PHOTOGENERATION OF REACTIVE TITANIUM AND ZIRCONIUM SPECIES: A CIDNP STUDY

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Summary

Chemically induced dynamic nuclear polarization (CIDNP) studies of the photolytically initiated reactions of $Cp'_2Ti(CH_3)_2$ (Cp' = methylcyclopentadienyl) and $Cp_2Zr(CH_3)_2$ (Cp = cyclopentadienyl) have revealed that homolysis of the metal—methyl bond takes place, followed by a rapid recombination. The metal radical is shown to be one of the partners in the polarizing radical pair. Only very fast scavengers such as nitroxides, dioxygen and thiophenol can compete with the recombination reaction. Dimethylzirconocene undergoes a photochemically-initiated ethylene insertion reaction in which the olefin is inserted into the zirconium—methyl bond via an unprecedented radical process.

Introduction

In recent years [1] the photochemistry of derivatives of titanocene and zirconocene, along with their thermal decomposition, has received a great deal of attention. The photochemical behaviour of Cp_2TiR_2 (Cp = cyclopentadienyl; $R = CH_3$, C_6H_5, Cl) has been explored in detail. It has been reported that dimethyltitanocene in alkane reacts to form methane via abstraction of hydrogen from the titanocene by methyl radicals [2]; in the presence of CO the titanocene dicarbonyl is formed [3], while with diphenylacetylene a metallacycle of titanacyclopentadiene is obtained [3]. Titanocene dichloride reacts with exchange of cyclopentadienyl groups [4], and in the presence of alcohols photochemical alcoholysis occurs [5]. Initially a homolytic cleavage of the titanium—carbon bond in dimethyltitanocene was proposed [3], but recently some doubt has arisen about the free radical nature of this process [1,2]. The reactions seem to follow very much the same pathways as radical processes, but they need not be true radical reactions. The occurrence of titanium(III) radicals has been proved during photolysis of diphenyltitanocene [6]; on the other hand,

attempts to demonstrate the presence of methyl radicals during irradiation of dimethyltitanocene by polymerization experiments were unsuccesful [7], though spin trap experiments led to a methyl spin adduct being observed by EPR [8].

We were interested in the photochemical generation of reactive, coordinatively-unsaturated titanium and zirconium species and in the reactions of these species with various olefins and other unsaturated compounds. A prerequisite for an investigation of the latter type of reactions turned out to be a better knowledge of the photochemistry of the metallocene derivatives and therefore a study of CIDNP effects [9], was initiated to answer at least some of the questions that have arisen recently.

Results and discussion

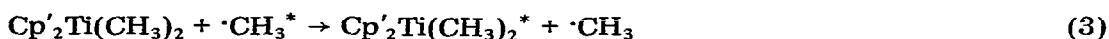### Irradiation of Cp₂Ti(CH₃)₂

Irradiation of $Cp_2Ti(CH_3)_2$

Previous investigations [1] have shown that several hours' irradiation of solutions of $Cp_2Ti(CH_3)_2$ in inert media leads to methane production, the hydrogen in the methane originating either from the second methyl group or from a cyclopentadienyl group but not from the solvent. When $Cp_2Ti(CH_3)_2$ or $Cp'_2Ti(CH_3)_2$ (where Cp' stands for methylcyclopentadienyl) in benzene in an NMR tube is irradiated with a UV-visible light source in the complete absence of water and oxygen, no change in the NMR spectrum is observed during irradiation, indicating the absence of CIDNP, or after 20 minutes of irradiation. However, when traces of oxygen are admitted to the reaction medium a three- to four-fold enhanced signal for the titanium-bonded methyl groups is observed during irradiation. After the light has been switched off the intensity of the methyl protons declines to its original value and no change in the spectrum of $Cp'_2Ti(CH_3)_2$ is observed. Raising the temperature to 80°C (with exclusion of oxygen) also leads to an enhanced absorption under irradiation. By changing the conditions, and, e.g., by taking a single spectrum, the occurrence of proton saturation effects is excluded. Further proof for the occurrence of CIDNP and its origin is obtained by studying the ^{13}C spectrum of $Cp_2Ti(CH_3)_3$ enriched with 40% ^{13}C in the methyl carbons under identical irradiation conditions. In this experiment an emission is observed for the methyl carbon of the irradiated compound. Though saturation cannot be rigorously excluded in this instance (repetition time 0.7 s, flip angle 40°, 1000 scans) the emission unequivocally proves the occurrence of CIDNP.

For polarization to occur a radical pair is needed involving radicals with different *g*-values, and since no polarizations are found in the other components (Cp, solvent) the two radicals involved must be titanium(III) and a methyl radical. Only very few examples are known of the participation of a transition metal in a CIDNP pair. One is $Mn(CO)_5$, observed during the reaction of $HMn(CO)_5$ with styrene [10], but in many cases no CIDNP originating from the metal is detected [11,12]. One reason for this may be a fast relaxation of the metal-centered radical, which destroys the spin correlation (relaxation times shorter than 10^{-9} s). Secondly, the difference in the *g*-factors may be too large [13]: a difference of more than 0.02 will start to destroy the net effect unless the reaction and the diffusion are extremely fast; CIDNP has been observed,

however, for thiophenoxyl radicals for which a g-value as high as 2.04 has been quoted [14]. The titanium radical involved in the present system is $Cp_2TiCH_3^{\cdot}$, for which (probably as the tetrahydrofuran complex) a g-value of 1.986 at $-65°C$ has been reported [15]. This is well within the limits mentioned [13]. Brintzinger [15] also recorded a hyperfine quartet ($a = 0.44$ mT), and the resolution suggests that the electronic relaxation time is larger than 10^{-7} s (no direct measurements were reported). In conclusion, there is no objection to participation of Ti^{III} as one of the radicals in the radical pair generating CIDNP. The photo-homolysis reaction leading to this pair can be represented as in eq. 1:

$$Cp'_2Ti(CH_3)_2 \xrightarrow{h\nu} \overline{Cp'_2TiCH_3 + \cdot CH_3} \tag{1}$$

The polarization found in the irradiated dimethyltitanocene may be due to recombination (2) or to an S_{H_2} reaction (3) (* denotes polarization):

$$Cp'_2TiCH_3 + \cdot CH_3^* \rightarrow Cp'_2Ti(CH_3)_2^* \tag{2}$$

$$Cp'_2Ti(CH_3)_2 + \cdot CH_3^* \rightarrow Cp'_2Ti(CH_3)_2^* + \cdot CH_3 \tag{3}$$

Furthermore, a very small emission is found for ethane and a small enhanced absorption for methane (non-deuterated in both perdeuterated benzene and toluene). The methane therefore shows the same polarization as the starting material, whereas ethane shows the opposite polarization. The most likely mechanism, which is supported by additional data (vide infra), is therefore a fast recombination (2), which causes the polarization. Methane is formed via reaction 4 confirming previous experiments [1—3]. The role of oxygen in the sys-

$$\overline{Cp'_2TiCH_3 + \cdot CH_3} \rightarrow \text{"}C_{13}H_{16}Ti\text{"} \quad CH_4^*$$
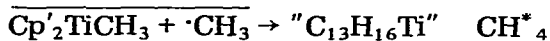
tem is to provide an escape route for the radicals in the radical pair, which is necessary for CIDNP to occur. We conclude that in the absence of an escape route the recombination (2) is an extremely efficient process and a few radicals of the pair have to be scavenged to give CIDNP. Oxygen is a fast methyl radical scavenger (diffusion controlled, rate constant 10^{8-10} mol^{-1} s^{-1}) and it may also scavenge Ti^{III}. we arrive at the given in Scheme 1.

SCHEME 1

* absorption

** emission
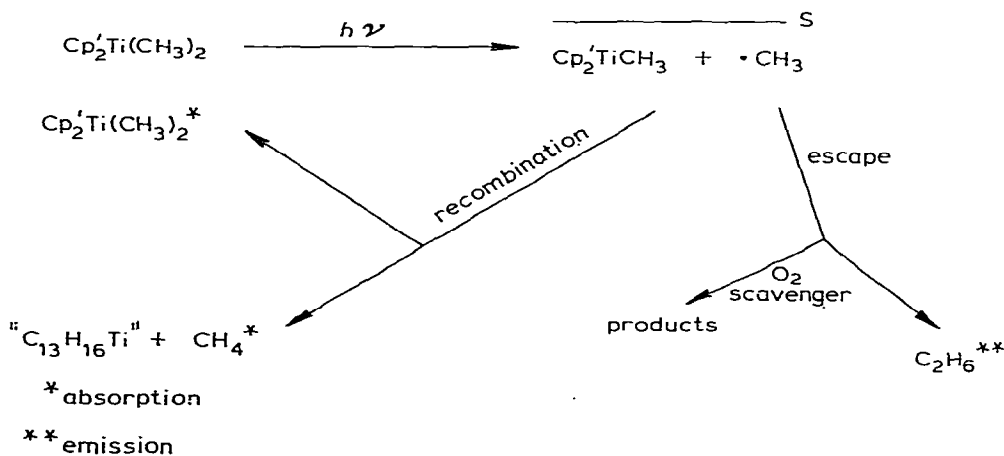
The main route is recombination of the Cp'_2TiCH_3 and $\cdot CH_3$ radicals to give the starting material, which can only be intercepted by fast scavengers and which occasionally yield CH_4 and other products. Abstraction of hydrogen (deuterium) from the solvent is far too slow and so is addition to the aromatic nucleus. (Abstraction of hydrogen from toluene by methyl radicals has a rate constant $< 10^2$ mol^{-1} s^{-1} and abstraction from the titanocene moiety seems more likely.) The traces of oxygen-containing products are not seen as polarized peaks, which is a common feature for the fast relaxing oxy-radicals in CIDNP studies [9].

The effect of higher temperatures can be explained by the higher rate of diffusion at lower viscosities, which facilitates escape, though again the escape polarization does not show in the spectrum (see Fig. 1).

Application of Kaptein's rule for net effects [9] indicates that the radical pair formed by the irradiation is a singlet pair * ($g(CH_3) > g(Ti)$, $a(CH_3)$ negative, enhanced absorption in recombination product), which is rather remarkable and which is in line with an effective recombination reaction (note that CIDNP is much less sensitive than EPR and that several percent of the complex has to "react" via this pathway for CIDNP to be observed). After 1 minute of irradiation with the powerful light source used, approximately 1 percent of the complex was decomposed.

A study of the wavelength dependence showed that irradiation at the wavelength at which the small shoulder in the UV spectrum occurs was sufficient to cause the homolysis. Filters transparent between 420 and 460 mμ gave the observed CIDNP, which amounts to only ~275 kJ/mol.

During irradiation of several minutes duration homolysis and recombination occur to an appreciable extent although the reaction with diphenylacetylene and carbon monoxide was very slow, and reactions with olefins were completely absent. We therefore thought that addition of methyl radical scavengers would open up the possibility of generating a reactive titanium species in apolar media. A hydrogen donor such as 9,10-dihydroanthracene seemed most attractive, since (a) it may inert towards the titanium complexes, and (b) it is approximately 40 times [16,17] more active per hydrogen atom than toluene. The scavenging action of this compound is still too slow (no CIDNP) to compete effectively with the recombination, which apparently has a rate close to the diffusion controlled limit.

Irradiation of $Cp'_2Ti(CH_3)_2$ in the presence of C_6H_5SH

Thiols react with methyl radicals with a rate constant of 10^6 M^{-1} s^{-1}. Figure 2 shows the result of irradiation of $Cp'_2Ti(CH_3)_2$ in the presence of thiophenol. Again an enhanced absorption is recorded for dimethyltitanocene (0.01 ppm) and methane (0.20 ppm) is seen in emission (escaped methyl radicals have opposite polarization). A small emission is also observed for $Cp'_2Ti(CH_3)SC_6H_5$ at 0.42 ppm. After irradiation the spectrum indicates hardly any reaction, but prolonged irradiation leads to the formation of $Cp'_2Ti(CH_3)SC_6H_5$ in high yield. Indeed thiophenyl effectively scavenges the methyl radicals from the titanium-

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* It should be noted here that the enhanced absorption in $Cp'_2Ti(CH_3)_2$ originating from the methyl radical (with a negative hyperfine constant of 2.30 mT) is countered by an emission of the other methyl group, which has a hyperfine splitting of only 0.44 mT, but the former effect will, of course, predominate.
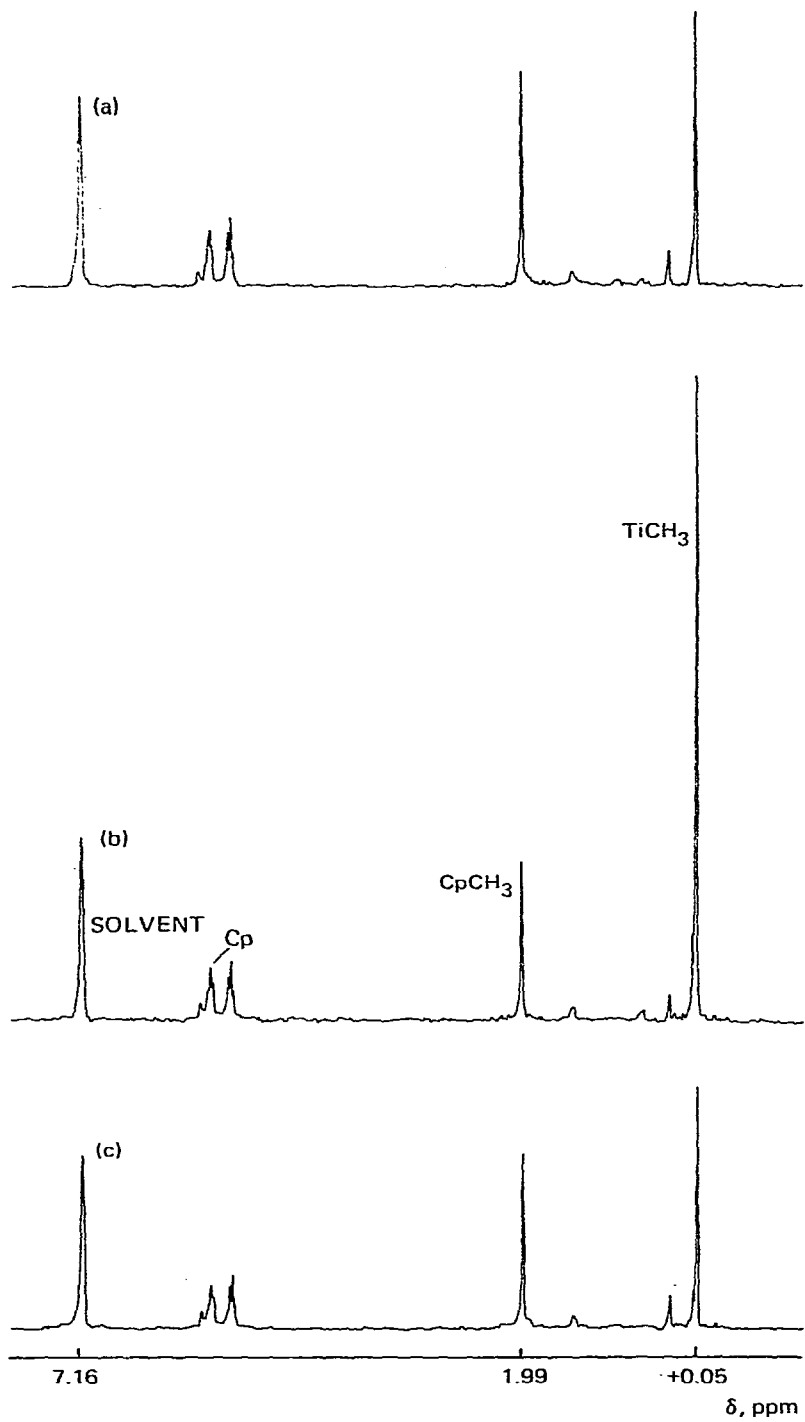
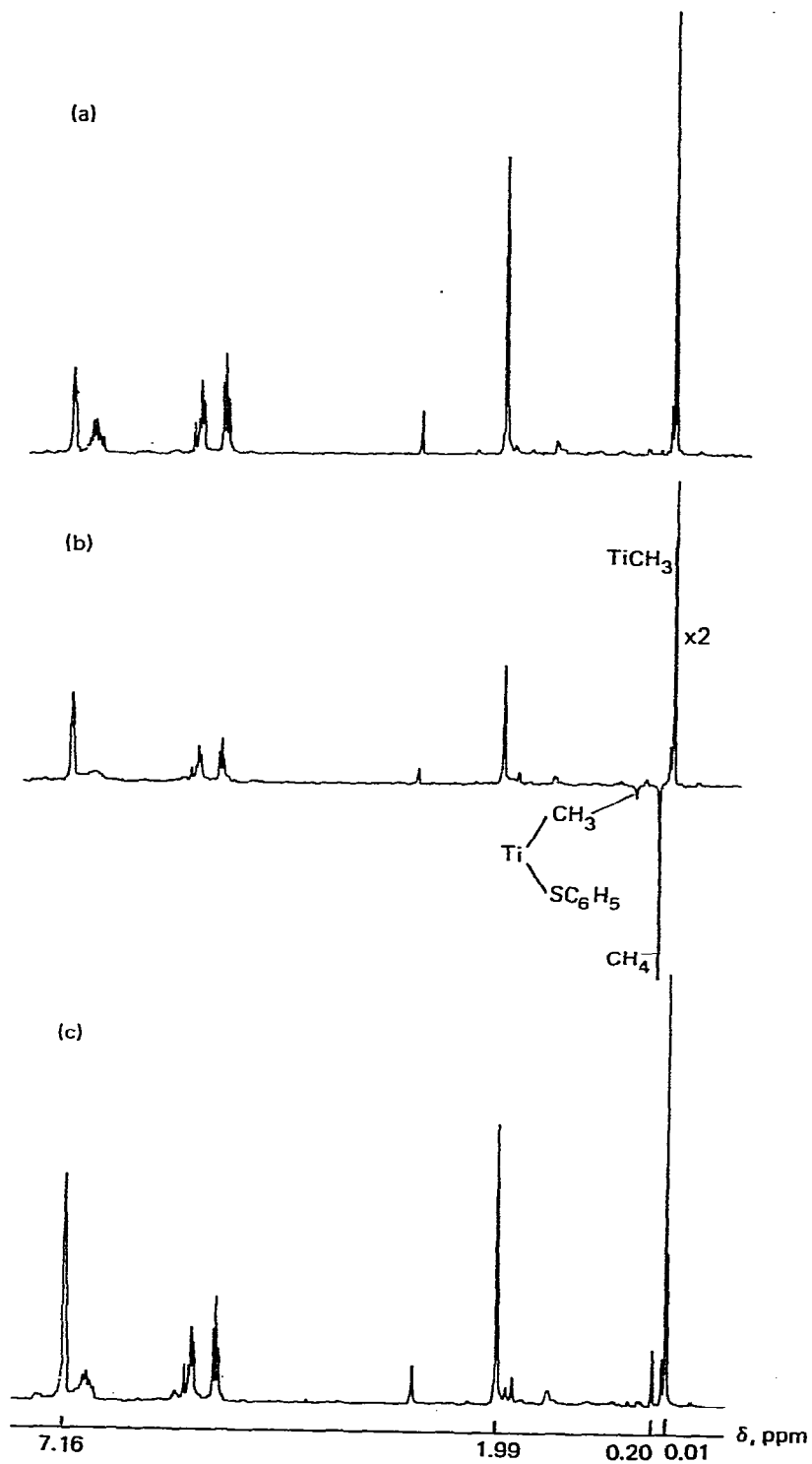Fig. 1. NMR spectra of Cp'$_2$Ti(CH$_3$)$_2$: (a) before, (b) during, and (c) after irradiation in C$_6$D$_6$ at 75°C.

(a)

(b)

TiCH$_3$

×2

Ti — CH$_3$
Ti — SC$_6$H$_5$

CH$_4$

(c)

7.16   1.99   0.20 0.01 δ, ppm

Fig. 2. NMR spectra of Cp$'_2$Ti(CH$_3$)$_2$ in the presence of C$_6$H$_5$SH: (a) before, (b) during, and (c) after irradiation.

methyl radical pair, but unfortunately the titanium(III) species reacts with thiophenol or the thiophenoxyl radicals formed.

Irradiation of Cp'$_2$Ti(CH$_3$)$_2$ in the presence of nitroxides

Nitroxides react efficiently with alkyl radicals to give the O—C combination product [18] with a rate constant [17] of ~10^7 M^{-1} s^{-1}. Figure 3 shows the result for Cp'$_2$Ti(CH$_3$)$_2$ irradiated in the presence of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TMPNO), which itself is relatively stable under these conditions. The scavenged methyl radicals appear as an emission at 3.57 ppm. Dimethyltitanocene exhibits the usual enhanced absorption. The nitroxyl also forms an adduct with Ti^{III}, as seen from the methyl absorption at 1.06 ppm assigned to Cp'$_2$Ti(CH$_3$)(TMPNO). The character of the absorptions and emission further supports the singlet nature of the initial titanium-methyl radical pair.

When di-*para*-nitrophenylamine-*N*-oxyl is used as the scavenger, spectra like those from TMPNO are not obtained. Only a very small enhancement for Cp'$_2$Ti(CH$_3$)$_2$ is found, together with minute emissions at 1.08, 0.96 and 0.79 (ethane) ppm. This nitroxyl is a few orders of magnitude slower in its action as an alkyl trap than TMNPO due to resonance stabilization, and apparently it is too slow to compete on the CIDNP time scale with the recombination reaction.

Other scavengers and Cp'$_2$Ti(CH$_3$)$_2$

In a completely oxygen-free atmosphere 2,6-di-tert-butyl-4-methylphenol likewise failed to intercept methyl radicals. The rate constant reported [17] for this scavenger is 10^4 M^{-1} s^{-1}. Triethylsilane was found to be ineffective. We estimate the rate constant [16,17] to be 10^3—10^4 M^{-1} s^{-1} at room temperature. Results with DPPH (2,2-diphenylpicrylhydrazyl) and galvinoxyl were also negative, which may be due to instability of the scavengers and/or to quenching or absorption of the scavengers.

The rate constant for hydrogen abstraction by methyl radicals for tin hydrides is 10^7 M^{-1} s^{-1} [17]. During the first few seconds of this reaction a strong emission for methane is observed but then a complicated pattern is formed stemming from several unidentified intermediates and products. The fast secondary reactions require no irradiation and do not exhibit polarization; they may be radical chain reactions.

Another clear example giving indications about the rates is provided by iodides. In the presence of CH$_3$I no CIDNP is observed. The rate constant for iodide transfer from CH$_3$I to methyl radicals is roughly 10^3 M^{-1} s^{-1} (at 65°C) [17]. With isopropyl iodide (rate constant 10^5 M^{-1} s^{-1}) an emission of methyl iodide (escape polarization) is seen, which is also the case with C$_3$F$_7$I (rate constant 10^7 M^{-1} s^{-1}). In addition enhanced absorptions for the starting dimethyl compound occur and in the former case polarizations stemming from isopropyl radicals are observed as well. These results are summarized in Scheme 2.

Photochemical methanolysis of Cp'$_2$Ti(CH$_3$)$_2$

Alcoholysis of dimethyltitanocene is very slow in the absence of radiation. Irradiation leads to a fast reaction giving methane and the monomethoxymethyltitanocene and at a later stage dimethoxytitanocene. Photochemical alcoholysis was reported previously [4] for Cp$_2$TiCl$_2$. Figure 4 proves the radical
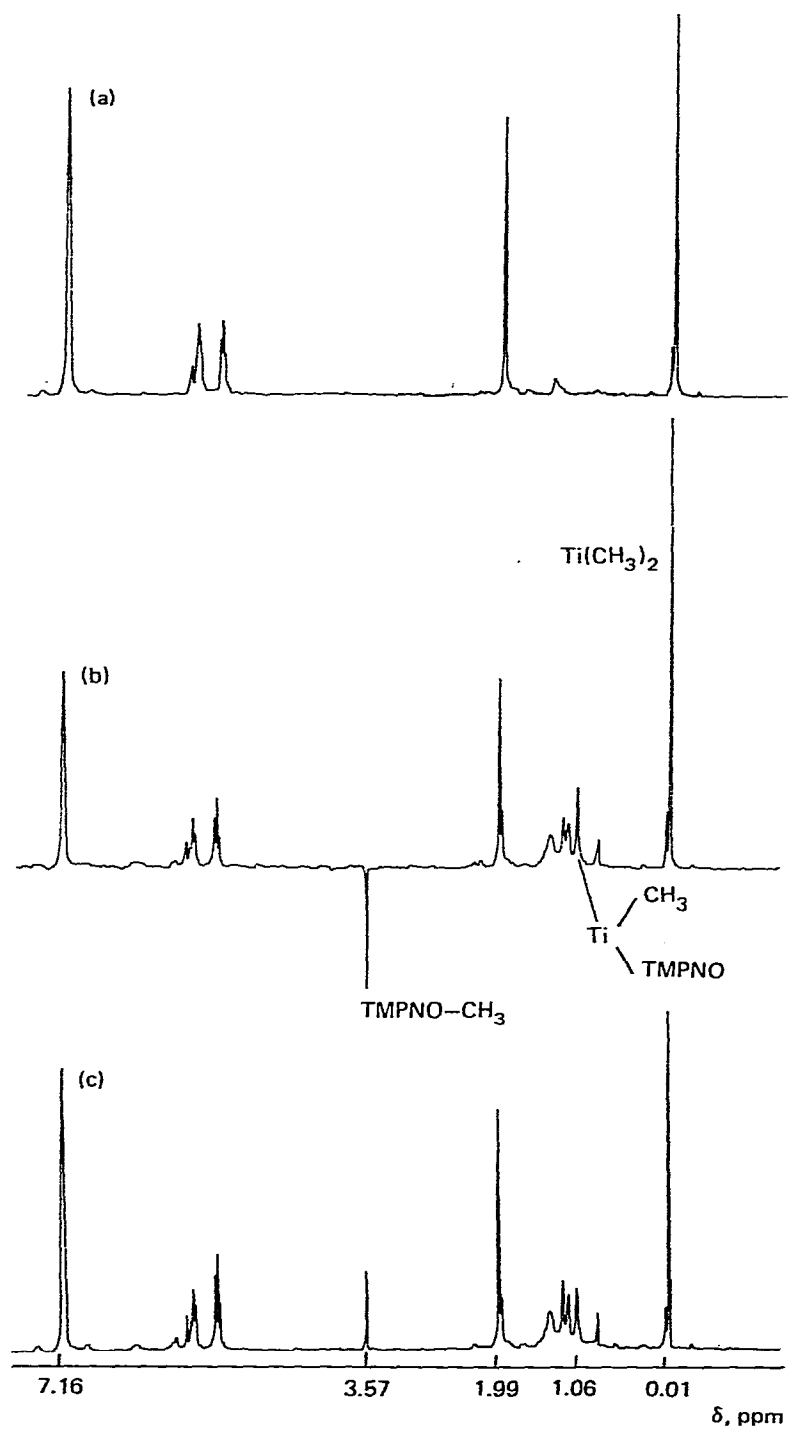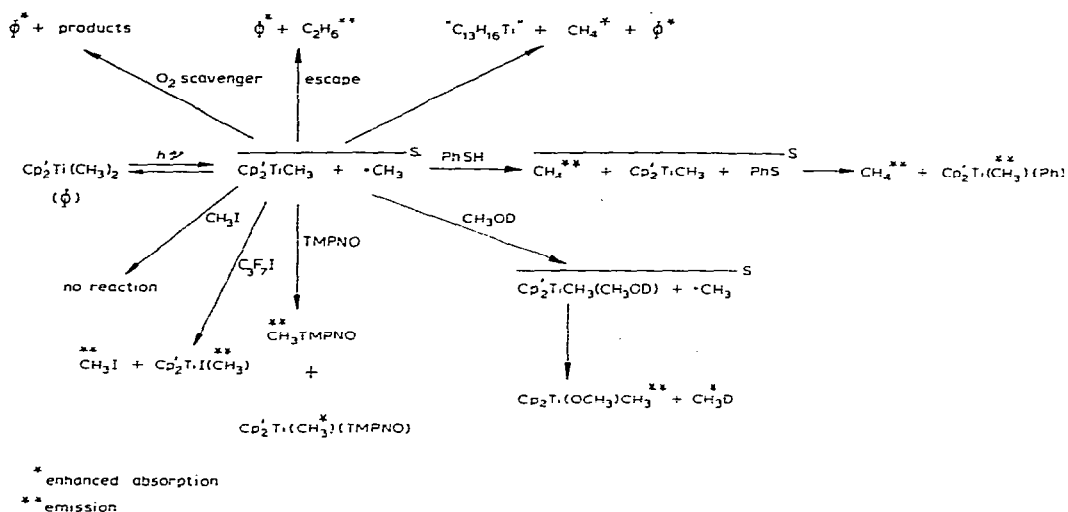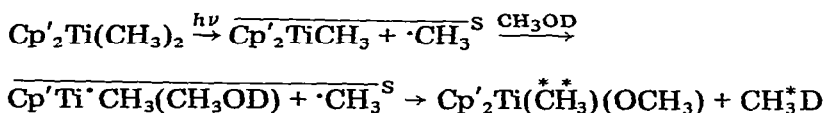
Fig. 3. NMR spectra of $Cp'_2Ti(CH_3)_2$ in the presence of TMPNO: (a) before, (b) during, and (c) after irradiation.

SCHEME 2

$\overset{*}{\phi}$ + products $\overset{*}{\phi}$ + $C_2H_6^{**}$ $^-C_{13}H_{16}Ti^-$ + CH_4^* + $\overset{*}{\phi}$

O_2 scavenger | escape

$Cp_2'Ti(CH_3)_2 \underset{(\phi)}{\overset{h\nu}{\rightleftharpoons}} Cp_2'TiCH_3 + \cdot CH_3 \xrightarrow[\text{PhSH}]{S} CH_4^{**} + Cp_2'TiCH_3 + PhS \xrightarrow{S} CH_4^{**} + Cp_2'Ti(CH_3)(Ph)$

no reaction

CH_3I / C_2F_5I | TMPNO | CH_3OD

$\overset{**}{CH_3}$TMPNO

$^{**}CH_3I + Cp_2'Ti \cdot I(CH_3)$

$Cp_2'Ti(CH_3^*)(TMPNO)$

$Cp_2'TiCH_3(CH_3OD) + \cdot CH_3 \xrightarrow{S}$

$Cp_2Ti(OCH_3)CH_3^{**} + CH_3^*D$

$\overset{*}{}$enhanced absorption
$\overset{**}{}$emission

nature of the process. With CH_3OD as the alcohol monodeuteriomethane is formed, which shows an enhanced absorption as does the starting material. It is concluded that both originate from combination of the geminate singlet radical pair. This involves coordination of methanol to titanium prior to abstraction, which turns out to be much faster than abstraction from free methanol. The broadening of the methoxy group of methanol during irradiation points to a fast exchange between free and coordinated methanol of which the latter experiences a contact shift and broadening. No concentration or temperature studies were undertaken to see whether the observed methanol signal is to be described in terms of a fast or slow exchange. The methyl group of $Cp'_2Ti(CH_3)$-(OCH_3) appears as an emission and although at first sight the emission might be regarded as the escape polarization complementing the absorptions mentioned, a mechanism for this is hard to envisage. It is proposed that this polarization does not stem from the methyl radicals but from the methyltitanium(III) radical. A geminate recombination and a negative hyperfine constant account for the emission. The escape polarization of either radical is lost or dominated by recombination. Scheme 3 summarizes the results:

SCHEME 3

$$Cp'_2Ti(CH_3)_2 \xrightarrow{h\nu} \overline{Cp'_2TiCH_3 + \cdot CH_3}^S \xrightarrow{CH_3OD}$$

$$\overline{Cp'Ti\cdot CH_3(CH_3OD) + \cdot CH_3}^S \rightarrow Cp'_2Ti(\overset{**}{CH_3})(OCH_3) + CH_3^*D$$

This reaction sequence differs from that involving thiophenol in the way methane is formed: in the latter the methyl radicals react with free thiophenol (escape polarization), followed by geminate combination of Ti^{III} and thiophenoxyl, while in the former methanol first forms a complex with titanium after which the activated methanol donates its hydrogen (deuterium) to the methyl radical (recombination polarization). The activation of CH_3OD is an interesting phenomenon, since a free methanol molecule would (a) react much
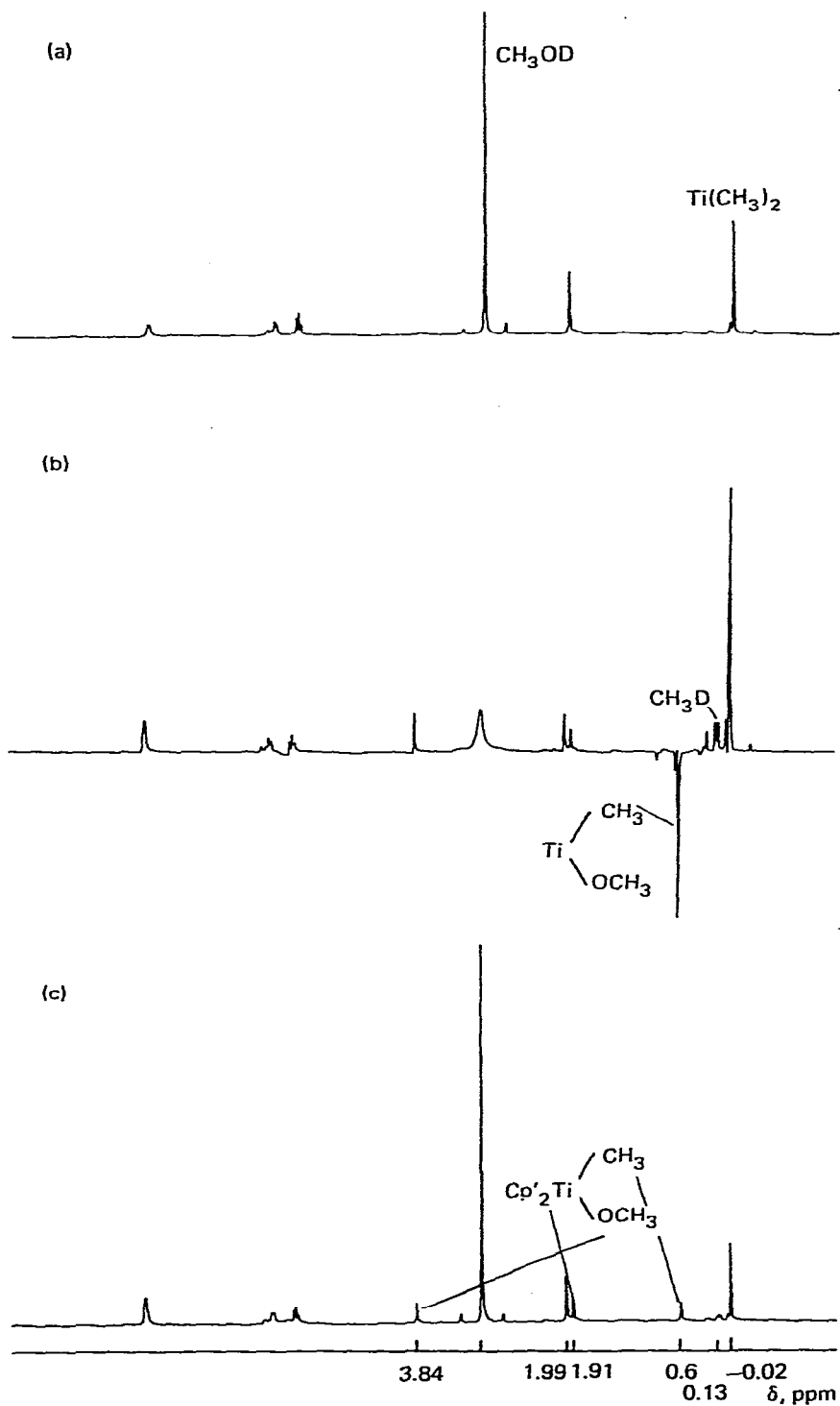
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Fig. 4. Photochemical methanolysis (with CuSO₄ filter) of Cp′₂Ti(CH₃)₂: (a) before, (b) during, and (c) after reaction.

more slowly and not exhibit CIDNP, and (b) would donate a hydrogen from the carbon rather than from the oxygen atom.

Thermal decomposition of $Cp_2Ti(CH_3)_2$

The thermal decomposition of dicyclopentadienyldimethyltitanium has been the subject of several studies [19,20]. It is described as a two-stage process, involving initial formation of methane via a first-order α-elimination followed by a catalysed second process in which ring protons are also found in the methane produced. Both concerted and radical pathways have been considered: after decomposition an EPR signal for Ti^{III} has been observed [21] and taken as an indication of homolysis, but often no abstraction of hydrogen from the aromatic or alkane solvent is found and this was taken to prove the absence of free methyl radicals. The latter conclusion is somewhat doubtful, since abstraction of hydrogen from the titanocene derivatives may be considerably faster than abstraction from the solvents, which is known [16,17] to be slow; in diethyl ether the hydrogens are mainly abstracted [22] from the solvent during the decomposition, which may be due to the effect of coordination and/or to the higher reactivity of ethers compared to that of benzene and hexane towards methyl radicals.

We thought it worthwhile to investigate the thermal decomposition of $Cp_2Ti(CH_3)_2$ by CIDNP. Typically the experiments were carried out in C_6D_5Br at 120°C and spectra were recorded at 3.5 s intervals starting 10 s after insertion of the tube into the hot probe. Within ten scans the absorptions of the starting compound descreased to one third of their original values, the cyclopentadienyl peak broadened and methane was formed. However, in none of our experiments were emissions or enhanced absorptions observed. The rate of decomposition is not a limiting factor. Homolysis similar to that in the photolysis does not occur. It can be argued that an escape route should be offered as in the case of photolysis in order to obtain spin selection, but addition of traces of dioxygen gave no CIDNP. Reactions in the presence of other scavengers turned out to be complex since induced decomposition (by thiophenol, nitroxides) complicates the picture. In strongly chlorinating solvents such as hexachlorocyclopentadiene and hexachloroacetone the observed reaction is

$$RCl + {\geq}Ti{-}CH_3 \rightarrow {\geq}Ti{-}Cl + CH_3{^\bullet} + R^\bullet$$
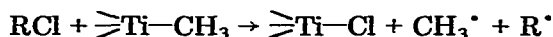
which is also found for chloroform * and tetrachloromethane under photolysis. This reaction exhibits the usual CIDNP for this rather general reaction [11,12]. However, the thermal decomposition taking place simultaneously (e.g. in C_6D_5Br with hexachloroacetone (1:1) at 120°C) gives methane but this is not polarized. The absence of CIDNP is usually only partial evidence for a non-radical mechanism (e.g. radical chain reactions may still occur; short relaxation times will hamper CIDNP) but the simultaneous occurrence of the two reactions described here and the similarity between the products from the thermal (no CIDNP) and photolytic reactions (CIDNP) points to a different mechanism for the two. Hence, it seems safe to conclude that the thermal decomposition does not lead
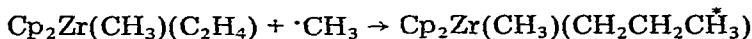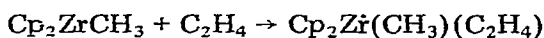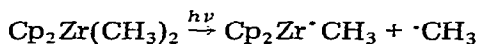
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* Irradiation of $Cp_2Ti(CH_3)_2$ leads to enhanced absorptions of CH_3CCl_3 and CH_3CDCl_2, and a strong emission of CH_3D and a weak one for C_2H_6. The reaction is slightly more complicated due to an enhanced absorption of the starting material caused by the simultaneous homolysis.

to free methyl radicals, free in the sense of being a partner in a radical pair showing CIDNP, i.e. with lifetimes $>10^{-10}$ s. Previously, Waters et al. [23] described the homolysis of $Cp_2Ti(CH_3)Cl$ as a homolytic cleavage whereby the methyl radical remains in the coordination sphere of the titanium before reacting with the titanocene moiety or another molecule. Our experiments have shown that under photolytic conditions a radical pair is formed (lifetime $>10^{-10}$ s) whereas the thermal reactions are most satisfactorily described as non-radical reactions.

Irradiation of $Cp_2Zr(CH_3)_2$

Photolysis of dimethylzirconocene produces, inter alia, methane and zirconocene. In the presence of CO dicarbonylzirconocene is formed, and in the presence of diphenylacetylene 1,1-bis-Cp-2,3,4,5-tetraphenylzirconacyclopentadiene is obtained, together with methyl adducts of diphenylacetylene. Irradiation of tetraallylzirconium leads to homolysis, as can be seen from the observed CIDNP in which one of the radicals causing polarization is a zirconium radical [24]. Photolysis of $Cp_2Zr(CH_3)_2$ in benzene in the presence of radical scavengers or hydrogen donors (nitroxide, thiophenol) yielded no information about the mechanism of the photolysis because of the occurrence of a thermal reaction. Sometimes, irradiation of dimethylzirconocene in the absence of scavengers did give enhanced absorptions or emission, but this turned out to be irreproducible. In the presence of 9,10-dideuterioanthracene CH_3D is formed; this is probably due to a radical reaction, though no polarization is observed.

An interesting phenomenon is observed when dimethylzirconocene in benzene is irradiated (using a $CuSO_4$/water filter) in the presence of ethylene. During irradiation an absorption of a triplet at $\delta = 1.01$ ppm ($J = 7$ Hz) is seen, and this disappears when irradiation is stopped. When tetradeuterioethylene is used an identical reaction takes place, but now the signal at 1.01 ppm is a broad singlet (no solution of deuterium couplings). The products are methane, ethane (in emission) and polyethylene. The triplet at 1.01 ppm is ascribed to a Zr-propyl group. This points to an insertion of ethylene into the zirconium—methyl bond via an unprecedented radical process. The reaction can be represented as follows:

$$Cp_2Zr(CH_3)_2 \xrightarrow{h\nu} Cp_2Zr^{\cdot}CH_3 + {}^{\cdot}CH_3$$

$$Cp_2ZrCH_3 + C_2H_4 \rightarrow Cp_2\dot{Z}r(CH_3)(C_2H_4)$$

$$Cp_2Zr(CH_3)(C_2H_4) + {}^{\cdot}CH_3 \rightarrow Cp_2Zr(CH_3)(CH_2CH_2\overset{\cdot}{C}H_3)$$

where the polarizing radical pair consists of Cp_2ZrCH_3 and the methyl radical. In the case of deuterated ethylene, $Cp_2Zr(CH_3)(C_2D_4CH_3)$ is formed. Synthesis of the observed propylzirconium compound led to a complex mixture, which did, however, show a triplet at $\delta = 1.01$ ppm.

Experimental

The compounds were prepared by literature methods. The solutions were made in the complete absence of oxygen and water, unless stated otherwise (1—2 mg in 0.3 ml).

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WH-90 NMR spectrometer in the FT mode. Photolysis with concomitant recording of the NMR spectra was performed with a Philips SP-1000 mercury light source. The filters used were: water, $NiSO_4$ in water, $CuSO_4$ in water, and commercially obtained interference filters. The light beam was focussed with two lenses ($f \sim 10$ cm) and directed into the probe via a quartz light tube (diameter 8 mm, length 30 cm). In a standard procedure the sample was irradiated for 45 seconds while ten spectra were recorded during the last 35 seconds (flip angle $<40°$).

Concluding remarks

The above described experiments yield definite proof for the occurrence of free radical reactions during photolysis of dimethyltitanocene and -zirconocene. The secondary reactions, however, are extremely fast, and this may often have led to the conclusion that the reactions taking place are "concerted". For instance, the remaining titanocene fragment is a very active hydrogen donor and the lack of formation of CH_3D in experiments in perdeuterotoluene does not prove the absence of methyl radicals. We have found that the competing reaction which may scavenge the methyl radicals so as to create spin selection pathways must be extremely fast. Another explanation for the absence of polarization might have been that spin correlation is preserved for too short a period (g-difference too large, or electron-relaxation time of Ti^{III} is very short [13]), but on the basis of other CIDNP work (see above) and the ESR line-width for "Ti—CH$_3$" this does not seem very likely.

In the present study the spin-state of the initial pair formed by photolysis is deduced from the polarizations observed. Unfortunately, a second unknown is involved in same cases, viz. the sign of the hyperfine constant of the hydrogens on the methyltitanium(III) radical. An independent determination of this sign would strengthen the formulated mechanisms. We have undertaken several experiments to determine the sign, such as anion exchange between Ti^{III} and Ti^{IV}, and an attempted electron exchange between $Cp_2Ti(CH_3)_2^-$ and excess $Cp_2Ti(CH_3)_2$, but, these attempts were unsuccessful because the exchange was too slow to cause a shift in the NMR signal of $Cp_2Ti(CH_3)_2$.

Selective scavenging of the methyl radicals so as to leave a reactive Ti^{III} species for, e.g., olefin reactions turned out to be virtually impossible. In this respect the insertion of ethylene into the zirconium—methyl bond via a radical mechanism is more promising.

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