevant as can be seen from the experimental results (vide infra).

The CA spectrum obtained for C₆H₆Fe⁺ from (C₅H₄CH₂-OC₂H₅)Fe(C₅H₅) (5) [Fig. 4(c)] is significantly different form the corresponding benzene–iron ion spectrum [Fig. 4(d)]. In addition to the peaks found in the benzene–iron spectrum, there are peaks at m/z 119 corresponding to loss of CH₃ and m/z 94 corresponding to loss of C₃H₄.

The CA spectrum obtained for C₆H₆Fe⁺ from (C₅H₄-
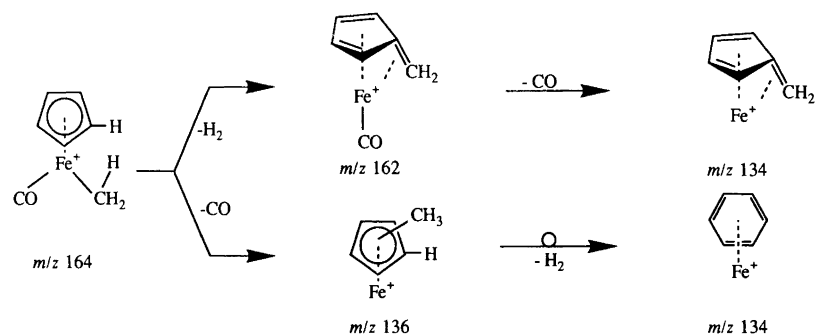
Scheme 3.

CH₂X)Fe(C₅H₅) for X = OH (**6**) [Fig. 4(e)] is different from the spectrum obtained from X = OC₂H₅ [Fig. 4(c)]. This may be attributed to the fact that OH is a poorer leaving group than OC₂H₅. The rather close resemblance between the spectra of Fig. 4(e) and 4(d) indicates a high degree of isomerization to the benzene–iron structure during ionization/dissociation of **6**.

The CA spectrum of $C_6H_6Fe^+$ from η^4-CH₃C₅H₅Fe(CO)₃ (**7**) is shown in Fig. 4(b). Except for small intensity differences the spectrum is identical with the spectrum of the assumed fulvene–iron ion [Fig. 4(c)]. The intensity variations may be attributed to differences in internal energy of the $C_6H_6Fe^+$ ions produced via the two independent routes.

When we compare the CA spectrum of $C_6H_6Fe^+$ produced from C₅H₅Fe(CO)₂CH₃ [Fig. 4(a)] with the two references [Fig. 4(c) and 4(d)] it is obvious that it is different. However, there are great similarities in all three; almost 100 % fit is achieved if one assumes that the $C_6H_6Fe^+$ generated from C₅H₅Fe(CO)₂CH₃$^+$ consists of a 1:1 mixture of benzene–iron and fulvene–iron.

Conclusions

The results from this work have been summarized in Scheme 3. There exist two independent routes for formation of $C_6H_6Fe^+$ from C₅H₅Fe(CO)₂CH₃$^+$, both via routes from the common intermediate C₅H₅Fe(CO)CH₃$^+$.

Ions which first lose H₂ and then CO produce $C_6H_6Fe^+$ ions which most probably have the fulvene–iron structure. This is because H₂ is lost specifically in the sense that one of the hydrogen atoms originates from the CH₃ group and the other from the C₅H₅ group. The loss of H₂ either precedes the formation of the C–C of the fulvene moiety or it occurs simultaneously.

The second route applies to ions which first lose CO and then H₂. In this mechanism the methyl group migrates to the C₅H₅ ligand prior to H₂ loss. This can be deduced from the fact that all eight hydrogens are randomized prior to loss of H₂. The product formed by this mechanism most probably has the benzene–iron structure.

References

1. King, R. B. *J. Am. Chem. Soc.* **90** (1968) 1417.
2. Müller, J. and Lüdemann, F. *Z. Naturforsch., Teil B36* (1981) 74.
3. Nekrasov, Yu. S., Sizoi, V. F., Orlova, T. Yu. and Kursanov, D. N. *Proc. Acad. Sci. USSR, Chem. Sect. 222* (1975) 368.
4. Howe, I., Williams, D. H. and Bowen, R. D. *Principles of Organic Mass Spectrometry*, 2nd ed., McGraw-Hill; New York 1981, p. 24.
5. Cooks, R. G., Beynon, J. H., Caprioli, R. M. and Lester, G. R. *Metastable Ions*, Elsevier, Amsterdam 1973.
6. Boyd, R. K. and Beynon, J. H. *Org. Mass Spectrom. 12* (1977) 163.
7. Stenstrøm, Y., Koziol, A. E., Palenik, G. J. and Jones, W. M. *Organometallics 6* (1987) 2079.
8. Misterkiewicz, B. *J. Organomet. Chem. 224* (1983) 43.
9. Nesmeyanov, A. N., Perevalova, É. G. and Ustynyuk, Yu. A. *Proc. Acad. Sci. USSR, Chem. Sect. 133* (1960) 921.
10. Akiyama, T., Hoshi, Y., Gato, S. and Sugimoro, A. *Bull. Chem. Soc. Jpn. 46* (1973) 1851.
11. Green, M. L. H., Pratt, L. and Wilkinson, G. *J. Chem. Soc.* (1960) 989.
12. Khand, I. U., Pauson, P. L. and Watts, W. E. *J. Chem. Soc. C* (1968) 2257.
13. Kochhar, R. K. and Pettit, R. *J. Organomet. Chem. 6* (1966) 272.

Received April 11, 1991.