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PHOTOLYSIS OF ISOPROPYLTRICYCLOPENTADIENYLURANIUM(IV): HOMOLYSIS RATHER THAN β-HYDRIDE ELIMINATION

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Summary

Photolytic decomposition of the title compound (Cp_3U-i-Pr) proceeds by homolytic cleavage of the U—C σ-bond and not by β-hydride elimination. The presence of free alkyl radicals was demonstrated by the ESR spin-trapping technique and the reaction shown to be first order in uranium alkyl. The major organouranium product is Cp_3U^{III} THF.

Introduction

As part of our continuing interest in the chemistry of organouranium complexes containing a U—C σ-bond we recently reported our findings on the photolysis and thermolysis of U^{IV} compounds of the type Cp_3UR ($Cp = \eta^5$-C_5H_5, R = CH_3, n-Bu) [1]. These compounds photolysed readily at 60°C in THF and the final product of reaction was the uranium(III) derivative, Cp_3U^{III} THF [2]. Kinetic, ESR and NMR data for these reductions, together with mass spectroscopic and gas chromatographic analyses of the organic products pointed strongly to an initial homolysis of the U—C σ-bond to produce a cage radical pair, decomposition of which was assisted by the solvent, THF. With Cp_3U-n-Bu no evidence was found for any significant amount of decomposition via a β-hydride elimination mechanism, a pathway frequently followed by suitably substituted organometallic compounds [3]. (Cp_3UCH_3 of course cannot react by this mechanism.) Indeed, it has already been well established by Marks and his co-workers [4] that thermal decomposition of $Cp_3U^{IV}R$ species (R = e.g. CH_3, n-Bu, t-Bu, i-Pr) in toluene does not involve β-hydride elimination but rather quantitative intramolecular hydrogen abstraction from a Cp group with liberation of an alkane. The nature and fate of the organometallic residue in these reactions could not

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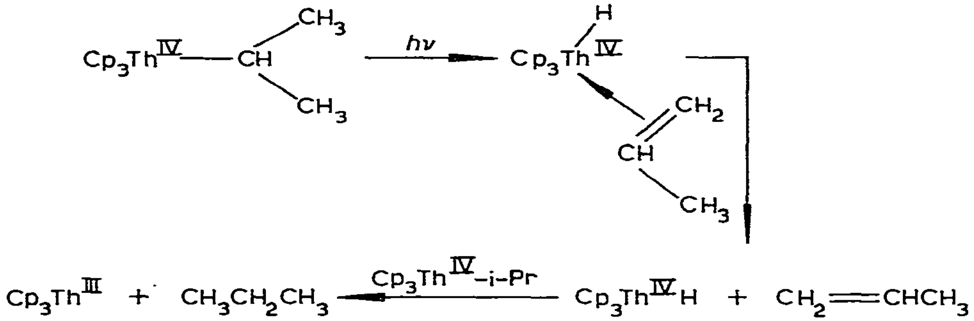
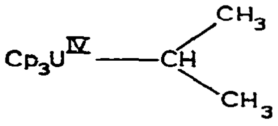
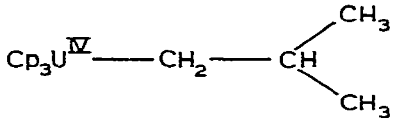
be definitively established, although the formula $(\eta^5\text{-}C_5H_5)_2U^{IV}(\eta^1\text{-}C_5H_4)_2U^{IV}\text{-}(\eta^5\text{-}C_5H_5)_2$ was suggested [5]. In contrast, the related thorium(IV) complexes [6] ($Cp_3Th^{IV}R$, R = e.g., i-Pr, n-Bu, neopentyl) thermolyse cleanly in toluene at 170°C, again with intramolecular abstraction of a Cp hydrogen to give alkane and $(\eta^5\text{-}C_5H_5)_2Th^{IV}(\eta^1\text{-}C_5H_4)_2Th^{IV}(\eta^5\text{-}C_5H_5)_2$, the X-ray structure of which has been determined [5]. In addition, photolysis of Cp_3Th^{IV}i-Pr in benzene [7] proceeds by a different route, leading to the dark green Cp_3Th^{III} [8] and almost equal quantities of propane and propene. This was explained in terms of the following mechanism involving a photo-induced β-hydride elimination.



This difference in photolytic and thermolytic behaviour of Cp_3Th^{IV}i-Pr prompted us to a detailed study of the uranium analogue, Cp_3U^{IV}i-Pr (I).



(I)



(II)

Cp_3U^{IV} —$CH_2CH_2CH_2CH$

(III)

The kinetics of the photolytic decompositions of Cp_3U-i-Bu (II) and Cp_3U-n-Bu (III) in THF solution are also presented here for comparison. Cp_3U-i-Pr (I) contains six hydrogens in the β-position and should be a very favorable candidate for β-elimination, in contrast to the isobutyl (II) and n-butyl (III) compounds which possess only one and two β-hydrogens, respectively.

Experimental

All operations were performed under dry argon as the uranium alkyls are extremely sensitive to oxygen and water. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone under Ar. Cp_3U-n-Bu (III) was prepared as before [1]. I and II were made by dropwise addition of a THF solution of the appropriate Grignard reagent (RMgBr) to a cooled (0°C) and stirred solution of Cp_3UCl [9] in THF. The purity of the Cp_3UR complexes was checked by ^1H NMR on a Varian NV 14 (60 MHz). One THF resonance was used as lock and the large paramagnetic shifts of these compounds permitted the routine use of non-deuterated THF. Values are quoted in ppm relative to benzene with upfield shifts positive.

Cp_3U-i-Pr (I) in THF 10.5 s (15 H), 3 × Cp; 19.7d, $J = 7$ Hz (6 H), 2 × CH_3; 184 septet, $J = 7$ Hz (1 H), CH. (literature [4], 10.9; 19.3; 190 in toluene).
Cp_3U-i-Bu (II) in THF: 10.2s (15 H), 3 × Cp; 24.5d, $J = 7$ Hz (6 H), 2 × CH_3; 24.7 broad, (1 H), CH; 185d, $J = 7$ Hz, (2 H), CH_2-(literature [10], 10.5; 24.7; 26.1; 194.3 in toluene-d_8).

Gas chromatographic analyses were carried out on a Perkin-Elmer 3920 B instrument equipped with a 0.5 m phenylisocyanate column (60°C); aliquots of the gases above the solutions were removed through a septum with a gas syringe. Infrared spectra were obtained between AgCl plates using degassed Nujol on a Perkin-Elmer 580 instrument, and mass spectra were run on a VG 305 F instrument. ESR spectra were performed using a Bruker ER 420 spectrometer fitted with B-ST 100/700, B-MN 12 and B-A6 variable temperature accessories. The following spin-trap reagents were employed: nitrosodurene (ND), phenyl-1-t-butylnitrone (PBN) and 5,5'dimethylpyroline-*N*-oxide (DMPO).

All irradiations and thermolyses were carried out as described previously [1].

Results

Kinetics

The kinetics were determined from the intensity of the NMR signals and are first order in respect to the uranium alkyl (Table 1).

Table 1 shows the very marked effect of photolysis, as all three compounds are stable in the dark for several weeks at 10°C. In addition the Table highlights the well known thermal stability of Cp_3U-n-Bu [4], although Cp_3U-i-Bu is in the same range. As already noted for Cp_3UCH_3 and Cp_3U-n-Bu [1], the thermal stability of Cp_3U-i-Pr in THF is significantly lower than in toluene, but the overall thermal stability follows the trend primary > secondary as pointed out by Marks et al. [4]. Under photolysis, however, Cp_3U-i-Pr(I) and Cp_3U-i-Bu (II) have a very similar stability, and this is much lower than that of Cp_3U-n-Bu (III). Clearly, factors other than branching at the first carbon are involved in the photo-assisted decompositions.

Analysis of the hydrocarbons evolved

Both irradiation and thermolysis experiments were accompanied by a large increase in hydrocarbon content in the gases above the solutions but the rela-

TABLE 1

KINETIC DATA FOR Cp_3UR IN THF

Complex	Photolysis at 10°C		Thermolysis at 60°C	
	$k \times 10^{-1}$ (h^{-1})	$t_{1/2}$ (h)	$k \times 10^{-1}$ (h^{-1})	$t_{1/2}$ (h)
Cp_3U-i-Pr (I)	7.8	0.88	2.3	3.0
Cp_3U-i-Bu (II)	8.25	0.84	0.115	60
Cp_3U-n-Bu (III)	0.82	8.33	0.0686	101

tive proportions of alkane/alkene remained constant throughout any one experiment (Table 2).

The analyses show that in all experiments there is predominant alkane formation at the expense of alkene. This result clearly demonstrates that a β-elimination mechanism cannot be involved to any major extent. Moreover, the relative ratio of alkane/alkene varies little between thermolysis and photolysis, implying essentially the same mechanism in both cases, although the reaction is much faster for photolysis. The relative proportions of gases found in all experiments can be explained in terms of an initial homolytic cleavage of the U—alkyl bond which gives rise to free radicals contained initially within, and stabilised by [19], a solvent (THF) cage [11]. Hydrogen abstraction from THF or a Cp produces an alkane, whilst some radical disproportionation forms the observed alkene plus further alkane. Radical combination products (R—R), although detected, could not be determined quantitatively due to experimental difficulties. Further support for this mechanism is provided by the ESR studies (described below) which showed the release of alkyl radicals on irradiation.

ESR studies

We investigated the photolysis of $Cp_3U—R$ in THF both in the presence and absence of the spin-trap reagents.

In the absence of spin-traps, photolysis of $Cp_3U—R$ ($R = CH_3$, $CH(CH_3)_2$, $CH_2CH(CH_3)_2$) at room temperature (295 K) gave no detectable signal but at low temperature (120 K) a signal with five hyperfine lines appeared. $R = CH_3$ g_{iso} 2.0099 ± 0.0002; $a_H = 20.99$; $R = i\text{-}C_3H_7$ $g_{iso} = 2.0032 \pm 0.0002$; $a_H = 18.33$; with $R = i\text{-}C_4H_9$ the signal was not well resolved $g_{iso} = 2.0005 \pm 0.0002$ and showed no hyperfine splitting. The spin density, measured using DPPH * as external standard, gave approximately 1% of free radical compared to the concentration of Cp_3UR in solution. The signal increased under continuous photolysis and reached a steady state after thirty minutes of continuous irradiation. The signal was stable between 110 K and 150 K but disappeared above that temperature.

The two most plausible explanations for this type of signal are:

1. A geminate reaction, in the frozen solvent cage, of $R^\bullet$ with one hydrogen atom of a cyclopentadienyl ring leading to the radical $Cp_2U^{III}Cp'^\bullet$ as indicated below

$$Cp_3U^{IV}R \rightarrow Cp_3U\cdots R \rightarrow Cp_3U^{III}R^\bullet \rightarrow Cp_2U^{III}Cp'^\bullet + RH$$

$$Cp'^\bullet = (C_5H_4)^\bullet$$

2. Intermolecular reaction in the frozen solution between $Cp_3U^{IV}R$ and $R^\bullet$ diffused from an adjacent solvent cage molecule leading to $Cp_2(Cp'^\bullet)U^{IV}R$.

The possibility that the spectra arose from free alkyl radicals can be excluded because $Cp_3U\text{-}i\text{-}Pr$ and Cp_3UCH_3 gave the same ESR signal. Likewise, THF can also be discounted as the radical source because this would have produced identical g_{iso} values and hyperfine splitting in all spectra, and this was not observed in practice.

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[*] DPPH = α,α'-diphenyl-β picrylhydrazyl.

TABLE 2

RELATIVE PROPORTIONS OF HYDROCARBONS EVOLVED IN THF SOLUTION

Complex	Products	Relative yields (%)		
		Photolysis		Thermolysis
		10°C	60°C	60°C
Cp_3U-i-Pr (I)	Propane	76	76	85
	Propene	24	24	15
Cp_3U-i-Bu (II)	Isobutane	92	—	95
	Isobutene	8	—	5
Cp_3U-n-Bu (III)	n-Butane	88	—	—
	1-Butene	12	—	—

On irradiating Cp_3U-i-Pr and Cp_3U-i-Bu at ambient temperature using ND as the spin-trap, we initially obtained ESR spectra corresponding to ND-alkyl spin-adducts with the following parameters: R = i-Pr, $a_N = 13.49$ G, $a_H = 5.99$ G, $g_{iso} = 2.0070 \pm 0.0001$, R = i-Bu, $a_N = 12.47$ G, $a_{H\alpha} = 3.99$ G, $g_{iso} = 2.0038 \pm 0.0002$. Towards the end of the photolysis, we observed the triplet previously described [1] in the photolysis of Cp_3UCH_3 and Cp_3U-n-Bu, which can be attributed to either the adduct $[Cp_3U—ND]^{\bullet}$ or the radical anion $ND^{\bullet}$ produced by a slow photolytic reduction. Photolysis of Cp_3U-i-Bu with PBN gave a six-line spectrum characteristic of a PBN—alkyl spin-adduct $a_H = 3.17$ G; $a_N = 14.69$ G; $g_{iso} = 2.0073 \pm 0.0001$.

With DMPO two types of spin adducts were encounter. An initial thermal reaction of the spin-trap with Cp_3U-i-Bu led to the spin-adduct DMPO—C_5H_5 ($a_H = 28.26$ G; $a_N = 16.82$ G) which was stable at ambient temperature but rapidly disappeared on photolysis, to be replaced by the spin adduct DMPO—i-Bu ($a_N = 14.13$, $a_H = 21.08$ G).

Nature of the resulting organometallic systems

The mole ratio of i-PrMgBr and Cp_3UCl used in forming Cp_3U-i-Pr has an important bearing on the uranium species observed by NMR, and we encountered three distinct situations, as follows.

1. i-PrMgBr in large excess. The presence of a large excess of the Grignard reagent led to direct reduction of the Cp_3U-i-Pr initially formed [12] to produce Cp_3U^{III} THF in approximately 90% yield. The U^{III} compound, which exhibits a single broad resonance in the NMR at 21.7 ppm, was identified by its electronic spectrum [2d]. The mechanism of its formation and possible synthetic applications of this reaction are currently being explored [13].

2. Equimolar quantities of i-PrMgBr and Cp_3UCl. In order to avoid the above reduction, solutions of Cp_3U-i-Pr were carefully prepared to avoid an excess of either the Grignard reagent or Cp_3UCl. Irradiation at 60°C for 45 min gave ~75% yield of Cp_3U^{III} THF (NMR, 21.7 ppm) identified by its visible spectrum [2d] as above, together with a small amount of a non-crystalline brown precipitate (vide infra). No other signals were observed in the NMR spectrum.

3. Cp_3UCl in excess. Normally, solutions were prepared with a 10—30% excess of Cp_3UCl, and two Cp signals, 10.5 ppm (Cp_3U-i-Pr) and 10.2 ppm (Cp_3UCl), could be clearly distinguished in the NMR spectrum. On irradiation at 60° C the resonances corresponding to Cp_3U-i-Pr diminished and were replaced by a broad resonance resulting from an exchange between the Cp_3U^{III} produced and the photolytically inactive Cp_3UCl [1]. This exchange, which may best be represented as:

$$Cp_3U^{III}\cdots Cl{-}U^{IV}Cp_3 \rightleftharpoons Cp_3U^{IV}{-}Cl\cdots U^{III}Cp_3$$

is fully described elsewhere [14]. In a typical experiment, 60—70% of the Cp_3U-i-Pr initially present was converted into Cp_3U^{III}. The chemical shift of the resonance corresponding to the above exchange depends upon the relative concentrations, but was normally observed in the range 11 to 20 ppm. Concurrently a substantial non-crystalline brown precipitate was formed. We have been unable to find any solvent for this solid, which is not stable to the atmosphere, and consequently purification has been impossible. However, on the basis of the following information obtained from the crude precipitate after several washings with THF and drying "in vacuo", we believe the solid to be an insoluble dimeric, or possibly polymeric, form of Cp_3U^{III}. The infrared spectrum (ν_{max}, Nujol, 1062w, 1010s, 910—880m and 810—720s cm^{-1}) is identical in all important aspects to that already reported for Cp_3U^{III} [2d], and these values differ from those presented by Marks et al. [4] for the insoluble product from Cp_3UR thermolysis in toluene (i.e. ν_{max}, Nujol, 1260vw, 1205vw, 1010m, 900w and 780vs cm^{-1}), a product later formulated as $Cp_2U(C_5H_4)_2UCp_2$ [5]. The mass spectrum of our product, which was obtained with difficulty owing to the extremely low volatility of the substance (210°C/70 eV), contained two important high mass fragments at *m/e* 446 (25%) and 866 (3%). Although the possible composition of *m/e* 446 is unclear the peak at *m/e* 866 may be attributed to Cp_3U dimer (2 × Cp_3U requires *m/e* 866). In addition, peaks were also observed at values (*m/e* > 1200) beyond the accurate resolution range of the apparatus, and might correspond to $(Cp_3U)_n^+$ ($n = 3, 4$ ... etc.). Further conformation of the nature of the solid came from elemental analysis, which revealed the overall composition of "Cp_3U". Evidence implying Cp_3U^{III} as precursor of the solid was gathered in the following way. An irradiated solution showing the exchange peak (15.3 ppm) was filtered and stored in the dark at ambient temperature for several weeks, during which the non-crystalline brown solid slowly separated. Subsequent re-examination of the NMR spectrum of the solution showed essentially pure Cp_3UCl only slightly displaced from its normal position (10.7 ppm instead of 10.2 ppm) indicating only a trace of Cp_3U^{III} still in solution.

When the irradiation was carried out at 10° C another resonance appeared in the NMR spectrum at 13.5 ppm, which reached 5—10% of the initial product concentration after 5 minutes of irradiation and remained practically constant until the concentration of Cp_3U-i-Pr became relatively minor, and disappeared altogether when all the Cp_3U-i-Pr was used up. This illustrated its intermediacy in the initial decomposition of Cp_3U-i-Pr and not, for example, in the transformation of Cp_3U^{III} to the brown precipitate. The intermediate, which by its narrow linewidth is undoubtedly a U^{IV} species, is relatively stable in the absence of light ($t_{1/2} \simeq 1$ day at 5°C) but is readily destroyed at 60°C, and this explains why it could not be observed in either the thermolysis experiments or on irradiation at 60°C, which in all other respects provided exactly the same reaction.

Discussion

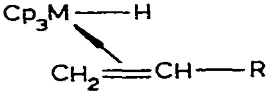
The photolysis of Cp_3U-i-Pr(I) in THF is interesting from several points of view. It represents the first such study of a Cp_3U—alkyl in which the alkyl group is branched, and in particular provides a direct analogy with the photochemistry of Cp_3Th-i-Pr. This permits the examination of a certain number of differences in behaviour between the uranium and thorium compound.

The unequivocal demonstration of alkyl radicals by ESR, the mixture of hydrocarbons obtained, and the first order reaction kinetics are not consistent with a β-hydride elimination as a major pathway, and can best be explained by initial homolysis of the U—C σ-bond as in the case of Cp_3UCH_3 and Cp_3U-n-Bu [1]. This reaction, which represents a formal reduction of U^{IV} to U^{III}, is therefore in contrast to the photo-induced β-elimination in Cp_3Th-i-Pr [7]. A key factor in this divergence of mechanism may be understood by considering the respective reduction potentials.

$U^{IV} \xrightarrow{-0.63\,V} U^{III}$ [15]

$Th^{IV} \xrightarrow{-3.7\,V} Th^{III}$ [16]

Because uranium(IV) is comparatively much easier to reduce than thorium(IV), the initial homolysis/reduction should be far more favourable with the former element, and in consequence there should be no need to resort to the coordinatively-saturated intermediate A, which is a necessary structure in the β-elimination mechanism for Cp_3Th-i-Pr and other organometallic complexes.



(A)

(M = U or Th)

An alternative argument which can be advanced is that the Cp ligands in Cp_3Ualkyl remain photochemically inflexible. This phenomenon has a useful analogy in organotitanum chemistry, for while photolysis of Cp_2TiCl_2 affords scission of the Ti—Cp linkage [17], the photolysis of Cp_2TiMe_2 proceeds by homolytic cleavage of the Ti—C σ bond [18]. Without the temporary promotion of a Cp to an η^1 or η^3 state, as postulated in other systems [20], process A might be disfavoured due to steric encumbrance around the metal atom. In this respect it is interesting to note that photolysis and thermolysis reactions are comparable in all but rate for a given uranium complex, suggesting essentially the same mechanism with light merely causing acceleration.

Conclusion

Both the photolysis and thermolysis of Cp_3U-i-Pr in THF lead to soluble U^{III} species in high yields. In the presence of $Cp_3U^{IV}Cl$ the adduct "$Cp_3U^{IV}—Cl\cdots U^{III}Cp_3$" is formed, otherwise the product is Cp_3U^{III} THF.

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References

1 E. Klähne, C. Giannotti, H. Marquet-Ellis, G. Folcher and R.D. Fischer, J. Organometal. Chem., 201 (1980) 399.

2 Cp_3U^{III}THF has also been obtained by chemical reduction of U^{IV} complexes:
(a) D.G. Karraker and J.A. Stone, Inorg. Chem., 11 (1972) 1742.
(b) H. Marquet-Ellis and G. Folcher, J. Organometal. Chem., 131 (1977) 257.
(c) P. Zanella, G. Rosetto, G. de Paoli and O. Traverso, Inorg. Chim. Acta, 44 (1980) L155: or from UCl_3 in THF;
(d) B. Kanellakopulus, E.O. Fischer, E. Dornberger and F. Baumgärtner, J. Organometal. Chem., 24 (1970) 507;
(e) D.C. Moody and J.D. Odom, J. Inorg. Nucl. Chem., 41 (1979) 533.

3 (a) G. Wilkinson, Science, 185 (1974) 109;
(b) P.J. Davidson, M.F. Lappert and R. Pearce, Chem. Rev., 76 (1976) 219;
(c) G.W. Parshall and J.J. Mrowca, Adv. Organometal. Chem., 7 (1968) 157.
(d) H. Schumann, W. Genthe and N. Brunks, Angew. Chem. Int. Ed., 20 (1981) 119.

4 T.J. Marks, A.M. Seyam and J.R. Kolb, J. Amer. Chem. Soc., 95 (1973) 5529.

5 E.C. Baker, K.N. Raymond, T.J. Marks and W.A. Wachter, J. Amer. Chem. Soc., 96 (1974) 7586.

6 T.J. Marks and W.A. Wachter, J. Amer. Chem. Soc., 98 (1976) 703.

7 D.G. Kalina, T.J. Marks, W.A. Wachter, J. Amer. Chem. Soc., 99 (1977) 3877.

8 Kanellakopulos et al. obtained a deep purple "Cp_3Th" by reduction of Cp_3ThCl with sodium/naphthalene in THF, B. Kanellakopulos, E. Dornberger and F. Baumgärtner, Inorg. Nucl. Chem. Lett., 10 (1974) 155.

9 H. Marquet-Ellis and G. Folcher, Rapport CEA, 1975, R4668.

10 V.K. Vasil'ev, V.N. Sokolov and G.P. Kondratenkov, J. Organometal. Chem., 142 (1977) C7.

11 The existence of constrained solvent cages was considered by Marks et al. [4,6] in the thermolysis of Cp_3MR (M = U, Th).

12 Cf. the reduction of $Cp_2Ti^{IV}Cl_2$ to $Cp_2Ti^{III}Cl$ by i-PrMgCl, E. Klei, J.H. Telgen and J.H. Teuben, J. Organometal. Chem. 209 (1981) 297.

13 L. Arnaudet and G. Folcher, unpublished results.

14 M. Burton, G. Folcher, C. Giannotti, H. Marquet-Ellis and P. Rigny, to be submitted.

15 C. Keller, The Chemistry of Transuranium Elements, Verlag Chemie, Weinheim/Bergstr., 1971, p. 212.

16 L.J. Nujent, R.D. Baybarz, J.L. Burnett and J.L. Ryan, J. Phys. Chem., 77 (1973) 1528, and references therein.

17 R.W. Harrigan, G.S. Hammond and H.B. Gray, J. Organometal. Chem., 81 (1974) 79; E. Vitz and C.H. Brubaker Jr., ibid., 82 (1974) C16; Z-T. Tsai and C.H. Brubaker Jr., ibid., 166 (1979) 199.

18 E. Samuel, P. Maillard and C. Giannotti, J. Organometal. Chem., 142 (1977) 289; M.D. Rausch, W.H. Boon and H.G. Alt, ibid., 141 (1977) 299; H. Alt and M.D. Rausch, J. Amer. Chem. Soc., 96 (1974) 5936.

19 E.M. Kosower, An Introduction to Physical Organic Chemistry, Wiley, New York, 1969, p. 352; T. Koenig, H. Fischer in J. Kochi (Ed.), Free Radicals, Vol. I, Wiley, New York, 1973, Chapter 4, p. 157.

20 M. Ephritikhine and M.L.H. Green, J. Chem. Soc., Chem. Commun., (1976) 926.