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PHOTOLYSIS OF DIALKYL METALLOCENES OF THE TITANIUM GROUP; AN ESR STUDY

E. SAMUEL *

Laboratoire de chimie organique industrielle de l'ENSCP, 11 rue P. et M. Curie, 75231 Paris Cédex (France)

P. MAILLARD and C. GIANNOTTI *

Institut de chimie des Substances Naturelles, C.N.R.S., Gif sur Yvette 91190 (France)

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Summary

Photolysis in the visible and the UV region of dialkyl metallocenes of the titanium group is studied by ESR. The primary process is shown to be homolytic cleavage of the metal—alkyl bond, with formation of paramagnetic metal species and organic free radicals. The first were identified from the ESR signal produced and the second from the spectra of their spin adducts with the appropriate spin trap. The M—C bond cleavage depends on the metal and on the radiation wavelength.

Introduction

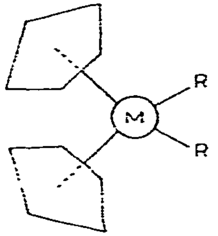
Dialkyl metallocenes of the titanium group provide an interesting model for the study of metal—carbon bond homolysis, a feature of major importance for the understanding of the catalytic reactivity of organo—transition metal compounds. Photolysis can be a neat method of provoking metal—ligand bond scission, and the study by ESR of the photo-generated species can be a rich source of information about the nature of both the metal-centered and organic fragments produced. The scarcity of data in literature on the photochemistry of early transition metallocenes prompted us to undertake this study.

Experimental

The compounds were prepared as indicated in the literature [1—3]. Solutions of 4×10^{-3} *M* concentration in carefully purified benzene or toluene were introduced in a 4 mm cylindrical quartz ESR tube in the dark and deoxygenated by bubbling through for 20 min a slow stream of argon. They were then introduced for spectral measurements into an ER 400 X-RL cavity of a Bruker ER-420 spectrometer equipped with a B-ST 100/700, B-MN-12 and B-A6 accessories of the same origin for variable temperature, magnetic field calibration and frequency measurements respectively. Irradiation was done with a Hanovia 977 B 0090, 1000 W Hg—Xe arc lamp in a Model LH 15 1H Schoeffel Lamp Housing. The light was focused through quartz lenses and filtered through a 15 cm flowing water filter and a Corning 3-73 or pyrex filter following the needs. The spin traps used were 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) [4,5] and nitrosodurene [6—8] synthesised by known methods [9,10], in 5×10^{-2} M concentrations.

Results

Photolysis of compounds I—V has been performed in the ESR cavity in order



(I) M = Ti, R = R′ = CH_3 (II) M = Ti, R = R′ = CH_2—Ph
(III) M = Ti, R = CH_3, R′ = Cl (IV) M = Zr, R = R′ = CH_3
(V) M = Hf, R = R′ = CH_3

to gain insight into the formation of paramagnetic short-lived intermediates during the photo-induced primary process. Both paramagnetic metal species and *organic free radicals have been detected, providing unequivocal evidence for* homolytic cleavage of the metal—carbon σ bond. The nature of the photo-generated species depend both on the metal and on the radiation wavelength. The *organic free radicals were identified from the ESR spectra of their spin adducts.* In all cases the signal growth and decay was dependant on the photolysis conditions.

Ti compounds I, II and III. The absorption spectra of these compounds display bands as indicated in Table 1. The absorptions at or below 300 nm are believed to be due to CT and the others to *d—d* transitions. Carefully degassed solutions prepared in the dark and introduced into the ESR cavity did not show any signal. Irradiation in the cavity with visible light ($\lambda > 420$ nm) generated within a few seconds a sharp signal centered at g 1.97. The g values and the presence of weak satellites due to hyperfine interaction with metal isotopes (^{47}Ti and ^{49}Ti, I 5/2 and 7/2 present in natural abundance 7.75 and 5.51% respectively) allow to attribute the signal as being unambiguously due to Ti^{III} species, Fig. 1 with the electron residing largely on a metal orbital [11]. The hyperfine constant is of the same magnitude (Table 2) as in other titanocene species studied earlier.

In the case of the dibenzyl compound II, the signal is stable under continuous

TABLE 1

ABSORPTION WAVELENGTHS AND EXTINCTION COEFFICIENTS OF SOME ALKYL TITANOCENES

Compound	λ (nm)	ϵ
I	225	27,142
	370	930
II	300	27,000
	490	1,160
III	212	18,400
	255	3,520
	385	333

photolysis and also for several minutes after shuttering the light. For the other two compounds, the signal is stable for a few minutes under continous photolysis and then slowly decays until complete disappearance, However, it reappears upon shutting the light and grows continuously until a steady state is reached;

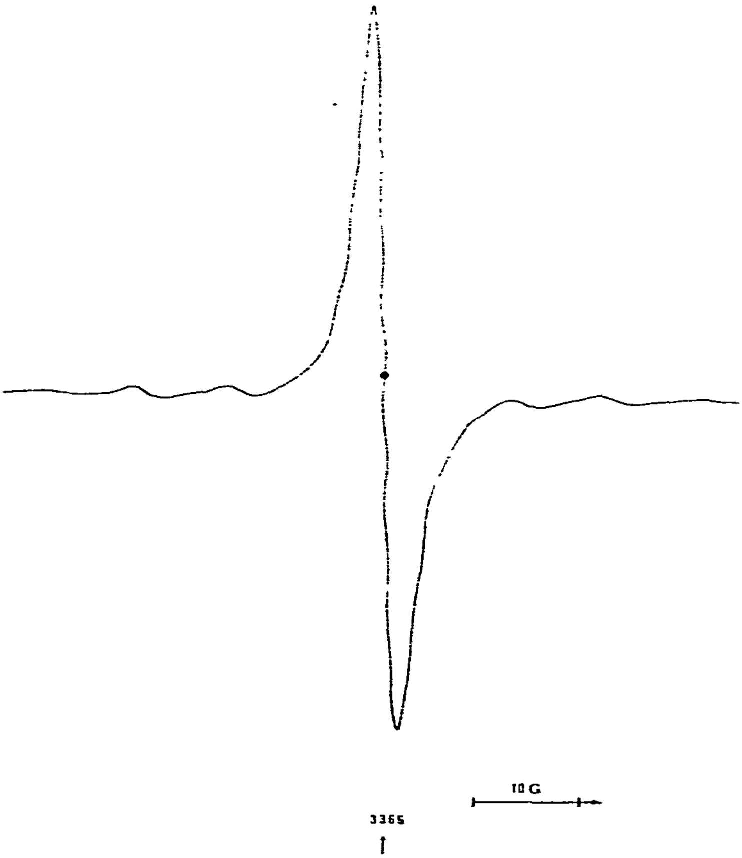


Fig. 1. ESR spectrum of the photolysis of I in toluene. Microwave frequence: 9.68 GHz. Microwave power: 5 mW. Frequency modulation intensity: 1 G. Microwave receiver gain 1.6×10^5.

TABLE II

ESR ISOTROPIC PARAMETERS OF METAL SPECIES GENERATED BY PHOTOLYSIS (UNLESS OTHERWISE STATED) OF ALKYL METALLOCENES. COUPLING CONSTANTS IN G

Parent compound	g	A_{Ti}	a_H
$Cp_2Ti(CH_2Ph)_2$	1.979	8.96	
$Cp_2Ti(CH_3)Cl$	1.980	8.80	
$Cp_2Ti(CH_3)_2$	1.981	8.66	
$Cp_2Zr(CH_3)_2$	2.000		7.00
$Cp_2Hf(CH_3)_2$	2.022		6.75
$(Cp_2TiCl)_2$ [a]	1.980		
$Cp_2Ti(CH_2Ph)$ [b]	1.97		
$Cp_2TiH_2^{(-)}$ [a]	1.979		
$\{Cp_2ZrH\}$ [c]	2.000		7.4

[a] Ref. 18. [b] Ref. 17. [c] Hypothetical structure, ref. 20 and unpublished studies. Stoechiometry unknown.

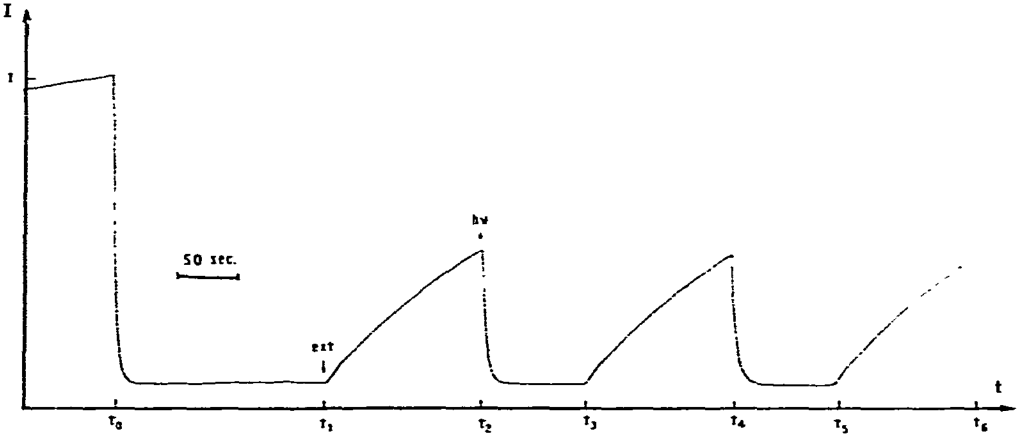


Fig. 2. Kinetics of ESR signal growth and decay of I in toluene on photolysis and extinction at alternate intervals.

it decays again upon further photolysis, and by repeating the operation at regular intervals, the kinetic spectrum presented in Fig. 2 is obtained. A rough determination of spin concentration in II by comparing the integrated signal with a known concentration of DPPH * indicates the presence of paramagnetic species in a ratio of about 10%.

Solutions of I, II and III containing DMPO as a spin trap exhibit instantaneously upon photolysis the characteristic 6-line spectra of methyl- or benzyl-trapped adducts, Fig. 3 (a_N 14.31, a_H 20.52 and a_N 14.16, a_H 20.66 G respectively). The use of nitrosodurene [8] allows to distinguish more clearly between these two types of radicals (a_N 13.61, a_H 12.17 for the methyl and a_N 13.61 and a_H 7.93 G for the benzyl adducts respectively), Fig. 4. Cooling these solutions

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* DPPH = α,α′-diphenylpicrylhydrazyl.

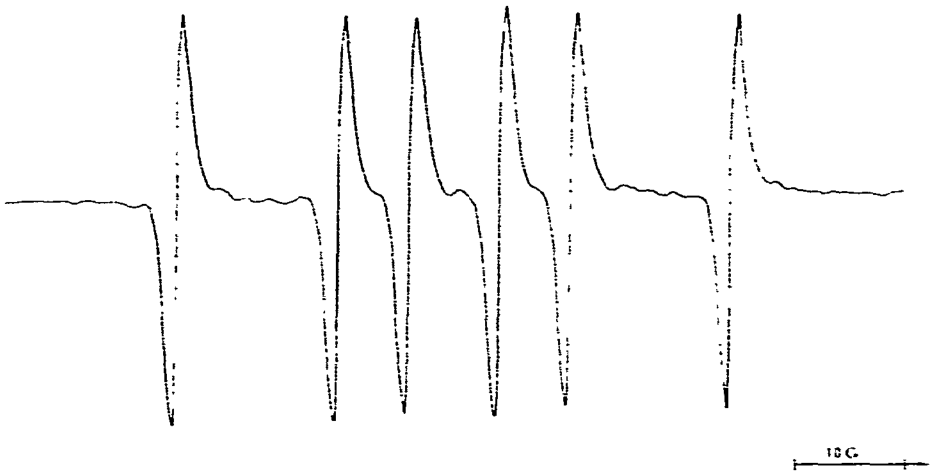


Fig. 3. ESR spectrum of DMPO-methyl spin adduct obtained by photolysis of I in presence of DMPO in toluene. Microwave frequency: 9.33 GHz. Field modulation intensity: 0.5 G. Microwave receiver gain 2×10^5. Microwave power: 5 mW.

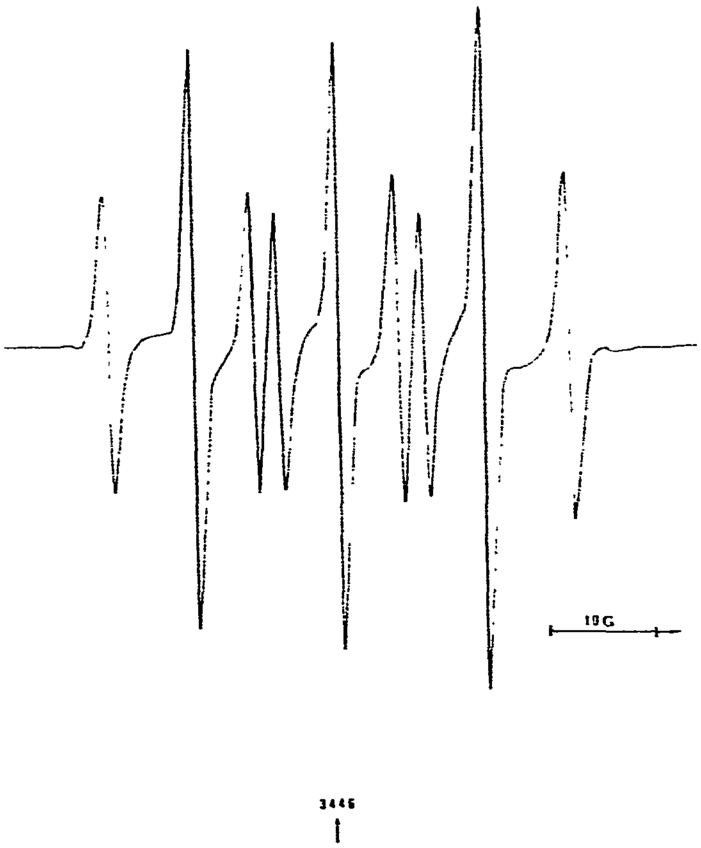


Fig. 4. ESR spectrum of nitrosodurene-benzyl adduct obtained by photolysis of II in presence of nitrosidurene in toluene. Microwave frequency: 9.68 GHz. Field modulation in intensity: 0.5 G. Microwave receiver gain: 1.6×10^5. Microwave power: 5 mW.

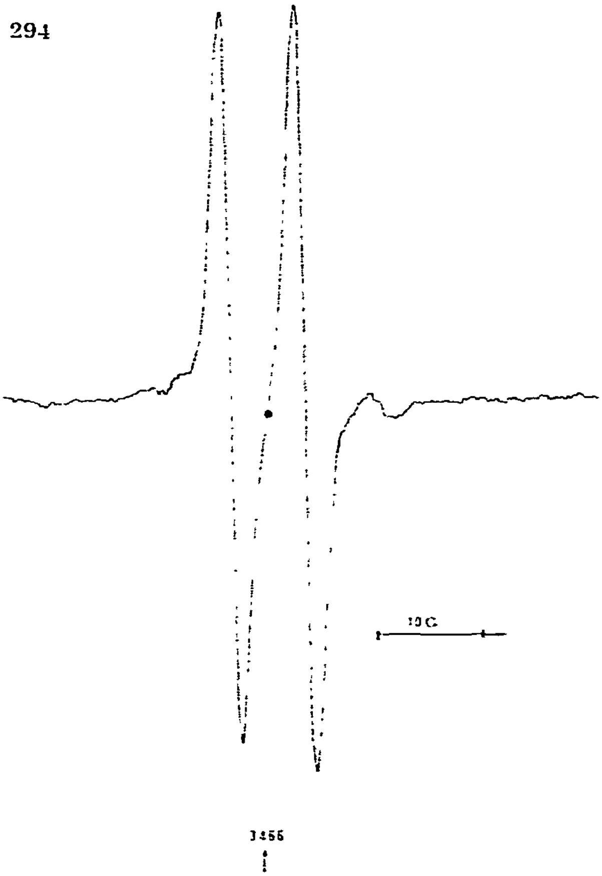


Fig. 5. ESR spectrum of photolysis of IV in toluene.

to low temperatures results by substantial decrease in signal intensity and band broadening. The presence of a single wide band in the spectrum of the frozen solution did not allow to obtain any indication about the symmetry of the photogenerated paramagnetic metal species.

Zr and Hf compounds IV and V. The absorption spectra of these compounds do not exhibit any detectable band in the visible or the near UV region besides a strong band at 300 nm due probably to charge transfer.

Photolysis of IV or V in benzene or toluene in the ESR cavity leads to similar results as above, but proceed differently. The use of visible light does not give any detectable ESR signal even after several minutes. However, irradiation with light of higher energy (UV light above 320 nm) gives a strong signal composed of a doublet of equal intensity within less than a minute, Fig. 5, in contrast to the singlet observed in titanocene compounds. Otherwise, the same phenomenon as in I obtains, namely decay of the signal upon prolonged irradiation and its growth upon shutting the light. Addition of DMPO to the solutions gives under photolysis the characteristic spectra of the methyl-trapped adducts in both cases.

It should be mentioned that the signals obtained in all these compounds are stable at room temperature for a period of approximately one hour.

The ESR parameters of the above photolysis products are set out in Table 2, together with data from literature on related species.

Discussion

In the last few years, work on thermal [12] and photochemical [13] cleavage of metal—carbon bonds in dimethyl metallocenes of the titanium group has been described. Thus it was reported that prolonged photolysis of I, IV and V in pentane yields methane together with diamagnetic "metallocenes" of the empirical formula $C_{10}H_{10}M$. Also, ring cleavage is believed to occur [14] upon irradiation of solutions of dichlorotitanocene in benzene for several hours. However, none of these reports mention the generation of trivalent metal species. Although in these as well as in other experimental investigations [14], M—C bond cleavage was suspected to be homolytic, the above results provide for the first time unequivocal evidence for this mechanism. Furthermore, the facility with which this homolysis seems to occur is rather rare in the chemistry of transition metal alkyl compounds and may be compared in this respect only with group A metal alkyls [15].

The primary photoprocess in all the compounds studied above is the immediate generation of trivalent d^1 metal species corresponding probably to the structure Cp_2MR. Moreover, from the kinetics of the appearance of the signal and its subsequent decay on photolysis, and its reappearance in the dark, it can be postulated that the paramagnetic metal species is photolabile and gives rise on continued photolysis to diamagnetic alkyl-free metallocene; this in turn disproportionates thermally with excess dimethyl leading to the monomethyl compound which is responsible for the signal growth observed on shutting the light.

Ti compounds. The following reaction sequence summarizes the above postulated mechanism

$$\mathrm{I} \xrightarrow{h\nu} \underset{(\mathrm{A})}{\mathrm{Cp_2Ti^{III}(CH_3)}} + \cdot\mathrm{CH_3} \text{ first step} \tag{1}$$

$$2\ \mathrm{A} \xrightarrow{\Delta} \underset{(\mathrm{B})}{[\mathrm{Cp_2Ti^{III}(CH_3)}]_2} \text{ dimer} \tag{2}$$

$$\mathrm{B} \xrightarrow{h\nu} \mathrm{Cp_2Ti} + \cdot\mathrm{CH_3} \tag{3}$$

$$\mathrm{Cp_2Ti} + \mathrm{I} \xrightarrow{\Delta} 2\ \mathrm{A} \rightarrow \mathrm{B} \tag{4}$$

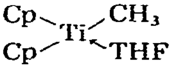
Dimerization of A is not unexpected and attempts to prepare A or B by chemical reactions led instead to Cp_2Ti^{IV} and Cp_2Ti^{II} species [16] believed to result from disproportionation. In contrast, compounds with R = Ph; CH_2Ph; *o,m,p*-tolyl; C_6F_5, where dimerization is inhibited by the nature of the ligands, were successfully isolated [17]. The fact that compound III shows a behavior identical to I (though after a somewhat longer period of photolysis) can be explained by the intermediate formation of $Cp_2Ti^{III}(CH_3)$ probably via the following pathway:

$$\text{III} \xrightarrow{h\nu} \text{Cp}_2\text{TiCl} + \cdot\text{CH}_3 \qquad (5)$$

$$\text{Cp}_2\text{TiCl} + \text{III} \xrightarrow{\Delta} \text{Cp}_2\text{TiCl}_2 + \text{I} \qquad (6)$$

which subsequently follows the same mechanism as in eq. 1, the dichloride remaining unaffected under the photolysis conditions employed. An equilibrium between III, the dichloride and the dimethyl is also to be considered.

If the formulation as $(\text{Cp}_2\text{TiCH}_3)_2$ of the paramagnetic photogenerated species responsible for the ESR signal is correct, then it can be argued that super-hyperfine interaction with the methyl protons or with the ring protons should be present in the spectrum. Indeed such interaction has already been observed in reactions of dichlorotitanocene with Grignard reagents [18]; however, the compounds obtained were formulated as monomeric dialkyl anions of Ti^{IV}. Hyperfine interaction with alkyl groups bonded to titanium was also observed in compounds suspected to have the following structure:



in which the monomeric alkyl has its vacant coordination site saturated with a THF solvent molecule [18]. In the case studied above, the equilibrium monomer—dimer is likely to reduce spin delocalization on the alkyl group.

Another argument in favor of the dimeric structure of the photogenerated monomethyl titanocene species under study is the dramatic loss of paramagnetism reflected by the decay of the ESR signal upon lowering the temperature; this phenomenon, thought to be due to progressive de-population of the triplet state at low temperatures is characteristic of dinuclear paramagnetic compounds [19]. On the other hand, the appearance in the dibenzyl compound II of a photoinduced signal which is not "quenched" upon further irradiation indicates that the process in this case is purely photochemical, and no thermal secondary reaction associated with dimerization or disproportionation is taking place. This observation can be reconciled with the existence of the monobenzyl titanocene monomer in the pure state (g 1.97) [17].

Zr and Hf compounds. The same arguments as above hold to explain the decay of the ESR signal upon prolonged photolysis and its growth in the dark, namely the thermal generation of the paramagnetic species subsequent to photoexcitation. However, a remarkable distinctive feature in this case is the appearance of a doublet in contrast to the singlet in the case of titanium, Fig. 5.

This doublet can only be attributed to hyperfine interaction of the unpaired electron with a hydride proton bonded to the metal on the basis of the coupling constant (a_H 7.0 G) which is of the same magnitude as in the $\text{Cp}_2\text{Ti}^{\text{III}}$ monohydride [18] obtained by reduction of dichlorotitanocene with isopropyllithium, or in the zirconocene hydride obtained by reduction of zirconocene dichloride with metallic magnesium in THF [20]. In the case of hafnium, it should be mentioned that the photolytically generated species is to our knowledge the first example of a paramagnetic hafnium compound.

The formation of the hydride species is not unusual in the chemistry of the early transition metals and can be accounted for in terms of proton transfer from the ring. The following reaction sequence is suggested to take place on photolysis:

$$\mathrm{IV} \xrightarrow{h\nu} \underset{(\mathrm{C})}{\mathrm{Cp_2Zr^{III}CH_3}} + \cdot\mathrm{CH_3} \qquad (7)$$

$$\mathrm{C} \overset{\Delta}{\rightleftharpoons} \text{dimer} \underset{h\nu}{\overset{\Delta}{\rightleftharpoons}} \underset{(\mathrm{D})}{\mathrm{Cp_2Zr}} + \mathrm{IV} \qquad (8)$$

$$\mathrm{D} \xrightarrow{\Delta} \underset{(\mathrm{E})}{\mathrm{CpCp'Zr^{III}H}} \xrightarrow{h\nu} (\mathrm{CpCp'Zr})_n + \cdot\mathrm{H} \qquad (9)^*$$

At the early stages of photolysis, cleavage of one metal—methyl bond gives rise to the monomethyl C or its dimer and subsequently to zirconocene D. The latter rearranges thermally to the hydride E, probably through an intermolecular process involving proton abstraction from the Cp ring **. This hydride is photolabile under the conditions used (high energy UV) and the Zr—H bond is cleaved to give the diamagnetic $\mathrm{Zr^{II}}$ compound $(\mathrm{CpCp'Zr})_n$ which explains the rapid decay of the signal upon photolysis. It is interesting to note that a similar observation has been reported on photolysis of $\mathrm{Cp_2NbH_3}$ where the ESR signal of the photogenerated dihydride $\mathrm{Cp_2NbH_2}$ decays quite rapidly on further irradiation [21].

It should be mentioned that we have been unable so far to detect the hydride spin adduct suspected to be generated photolytically from reaction 9, because of the complicated features exhibited by spectra of the compounds in presence of spin traps under continuous photolysis.

Finally, although the ESR spectra are expected to display hyperfine interaction due to ^{91}Zr (I 5/2, 11.23% and I 7/2, 18.39%) and ^{179}Hf. (I 9/2, 13.78%) isotopes, these could not be detected. The reason for this is not yet clear, the more so that no data in the literature are available to date on the magnitude of such interaction [11].

To summarize, it can be stated that the formation of trivalent metal species is an important preliminary step in the photodissociation of the metal—alkyl bond in the isoelectronic compounds $\mathrm{Cp_2MR_2}$ of the titanium group. The tendency to hydride formation in this process is particularly obvious in Zr and Hf, a behavior which finds its analogy in the chemistry of Nb and Ta metallocenes. Interestingly, this situation contrasts with recent reports on the photochemistry of the organoactinide compound $\mathrm{Cp_3ThR}$ (R = alkyl) of the same transition group, which undergoes clean homolysis of the M—R bond upon irradiation to yield $\mathrm{Cp_3Th}$ [22] whereas thermal dissociation yields the species $\mathrm{Cp_2Th(C_5H_4)}$ [23].

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* $\mathrm{Cp' = C_5H_4}$.

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