

THE MASS SPECTROMETRIC BEHAVIOUR OF TRICYCLOPENTADIENYLURANIUM η^2 -IMINOALKYL(CYCLOALKYL) DERIVATIVES; THE EVIDENCE FOR SOME CYCLOPENTADIENYLURANIUM HYDRIDE SPECIES PRODUCED BY ELECTRON IMPACT

G. PAOLUCCI,

Dipartimento di Chimica, Università di Venezia, Calle Larga S. Marta 2137, 30100 Venice (Italy)

S. DAOLIO and P. TRALDI

*Istituto di Polarografia ed Elettrochimica Preparativa del C.N.R.,
 Area di Ricerca C.N.R., Corso Stati Uniti 4, 35100 Padua (Italy)*

(Received January 15th, 1986)

Summary

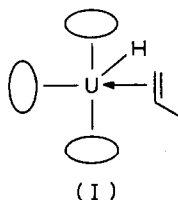
The previously unobserved fragmentation patterns of some Cp_3UX ($X = \eta^1\text{-N}(\text{C}_2\text{H}_5)_2$, $\eta^2\text{-C}(\text{CH}_3)=\text{N}(\text{C}_6\text{H}_{11})$, $\eta^2\text{-C}(\text{CH}_3)=\text{N}(\text{n-C}_4\text{H}_9)$) systems under electron impact, leading to some cyclopentadienyluranium hydride species are reported, and the mechanism of the β -hydride rearrangement and the role of the N-donor ligands are discussed on the basis of linked scans and MIKE spectrometry.

Introduction

In the last few years the chemistry of organoactinide derivatives has received increasing attention [1] because their reactions differ sometimes markedly, from those of the analogous transition metal derivatives.

Although bis(pentamethylcyclopentadienyl)uranium(IV) hydrides are known [2], there has until now been no report of the isolation, or even the detection, of unsubstituted cyclopentadienyluranium(IV) hydrides. Some attempts to isolate the " Cp_3UH " species failed because a reduction of U^{IV} to U^{III} occurred, although " Cp_3UH " was tentatively identified as an intermediate in the reduction of Cp_3UCH_3 by LiCH_3 [3]. However, the very low thermal stability of the " MR_4 " species ($\text{M} = \text{U}^{\text{IV}}$, Th^{IV} ; $\text{R} = \text{alkyls}$), which are coordinatively unsaturated, has been assigned to β -hydride elimination processes [4] through the formation of intermediate hydride species.

Increase in the coordinative saturation by introduction of cyclopentadienyl groups makes the Cp_3UR and Cp_3ThR compounds thermally stable, since β -hydride elimination can then occur only when alkene-hydride intermediates in transition states such as I [5] are energetically accessible which is not the case in the Cp_3MR derivatives.



However, there remains a theoretical possibility of lowering the energy of the transition states such as I, by using ligands containing both β -hydrogens and donor atoms.

The insertions of molecules containing multiple dipolar bonds into $\text{M}-\text{C}$ bonds of Cp_3MR systems have been described recently ($\text{M} = \text{U}^{\text{IV}}, \text{Th}^{\text{IV}}, \text{R} = \text{alkyls}$) [6,7]. In contrast to the results with the analogous transition metal complexes, the CO insertion into $\text{M}-\text{C}$ bonds of Cp_3MR ($\text{M} = \text{U}^{\text{IV}}$ and Th^{IV}) affords η^2 -acyl derivatives, in which the oxycarbenic character of the introduced group depends on the nature of the metal [7]. Thus, η^2 -acyl derivatives having a more pronounced carbenic character undergo in the condensed phase some β -hydride rearrangements typical of such species [7-11].

To date mass spectrometry has been used mainly as an analytical tool in determination of the molecular weights of organoactinide compounds and only a few reports, concerned with derivation of the mode of ligation from the fragmentation pattern of some Cp_3MX compounds, have been published [12].

We describe here the mass spectrometric behaviour of tricyclopentadienyl-uranium(IV) η^2 -iminoalkyl(cycloalkyl) derivatives [13] and the evidence of some cyclopentadienyluranium hydride species formed by electron impact, as obtained by linked scans [14], exact mass measurements, and mass analyzed ion kinetic energy (MIKE) spectrometry [15].

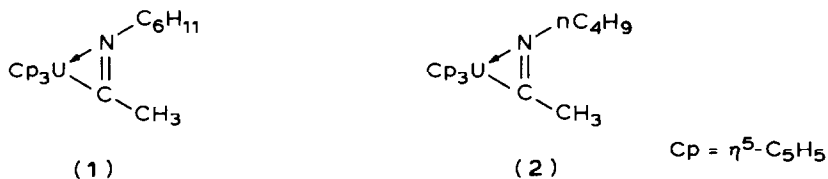
Experimental

The very air sensitive compounds $\text{Cp}_3\text{UC}_2\text{H}_5$, $\text{Cp}_3\text{UN}(\text{C}_2\text{H}_5)_2$, $\text{Cp}_3\text{UOC}_2\text{H}_5$, $\text{Cp}_3\text{U}(\eta^2\text{-COCH}_3)$, $\text{Cp}_3\text{U}(\eta^2\text{-CO-n-Bu})$, $\text{Cp}_3\text{U}[\eta^2\text{-C}(\text{CH}_3)=\text{N}(\text{C}_6\text{H}_{11})]$, and $\text{Cp}_3\text{U}[\eta^2\text{-C}(\text{CH}_3)=\text{N}(\text{n-C}_4\text{H}_9)]$ were prepared by published methods [6,16,17].

All mass spectrometric measurements were performed on a VG ZAB 2F instrument operating at 70 eV (200 μA) and with a source temperature of 200°C. The very air sensitive samples were introduced under nitrogen by the direct electron impact (DEI) [18] technique. Metastable transitions were detected by B/E , B^2/E linked scans [14]. Exact mass measurements were performed with the peak matching technique at 20 000 resolving power (10% valley definition). Mass analyzed ion kinetic energy spectra were obtained in the usual way [15].

Results and discussion

The 70 eV EI mass spectra of compounds **1** and **2** are presented in Fig. 1. By *B/E* linked scans and exact mass measurements, the fragmentation pattern reported in Scheme 1 (compound **1**) has been derived.



The primary decomposition pathways arise from losses of Cp[•] (*m/z* 492), H[•] (*m/z* 556), C₆H₁₁[•] (*m/z* 474), C₈H₁₄N[•] and C₈H₁₃N (*m/z* 433 and 434, respectively). The first four of these decomposition routes were to be expected, but it is the last one, involving a H rearrangement, which seems to be rather unusual for this class of compounds. Its occurrence could be attributed to the formation of tri-

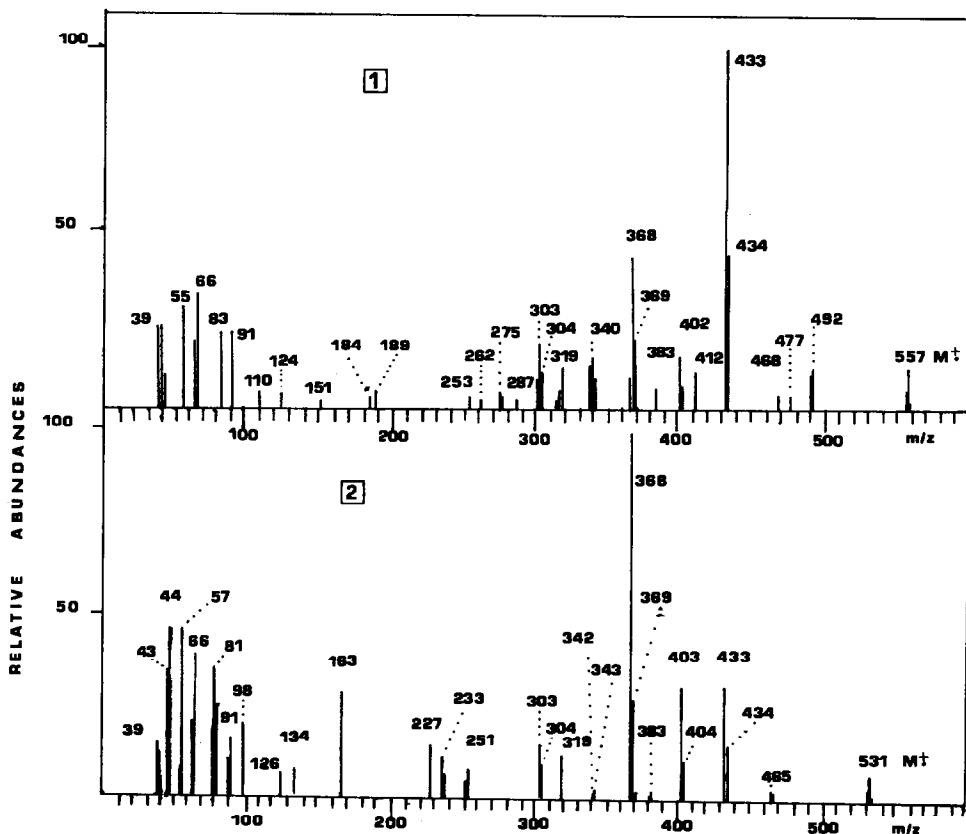
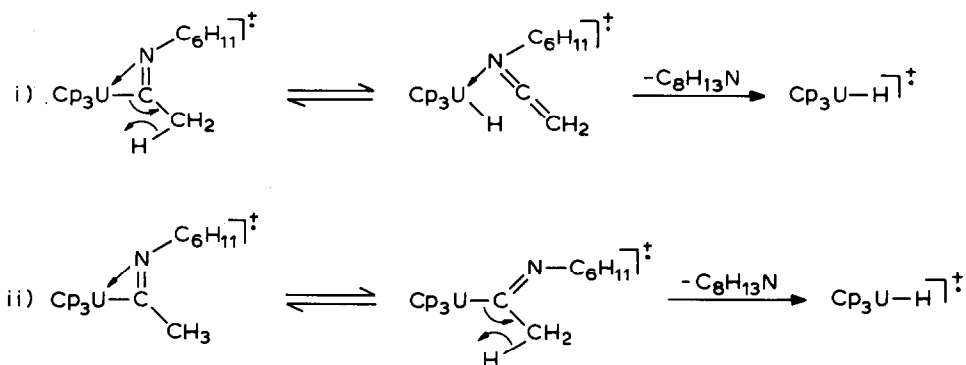


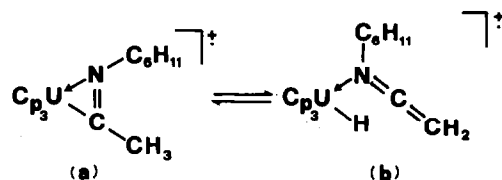
Fig. 1. Mass spectra (EI, 70 eV) of Cp₃U[η^2 -C(CH₃)=N(C₆H₁₁)] (1) and Cp₃U[η^2 -C(CH₃)=N(C₄H₉)] (2).

cyclopentadienyluranium(IV) hydride, a species occasionally detected but never isolated in the condensed phase chemistry of the tricyclopentadienyl(IV) compounds.

This hydride could be formed, in principle, through two different routes (i and ii),



the first of these a β -H rearrangement (i), involves immediately after the ionization process; this could take place through a concerted four center mechanism involving the simultaneous breaking of the U-C σ bond and formation of the U-H bond. The ionic product so obtained would be highly stabilized by the coordination with the iminoketene residue, the transition state being reminiscent of the previously supposed alkeneuranium hydride intermediate [5]. Thus the parent ion could be best represented by two forms **a** and **b** in equilibrium:



The second mechanism (ii) involves, initial cleavage of the coordinative bond between the U and N atoms, and then loss of the neutral species $C_6H_{11}N=C=CH_2$. If this second mechanism operates the role of the coordinated N atom would be unimportant, and the same behaviour should be shown by other tricyclopentadienyluranium(IV) derivatives containing β -hydrogens available for this rearrangement. However, when we examined $Cp_3UC_2H_5$ and $Cp_3U-n-C_4H_9$ under identical conditions we did not observe the presence of any cyclopentadienyluranium hydride species in their mass spectra. This result suggests that the η^2 -ligation mode of the iminoalkyl(cycloalkyl) arising from the presence of an additional coordinating atom could be the determining factor. Some η^2 -acyltricyclopentadienyluranium(IV) derivatives were studied under the same conditions, viz.: $Cp_3U(\eta^2-COCH_3)$, $Cp_3U(\eta^2-CO-n-C_4H_9)$ and $Cp_3U[\eta^2-CON(C_2H_5)_2]$, but in no case was there evidence for a cyclopentadienyluranium hydride species, indicating that the availability of oxygen as a donor atom in the η^2 -arrangements considered does not favour the β -H rearrangement; in other words the oxygen atom does not "assist" the β -H rearrangement. This behaviour was noted also in the comparative mass spectra of $Cp_3UOC_2H_5$ and $Cp_3UN(C_2H_5)_2$ (Tab. 1), thus while $Cp_3UOC_2H_5$ undergoes

TABLE 1

MASS SPECTROMETRIC DATA FOR COMPOUNDS $\text{Cp}_3\text{U}[\eta^2\text{-C}(\text{CN}_3)=\text{N}(\text{C}_6\text{H}_{11})]$ (1), $\text{Cp}_3\text{U}[\eta^2\text{-C}(\text{CH}_3)=\text{N}(\text{C}_4\text{H}_9)]$ (2) AND $\text{Cp}_3\text{U}[\text{N}(\text{C}_2\text{H}_5)_2]$ (EI, 70 eV)

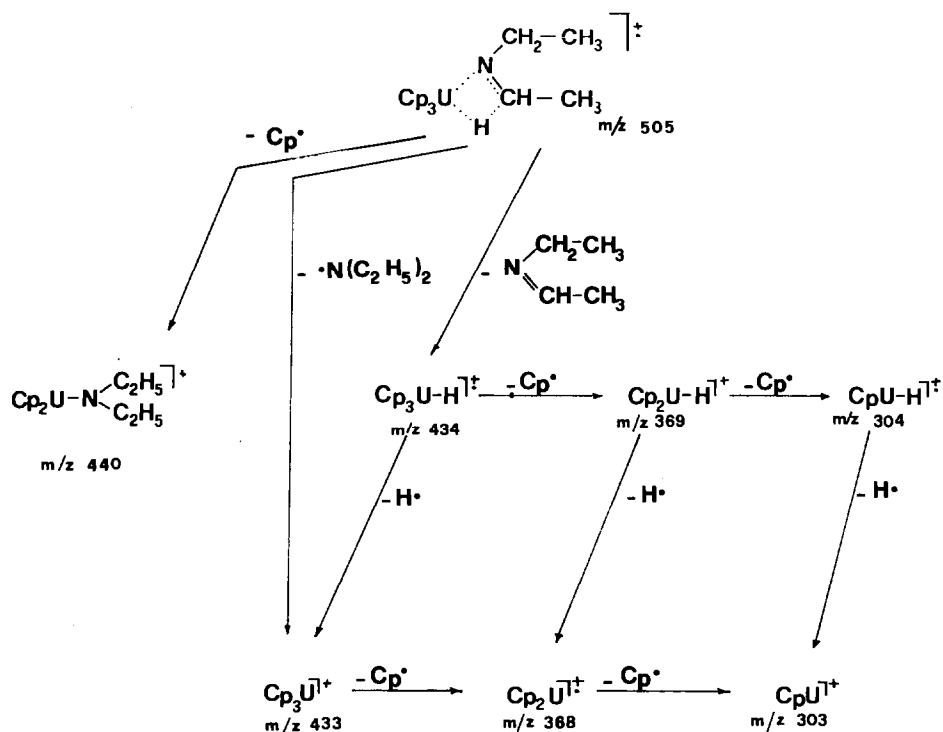
$\text{Cp}_3\text{U } \eta^2\text{-C}(\text{CH}_3)\text{N}(\text{C}_6\text{H}_{11})$		$\text{Cp}_3\text{U } \eta^2\text{-C}(\text{CH}_3)\text{N}(\text{C}_4\text{H}_9)$		$\text{Cp}_3\text{U-N}(\text{C}_2\text{H}_5)$	
Fragment	<i>m/z</i> relative abundance	Fragment	<i>m/z</i> Relative abundance	Fragment	<i>m/z</i> Relative abundance
M^+	557 24	M^+	531 12	$M^+ + 1$	506 8
$M^+ - 1$	556 2	$M^+ - 1$	530 2	M^+	505 28
$M^+ - \text{Cp}$	492 21	$M^+ - \text{C}_4\text{H}_9$	474 28	$M^+ - \text{Cp}$	440 10
$M^+ - \text{CpH}$	491 2	$\text{Cp}_3\text{UNCCH}_2^{\cdot+}$	473 3	$M^+ - \text{CpH}$	439 61
$\text{Cp}_2\text{UNC}_6\text{H}_{11}\text{C}^{\cdot+}$	477 8	$M^+ - \text{Cp}$	466 8	$\text{Cp}_3\text{UH}^{\cdot+}$	434 25
$M^+ - \text{C}_6\text{H}_{11}$	474 3	$M^+ - \text{CpH}$	465 10	$\text{Cp}_3\text{U}^{\cdot+}$	433 100
$\text{Cp}_3\text{UNCCH}_2^{\cdot+}$	473 2	$\text{Cp}_2\text{UNC}_4\text{H}_9\text{C}^{\cdot+}$	451 2	$\text{Cp}_2\text{UCH}_3^{\cdot+}$	383 10
$\text{Cp}_3\text{UH}^{\cdot+}$	434- 78	$\text{Cp}_3\text{UH}^{\cdot+}$	434 16	$\text{Cp}_2\text{UH}^{\cdot+}$	369 23
$\text{Cp}_3\text{U}^{\cdot+}$	433 100	$\text{Cp}_3\text{U}^{\cdot+}$	433 100	$\text{Cp}_2\text{U}^{\cdot+}$	368 98
$\text{CpUNC}_6\text{H}_{11}\text{C}^{\cdot+}$	412 19	$\text{Cp}_2\text{UNCCH}_3^{\cdot+}$	409 2	$\text{C}_3\text{H}_3\text{CpU}^{\cdot+}$	342 7
$\text{Cp}_2\text{UNHCCH}_3^{\cdot+}$	410 5	$\text{Cp}_2\text{UNCCH}_2^{\cdot+}$	408 2	$\text{C}_3\text{HCpU}^{\cdot+}$	340 8
$\text{Cp}_2\text{UCH}_3^{\cdot+}$	383 15	$\text{Cp}_2\text{UCH}_3^{\cdot+}$	383 18	$\text{CpUH}^{\cdot+}$	304 6
$\text{Cp}_2\text{UH}^{\cdot+}$	369 39	$\text{Cp}_2\text{UH}^{\cdot+}$	369 8	$\text{CpU}^{\cdot+}$	303 20
$\text{Cp}_2\text{U}^{\cdot+}$	368 90	$\text{Cp}_2\text{U}^{\cdot+}$	368 76		
$\text{CpUNHCCH}_3^{\cdot+}$	345 5	$\text{C}_3\text{H}_3\text{CpU}^{\cdot+}$	342 7		
$\text{C}_3\text{H}_3\text{CpUH}^{\cdot+}$	343 2	$\text{CpUCH}_3^{\cdot+}$	318 20		
$\text{C}_3\text{H}_3\text{CpU}^{\cdot+}$	342 2	$\text{CpUH}^{\cdot+}$	304 3		
$\text{CpUH}^{\cdot+}$	304 3	$\text{CpU}^{\cdot+}$	303 10		
$\text{CpU}^{\cdot+}$	303 38	$\text{C}_3\text{H}_3\text{U}^{\cdot+}$	277 2		

fragmentation by the usual pathways observed for other Cp_3UX systems (i.e. by loss either of Cp^{\cdot} and X^{\cdot} fragments), without the formation of any cyclopentadienyluranium hydride species, $\text{Cp}_3\text{UN}(\text{C}_2\text{H}_5)_2$ gives ions at *m/z* 434 ($\text{Cp}_3\text{UH}^{\cdot+}$), 369 ($\text{Cp}_2\text{UH}^{\cdot+}$), and 304 ($\text{CpUH}^{\cdot+}$) as expected for the fragmentation pattern depicted in Scheme 2 (determined by linked scans).

Examination of spectral data throws light on the origin of the β -H rearrangement process.

In Fig. 2 are presented plots of the absolute abundances of the ionic species at *m/z* 433, 434, 474, and 492 (corresponding to the four primary decompositions) against time. It is evident that the decrease of the ionic species at *m/z* 434 and *m/z* 433 suggests that the kinetic window of the decomposition processes leading to these ions is close to the residence time into the ionization chamber, while the opposite is the case for the ionic species at *m/z* 474. The ions at *m/z* 492, arising from loss of cyclopentadienyl, behave quite differently, showing an abundance maximum in the I FFR (First Free Field Region). Again the decrease of the hydride ions at *m/z* 434, proves that the process leading to them is particularly fast and parallels the loss of both cyclopentadienyl and cyclohexyl fragments.

From the metastable data and those for the other Cp_3UX systems, which reveal the dominant role of the N-donor atom in "assisting" the β -H, rearrangement, we believe that the mechanism (i) (which is surely faster than process (ii), and the only one which would lead to a molecular ion in the hydride structure, as observed in the II FFR - see discussion above) is more attractive than mechanism (ii). It is reasonable to assume the structure of M^+ shown in (i); the presence of the H-bridge between the U atom and the CH_3 group strongly stabilizes the positive charge.



SCHEME 2. Fragmentation pattern of $\text{Cp}_3\text{U}[\text{N}(\text{C}_2\text{H}_5)_2]$ as derived from *B/E* linked scans.

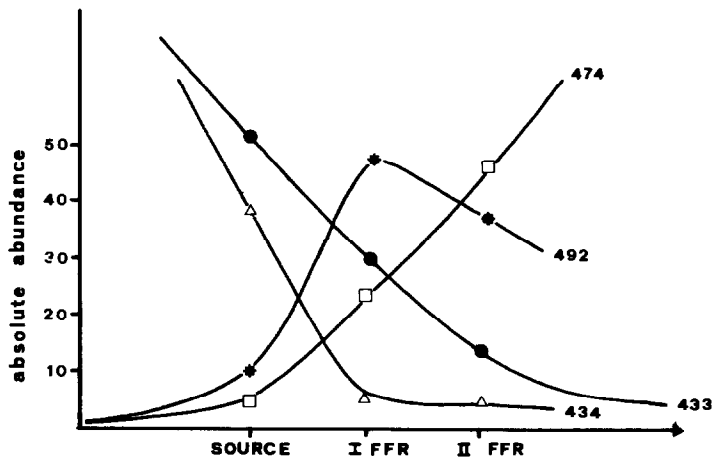


Fig. 2. Plots of absolute abundance vs. time for fragments of m/z , 492, 474, 434 and 433 from compound 1, as derived from metastable data.

m/z	Absolute Intensity			
	433	434	474	492
Source	51	37	3	9
I FFR	29	3	22	46
II FFR	15	3	43	39

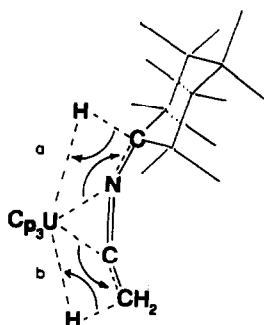


Fig. 3. Possible pathways for the β -H rearrangement in compound 1.

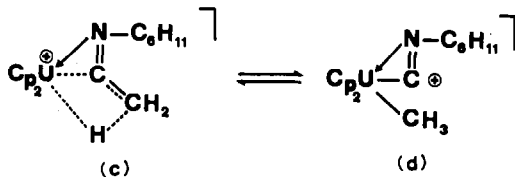
Furthermore this structure is consistent with the kinetic data, requiring the simple cleavage of the coordinative N-U bond to give the U hydride ionic species. For pathway (ii), a further cleavage of the U-C σ bond and a H rearrangement are required.

In conclusion, the molecular species of compound 1 are mainly present in two structures; the first of these (a), which decomposes with loss of $C_6H_{11}NCCH_3$; is strictly related to the neutral species, and the second (b), as discussed above, seems to have partial hydride character.

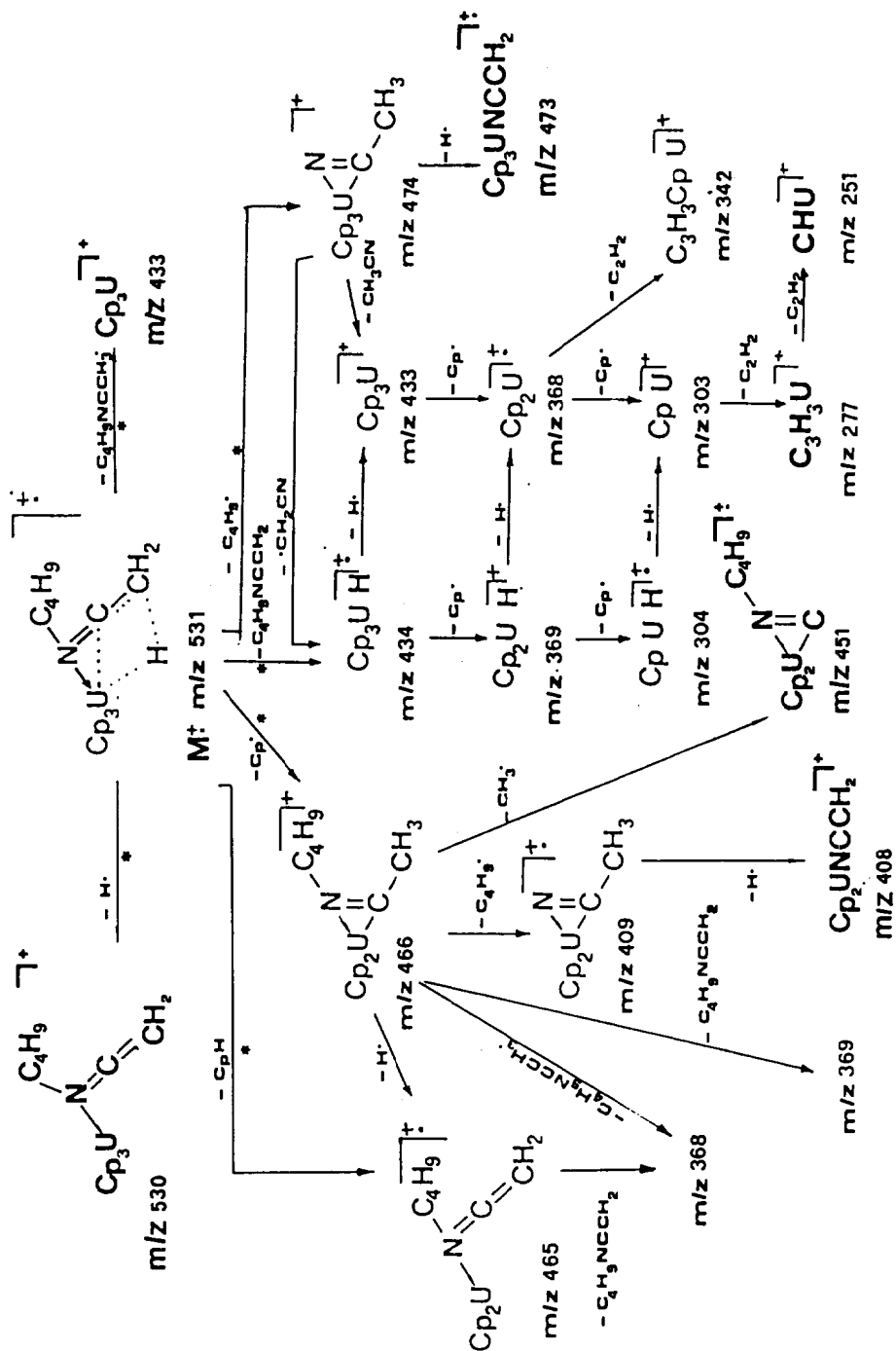
As far as the H transferred to the uranium is concerned, it may come, in principle, from any of the β -sites (i.e. from CH_3 or from the cyclohexyl group) as shown in Fig. 3.

The absence in the primary decomposition pattern of the fragment $M^+ - CH_3$ is in agreement with the presence of the molecular species b, in which the methyl has become a methylene group doubly bound to the iminoketene group.

On the other hand the behaviour of the ion at m/z 492 (Scheme 1), present as one of the most abundant fragments (21%), is consistent with its coming from two species in equilibrium c and d.



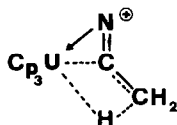
Form d has to be invoked to explain the formation of the ionic species at m/z 383 and 318, both containing the U- CH_3 bond, and those at m/z 477 and 412 arising from loss of CH_3 ; while form c is involved in the fragmentation leading to the ionic species at m/z 410 and 369. In this case also, a concerted four center mechanism has to be involved for the β -H rearrangement analogous to that suggested for the parent ion fragmentation to Cp_3UH^+ at m/z 434. Thus, it may be assumed that ions at m/z 492 are present in at least two different forms, in equilibrium with another, in which new U-H and U- CH_3 bonds have been formed. While compounds containing U- CH_3 bonds are well known and stable in the condensed phase, the formation of the U-H bond during the fragmentation pattern of compound 1 indicates a high stability of these hydride structures in the ionic gas



SCHEME 3

phase. In this connection it should be emphasized that the sequence: m/z 554 \rightarrow 434 \rightarrow 369 \rightarrow 304, resulting from a progressive loss of cyclopentadienyl radicals with formation of the very unusual hydride species Cp_3UH^+ , Cp_2UH^+ , and $CpUH^+$, has never been detected.

Finally, the ions at m/z 474, originating through initial loss of cyclohexyl must be of two different types, as argued for the ions at m/z 492. The metastable supported transitions leading to ionic species at m/z 433 and 434 indicate the precursors for these species are hydrides.



Analogous behaviour has been observed under the same conditions also for compound **2** (Table 1), confirming that its fragmentation pattern (Scheme 3) is typical of this class of compounds containing β -H.

Acknowledgments

We are indebted to Dr G. Rossetto of the Istituto di Chimica e Tecnologia dei Radioelementi C.N.R. (Padua) for preparation of the various samples, and to Prof. R.D. Fischer (University of Hamburg) for useful discussions, and are grateful to C.N.R. for valuable financial support.

References

- 1 T.J. Marks and R.D. Ernst, in *Comprehensive Organometallic Chemistry*, Pergamon Press, 1982, Vol. 6, p. 173.
- 2 P.J. Fagan, J.M. Manriquez, E.A. Maata, A.M. Seyam and T.J. Marks, *J. Am. Chem. Soc.*, 103 (1981) 6650.
- 3 E. Klahne, C. Giannotti, H. Marquet-Ellis, G. Folcher and R.D. Fischer, *J. Organomet. Chem.*, 201 (1980) 399.
- 4 T.J. Marks and A.M. Seyam, *J. Organomet. Chem.*, 67 (1974) 61.
- 5 J.K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic Press, New York, 1978, 247-261.
- 6 G. Paolucci, G. Rossetto, P. Zanella, K. Yunlu, R.D. Fischer, *J. Organomet. Chem.*, 272 (1984) 363.
- 7 D.C. Sonnenberger, E.A. Mintz and T.J. Marks, *J. Am. Chem. Soc.*, 106 (1984) 3484.
- 8 J.M. Manriquez, P.J. Fagan, T.J. Marks, C.S. Day, V.W. Day, *J. Am. Chem. Soc.*, 100 (1978) 7112.
- 9 T.J. Marks, J.M. Manriquez, P.J. Fagan, V.W. Day, C.S. Day and S.H. Vollmer, *Am. Chem. Soc. Symp. Ser.*, 131 (1980) 1.
- 10 P.J. Fagan, J.M. Manriquez, T.J. Marks, V.W. Day, S.H. Vollmer and C.S. Day, *J. Am. Chem. Soc.*, 102 (1980) 5393.
- 11 P.J. Fagan, F.A. Maatta and T.J. Marks, *Am. Chem. Soc. Symp. Ser.*, 152 (1981) 53.
- 12 J. Muller, *Chem. Ber.*, 102 (1969) 152.; G. Paolucci, P. Zanella and A. Berton, *J. Organomet. Chem.*, 295 (1985) 317.
- 13 G. Paolucci, G. Rossetto, P. Zanella and R.D. Fischer, *Abstr. 14èmes Journées des Actinides, Davos, Switzerland, 1984*, 71; G. Paolucci, S. Daolio and P. Traldi, *Abstr. XIIth Intern. Conf. Organomet. Chem., Wien, 1985*, p. 524.
- 14 A.P. Bruins, K.R. Jennings and S. Evans, *Int. J. Mass Spectrom. Ion Phys.*, 26 (1978) 395.
- 15 R.G. Cooks in *Collision Spectroscopy*, R.G. Cooks (Ed.), Plenum Press, New York, 1978, p. 357-450.
- 16 G. Paolucci, G. Rossetto, P. Zanella and R.D. Fischer, *J. Organomet. Chem.*, 284 (1985) 213.
- 17 P. Zanella, G. Paolucci, G. Rossetto, F. Benetollo, A. Polo, R.D. Fischer and G. Bombieri, *J. Chem. Soc. Chem. Commun.*, (1985) 96.
- 18 P. Traldi, U. Vettori and F. Dragoni, *Org. Mass Spectrom.*, 17 (1982) 587.