ON THE NATURE AND REACTIVITY OF Cp$_2$TiCH$_3$

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Summary

- Reaction of Cp$_2$TiCl with 1 eq. of CH$_3$Li in ether at $-78°$C yields the green, thermally unstable, trivalent Ti compound Cp$_2$TiCH$_3$. EPR studies on ether solutions of this compound reveal it to be present in solution as the adduct Cp$_2$TiCH$_3$ · OEt$_2$ · By reaction with DCl Cp$_2$TiCl$_2$ and CH$_3$D are formed. Reaction with 2,6 xylylisocyanide leads to insertion of the isocyanide into the Ti—CH$_3$ bond, while reaction with CS$_2$ yields the disproportionation products Cp$_2$-Ti(CH$_3$)$_2$ and Cp$_2$TiCS$_2$. Thermal decomposition studies on deuteriated analogues confirm the Ti—CH$_3$ structure. The rate determining step in the decomposition process is the abstraction of a Cp proton by the methyl group. Under nitrogen the decomposition reaction yields NH$_3$ and N$_2$H$_4$ in amounts of up to 0.28 moles N/Ti. Some catalytic applications of Cp$_2$TiCH$_3$ for hydrogenation and isomerisation of olefins and acetylenes are briefly mentioned.

Introduction

The paramagnetic compounds Cp$_2$TiR (Cp = η^5-C$_5$H$_5$, R = aryl) show very interesting activating properties towards donor molecules, such as molecular nitrogen [1], cyanides [2a,b], isocyanides [3] and carbon monoxide [4]. Even stronger activating properties can be expected for the compounds Cp$_2$Tialkyl, since these are expected to possess a higher electron density at the metal. A few compounds Cp$_2$Tialkyl have been isolated previously viz. Cp$_2$Tibenzyl [5], Cp$_2$-TiCH$_2$C(CH$_3$)$_3$ [6] and Cp$_2$TiCH$_2$Si(CH$_3$)$_3$ [7], but no particular activating properties were reported. However, attempts to prepare Cp$_2$TiR with R = Me, Et, i-Pr, n-Bu, t-Bu, n-C$_5$H$_{11}$ were unsuccessful [6].

We decided to try again to prepare Cp$_2$TiCH$_3$ and study its activating properties. We selected Cp$_2$TiCH$_3$ mainly for steric reasons: complexation of a substrate molecule to be activated to the Ti centre should be easier than for other Cp$_2$Tialkyl compounds. Moreover, Cp$_2$TiCH$_3$ is expected to show a higher ther-

mal stability than other n-alkyl derivatives because of the lack of β- and γ-hydrogens.

Cp_2TiCH_3 has been assumed to be formed in the electrochemical reduction of $Cp_2TiCl(CH_3)$ [8], and also during the photochemical decomposition of Cp_2-$Ti(CH_3)_2$ and $Cp_2TiCl(CH_3)$ [9]. Its existence was also inferred from EPR studies on mixtures of Cp_2TiCl and CH_3MgI in THF [10]. In none of these cases, however, were attempts to isolate or further characterize Cp_2TiCH_3 reported. In recent work, Holton et al. [11] suggest that reaction of Cp_2TiCl with CH_3Li in ether at $-78°C$ gives $(Cp_2TiCH_3)_2$, but attempts to isolate the compound were unsuccessful and no properties were described.

We decided to prepare Cp_2TiCH_3 from Cp_2TiCl and CH_3Li at low temperature and try to stabilize it by the addition of appropriate ligands. Phosphines such as diphenyl, o-tolyl phosphine or sulphides like 2-methyl thiophene were not suitable ligands, and no characterizable products could be isolated. In reaction with 2-substituted pyridines and quinolines, however, α-metallation of the ligands was observed; this C—H activation reaction is assumed to proceed via the adduct $CpTiCH_3 \cdot L$ (L = 2-substituted pyridine or quinoline) [12].

In this report we describe our studies on the product formed in the low-temperature reaction of Cp_2TiCl and CH_3Li in ether.

Results and discussion

Reaction of Cp_2TiCl with 1 eq. of CH_3Li in ether at $-78°C$ for about 10 minutes gives a green solution and a white precipitate. The solution (0.1 M) is stable at $-78°C$, but decomposes above about $-50°C$ with formation of methane (0.93 moles CH_4/Ti) and a purple solution, which on further warming changes into a dark-brown, moderately soluble product.

Attempts to isolate Cp_2TiCH_3, or the adducts $Cp_2TiCH_3 \cdot L$ (L = ether, THF, diphenyl o-tolylphosphine, 2-methylthiophene, 2,6-xylylisocyanide, 2-substituted pyridines or quinolines) failed, although the presence of these ligands does stabilize the solution.

Elemental analyses of the green solution show that it contains the expected amount of Ti, and only traces of Li (and Mg if Cp_2TiCl is prepared in situ from Cp_2TiCl_2 and i-C_3H_7MgCl, see experimental). This clearly indicates that no methyl or halogen bridged binuclear Ti—Mg or Ti—Li compounds or complexes of the type $[Cp_2Ti(CH_3)_2]^-Li^+$ are formed.

Spectroscopic characterization

The UV-VS spectrum of the green solution at $-75°C$ shows a low-intensity absorption at 610 nm resulting the absorptions at 646 nm ($\epsilon = 50$) for Cp_2Ti-$CH_2C(CH_3)_3$ [6] and 632 nm ($\epsilon = 40$) for $Cp_2TiCH_2Si(CH_3)_3$ [7]. This suggests that a similar product is formed in the reaction described here. The EPR spectrum of the green solution at $-80°C$ shows a singlet at $g = 1.980$ as depicted in Fig. 1a. Upon addition of THF ($-80°C$) this signal disappears completely and immediately a quartet signal appears ($g = 1.981$, a 4.4 G, Fig. 1b). This quartet is very similar to that reported by Brintzinger, and ascribed to $Cp_2TiCH_3 \cdot$ THF [10]. We conclude that in our case $Cp_2TiCH_3 \cdot$ THF is formed from the ether adduct $Cp_2TiCH_3 \cdot OEt_2$, which gives the first observed singlet. Similarly,
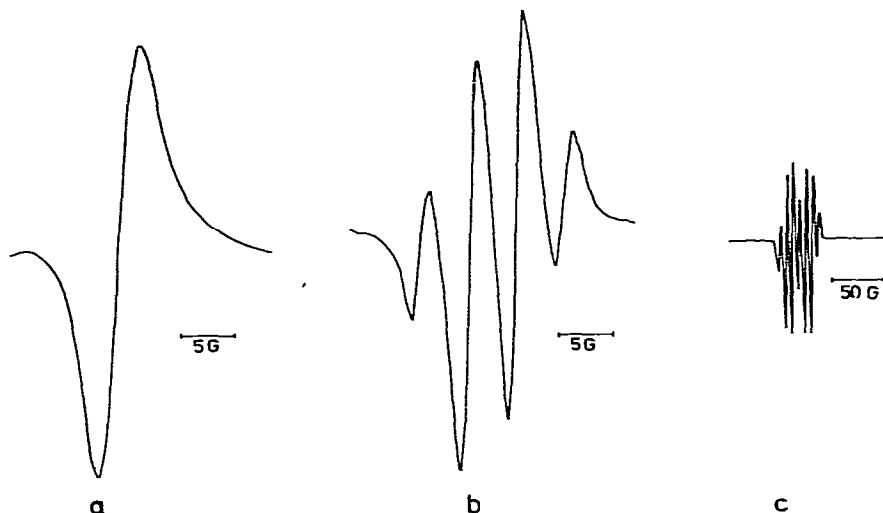
Fig. 1. EPR spectra ($-80°$C; DPPH external reference) a) $Cp_2TiCH_3 \cdot OEt_2$ ($g = 1.980$) b) $Cp_2TiCH_3 \cdot$ THF ($g = 1.981$, a 4.4 G) c) $Cp_2TiCH_3 \cdot PPh_3$ ($g = 1.999$, a 18.9 and 6.0 G).

addition of PPh_3 to this ether solution leads to the formation of $Cp_2TiCH_3 \cdot PPh_3$ which shows two partly overlapping quartet signals at $g = 1.999$ due to a Ti—P coupling (a 18.9 G) and a Ti—H coupling (a 6.0 G; Fig. 1c).

It is unlikely that molecules of Cp_2TiCH_3 exist as such in ether solution since they would be coordinatively highly unsaturated and are expected to relieve this unsaturation, either by forming an adduct or by dimerisation to $(Cp_2Ti-CH_3)_2$. The latter dimer is believed to be EPR inactive because of Ti—Ti interaction. Monomeric Cp_2TiCH_3 is expected to show a singlet at $g = 1.96-1.97$ comparable to the values of related compounds Cp_2TiR (R = $CH_2C(CH_3)_3$, $g = 1.960$ [6]; R = $CH_2C_6H_5$, $g = 1.966$ [5], R = $CH\{Si(CH_3)_3\}_2$, $g = 1.96$ [13]). No signals in this region are observed in our case. We believe, therefore, that in ether solution the compound exists as the adduct $Cp_2TiCH_3 \cdot OEt_2$, although some dimerisation cannot be excluded.

The intensity of the singlet signal in ether solution decreases on warming, but above about $-50°$C a new singlet appears at $g = 1.981$, which decays slightly upon standing at room temperature. Although the quartet signal of $Cp_2TiCH_3 \cdot$ THF is thermally more stable than the signal of $Cp_2TiCH_3 \cdot OEt_2$, it also disappears on warming and is again replaced by a singlet signal at $g = 1.981$. This is in contrast with the observations of Brintzinger who reported that in pure THF the quartet is stable [10]. It is quite possible that in the solutions under discussion an equilibrium exists:

$$Cp_2TiCH_3 \cdot THF + Et_2O \rightleftharpoons Cp_2TiCH_3 \cdot OEt_2 + THF$$
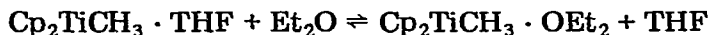
and that decomposition of the ether adduct is responsible for the decay of $Cp_2TiCH_3 \cdot$ THF. Samuel et al. reported the generation of Cp_2TiCH_3 by photochemical decomposition of $Cp_2Ti(CH_3)_2$ in toluene [9]. The product thus prepared shows a singlet at $g = 1.980$, exactly the value as found for our $Cp_2TiCH_3 \cdot OEt_2$. It is not clear whether identical Cp_2TiCH_3 species are concerned,

since the EPR signal of the photochemically prepared compound is reported to be stable at room temperature, which is in contrast to our observations. It is possible, however, that Cp_2TiCH_3 is much more stable in toluene than in the presence of donor ligands such as ether or THF. The observations by Holton et al. on the stability of the related complex $Cp_2Ti(\mu\text{-}CH_3)_2Al(CH_3)_2$ do not seem to support this view, however [11].

Chemical characterisation

Reaction of the green solution of Cp_2TiCH_3 with an excess of HCl/ether yields Cp_2TiCl_2 (90%) and CH_4 in a quantitative yield according to

$$Cp_2TiCH_3 + HCl \rightarrow Cp_2TiCl + CH_4$$

$$Cp_2TiCl + HCl \text{ (excess)} \rightarrow Cp_2TiCl_2 + \tfrac{1}{2}H_2$$
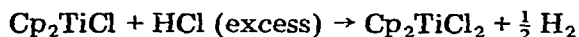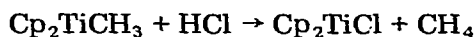
which clearly indicates retention of the Cp_2Ti structure. Reaction with DCl/ether results in the formation of CH_3D as the only deuteriated methane. The absence of CH_2D_2 and CHD_3 excludes the presence of Ti—methylene or Ti—carbyne species. Mass spectrometry shows that with excess DCl no deuterium is incorporated in the Cp ligands.

Reaction with 2,6-xylylisocyanide

Reaction of Cp_2TiCH_3 with 2,6-xylylisocyanide in ether at $-78°C$ results in the formation of the η^2-iminoacyl compound $Cp_2TiC(CH_3)=N\text{-}2,6(CH_3)_2C_6H_3$ (Scheme 1). This reaction is similar to the insertion of isocyanides into the

SCHEME 1
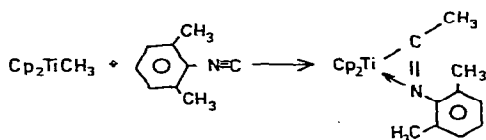
Ti—C bond of $Cp_2Tiaryl$ compounds [3]. The red-brown product is characterized by elemental analysis (Table 1), IR (Table 2) and molecular weight determination (monomeric, Table 2). The compound is stable up to about $140°C$ and is paramagnetic in solution, as expected for a Ti^{III} compound. Its IR spectrum shows, in addition to the characteristic $\eta^5\text{-}C_5H_5$ and phenyl absorptions,

TABLE 1

ANALYTICAL DATA FOR $Cp_2Ti\text{-}\eta^2\text{-IMINOACYL COMPOUNDS}$

Compound	Yield (%)	Colour	Analysis (found (calcd.) (%))		
			C	H	Ti
$Cp_2TiC(CH_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$	10	red-brown	73.59(74.07)	7.14(6.83)	13.77(14.77
$Cp_2Ti(I)C(CH_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$	82	yellow		a	
$Cp_2Ti(SC_6H_5)C(CH_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$	36	yellow	17.85(72.04)	6.48(6.28)	11.13(11.05

a not obtained in sufficiently pure form.

the ν(CN) band at 1578 cm^{-1} (free isocyanide 2115 cm^{-1}) which is comparable to the ν(CN) band at 1573 cm^{-1} of the phenyl analogue $Cp_2TiC(C_6H_5)$=N-2,6-$(CH_3)_2C_6H_3$, a value that was assigned to a η^2-coordination of the iminoacyl ligand [3]. The iminoacyl compound $Cp_2TiC(CH_3)$=N-2,6$(CH_3)_2C_6H_3$ with tri-valent Ti is readily oxidized by $C_6H_5SSC_6H_5$ or I_2 to derivatives of tetravalent Ti in which the iminoacyl ligand is still η^2-coordinated (Scheme 2). The yellow

SCHEME 2
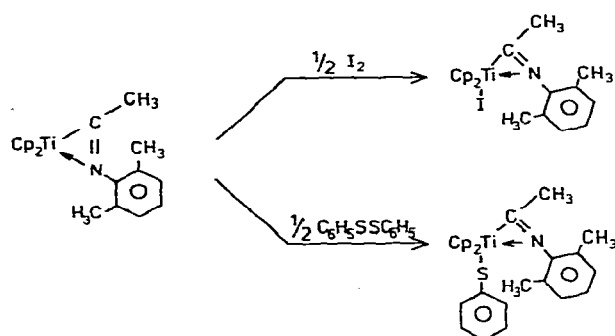
diamagnetic compounds formed were characterized by elemental analyses (Table 1), IR (Table 2), ^{1}H NMR (Table 3) and ^{13}C NMR (Fig. 2). The IR spectra show ν(CN) at 1677 cm^{-1} for $Cp_2Ti(I)C(CH_3)$=N-2,6$(CH_3)_2C_6H_3$ and 1662 cm^{-1} for $Cp_2Ti(SC_6H_5)C(CH_3)$=N-2,6$(CH_3)_2C_6H_3$ (Table 2). The presence of the methyl group is clearly shown in the ^{1}H and ^{13}C NMR spectra (Table 3).

The $-CH_3$ absorption in the ^{1}H NMR spectrum is centred at δ 2.63 ppm for the iodine derivative and at δ 2.44 ppm for the $-SC_6H_5$ derivative. The ^{13}C NMR spectrum of the latter compound is shown in Fig. 2. The resonance of the $-CH_3$ carbon atom of the Ti$-$C$-$CH$_3$ fragment is centred at 23.6 ppm ($^1J(^{13}$C$-^1$H) 132 Hz). The Cp carbon atoms are found at 108.7 ppm whereas the iminoacyl carbon shows a low-field resonance signal at 231.2 ppm ($^2J(^{13}$C$-^1$H) 9 Hz). The phenyl carbon atoms are found in the range 122.5 ppm to 148.3 ppm.

Reaction with CS_2

Reaction of Cp_2TiCH_3 with CS_2 in ether at $-78°$C results in the formation of

TABLE 2

INFRARED AND PHYSICAL DATA FOR Cp_2Ti-η^2-IMINOACYL COMPOUNDS

Compound	Mol. weight [a] (calcd.)	Magn. [b]	DTA		IR [e] ν(CN) (cm^{-1})
			endo (°C) [c]	exo (°C) [d]	
$Cp_2TiC(CH_3)$=N-2,6-$(CH_3)_2C_6H_3$	304(324)	paramagn.	88	142	1578 [f]
$Cp_2Ti(I)C(CH_3)$=N-2,6-$(CH_3)_2C_6H_3$		diamagn.			1677
$Cp_2Ti(SC_6H_5)C(CH_3)$=N-2,6-$(CH_3)_2C_6H_3$		diamagn.			1662

[a] Cryoscopically in benzene. [b] In solution. [c] Reversible; melting point. [d] Irreversible; decomposition temperature. [e] KBr/nujol. [f] ν(CN) in 2,6-xylylisocyanide 2115 cm^{-1}.

TABLE 3

^{1}H NMR SPECTRAL DATA OF TETRAVALENT Ti-η^2-IMINOACYL COMPOUNDS

Compound	δ(Cp) (ppm)	δ(Ti—C—CH$_3$) (ppm)	δ(CH$_3$) (ppm)	δ(fenyl-H) (ppm)
Cp$_2$Ti(I)C(CH$_3$)=N-2,6-(CH$_3$)$_2$C$_6$H$_3$ [a]	5.87 (s, 10)	2.63 (s, 3)	2.07 (s, 6)	7.09 (s, 3)
Cp$_2$Ti(SC$_6$H$_5$)C(CH$_3$)=N-2,6-(CH$_3$)$_2$C$_6$H$_3$ [b]	5.58 (s, 10)	2.44 (s, 3)	2.09 (s, 6)	6.8—7.2 (m, 8)

[a] CD$_3$CN, TMS, 30°C. [b] CDCl$_3$, TMS, 30°C.

Cp$_2$Ti(CH$_3$)$_2$ (IR, NMR) and Cp$_2$TiCS$_2$ (IR [4]) in very high yields according to

$$2\ Cp_2TiCH_3 + CS_2 \rightarrow Cp_2Ti(CH_3)_2 + Cp_2TiCS_2$$

Since a disproportionation reaction is thought to require a dimeric type of precursor [14], one might conclude that Cp$_2$TiCH$_3$ is present as a dimer. However addition to the reaction mixture of THF or even pyridine, ligands which yield ligand stabilized monomeric Cp$_2$TiCH$_3$ · L, as mentioned above, does not affect the product formation.

The observations can be explained by assuming that the CS$_2$ ligand is initially (σ, π) bridging between two Cp$_2$TiCH$_3$ fragments, thus creating a "dimeric type" intermediate [15].

Thermal decomposition

0.1 *M* solutions of Cp$_2$TiCH$_3$ in ether (under Ar) decompose above about —50°C with formation of methane (0.93 mole CH$_4$/Ti) and a dark brown mixture. The decomposition temperature is concentration dependent: 0.01 *M* solutions decompose above about —30°C.

Neither H$_2$ or other gaseous products in the C$_2$—C$_6$ rangs are observed from this decomposition reaction. Therefore homolytic fission of the Ti—CH$_3$ bond
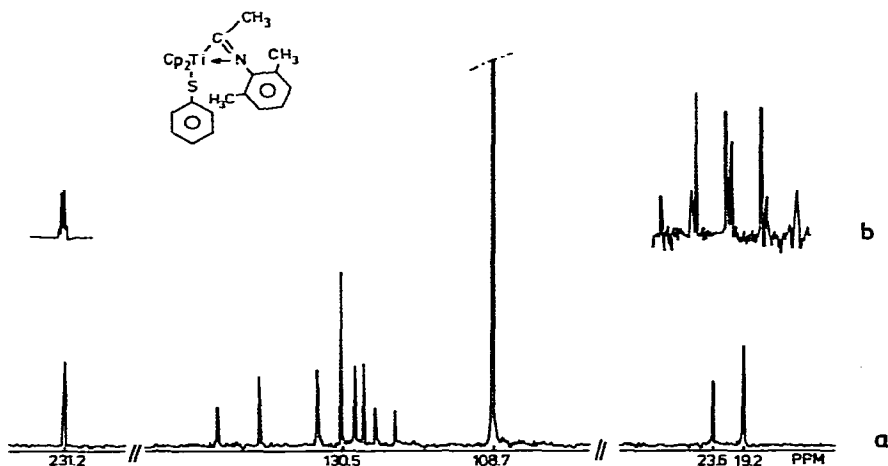

Fig. 2. Decoupled (a) and coupled (b) ^{13}C NMR spectra of Cp$_2$Ti(SC$_6$H$_5$)C(CH$_3$)=N-2,6-(CH$_3$)$_2$C$_6$H$_3$ (CDCl$_3$; TMS; —20°C; solvent peaks are omitted).

TABLE 4

DEUTERIUM CONTENT OF THE METHANE OBTAINED FROM THERMAL DECOMPOSITION OF $(C_5H_5)_2TiCH_3$ AND SPECIFICALLY DEUTERIATED ANALOGUES UNDER Ar

Compound	solvent; added	D-incorporation in methane, content [a] (%)				
		CH_4	CH_3D	CH_2D_2	CD_3H	CD_4
$(C_5H_5)_2TiCH_3$	ether	100				
$(C_5H_5)_2TiCH_3$	ether-d_{10}	100				
$(C_5H_5)_2TiCD_3$	ether				100	
$(C_5D_5)_2TiCD_3$ [b]	ether			11	66	23
$(C_5H_5)_2TiCH_3$	ether; THF-d_8	100				
$(C_5H_5)_2TiCD_3$	ether; THF-d_8				100	

[a] From peak ratio in mass spectrum at 15.5 eV (100°C). [b] Cp ligands are 89% deuteriated.

with formation of methyl radicals is not likely. In order to obtain more insight in the thermal decomposition pathway, and to find the source of the hydrogen for the methane formation, the CH_3 and Cp groups of the starting material Cp_2-$TiCH_3$ and also the solvent ether were (separately) deuteriated and the incorporation of D in the methane measured (Table 4). Decomposition of $(C_5H_5)_2Ti$-CD_3 in ether results in the formation of pure CD_3H and no other methanes such as CD_2H_2 or CD_4. This clearly shows that the starting material is a Ti—methyl compound and not a Ti—methylene species, which upon decomposition would produce CD_2H_2. Moreover, the decomposition temperature of Cp_2TiCD_3 does not differ from that of Cp_2TiCH_3 (—50°C at 0.1 M), which indicates a comparable activation energy for the decomposition process of the two compounds. This leads to the conclusion that a methyl C—H bond rupture is not the rate-determining step of the decomposition of Cp_2TiCH_3. Replacement of ether by ether-d_{10} as a solvent gives no D incorporation in the product methane, and again no change in the decomposition temperature is observed, which means that the solvent (ether) is not involved in the rate determining step (a similar observation was made for the photochemical decomposition of $Cp_2Ti(CH_3)_2$ [16]). For the same reason we conclude that THF, although it has a markedly stabilizing effect on Cp_2TiCH_3, does not participate in its decomposition.

As neither the methyl group nor the solvent ether are involved in the decomposition process, the only hydrogen sources can be the Cp groups. It is concluded that Cp_2TiCH_3 decomposes exclusively with abstraction of cyclopentadienyl protons by the methyl group to form methane. Concerning the question of whether this process is intra- or inter-molecular, it must be noted that the decomposition temperature is concentration dependent (higher thermal stability at lower concentrations) which suggests an inter molecular decomposition process. The fact that the Cp groups are the exclusive proton donors explains the observed kinetic isotope effect in the decomposition process of $(C_5D_5)_2Ti$-CD_3. This compound decomposes above about —30°C ($(C_5H_5)_2TiCH_3$ at —50°C) with formation not only of CD_4 but of CH_2D_2 (11%), CHD_3 (66%) *

* Since the Cp ligands in the compound $(C_5D_5)_2TiCD_3$ are only 89% deuteriated the non-deuteriated part of these ligands can be also involved in the CHD_3 formation.

TABLE 5

PRODUCT FORMATION IN HCl/ETHER REACTIONS OF DECOMPOSED REACTION MIXTURES
OF Cp_2TiCH_3 UNDER VARIOUS CONDITIONS

Solvent	Atmosphere	$CpTiCl_3$ (%)	Cp_2TiCl_2 (%)	"$C_{10}H_9TiCl_2$" (%)
ether	Ar	12	26	52
ether	N_2	21	63	12
ether + THF	Ar	7	27	58
ether + THF	N_2	10	85	traces

and CD_4 (23%). Obviously the replacement of cyclopentadienyl hydrogens by deuterium changes the activation energy of the rate determining step of the decomposition, which means that other decomposition pathways, with lower activation energies, are introduced (similar observations have been made in the decomposition of $(C_5H_5)_2Ti(CD_3)_2$ and $(C_5D_5)_2Ti(CD_3)_2$ [17]). The formation of CH_2D_2 indicates that C—D bond rupture in the methyl group, with formation of Ti—methylene species, is one of the processes that is now more involved. These observations indicate that there are only very small differences in activation energies between the various reaction possibilities and this is possibly the reason for the large number of rather conflicting data on the decomposition of low valent Ti compounds.

The Ti containing residue formed upon decomposition of Cp_2TiCH_3, was not studied in detail, but it may be expected to posess a highly unsaturated character, probably with $(\eta^1—\eta^5)$ bridging C_5H_4 groups or a fulvalene type structure; it may well be a mixture. Therefore, it might show interesting activating properties towards certain donor molecules. Indeed, as is reported below, it seems to be an active catalyst in isomerisation and hydrogenation reactions of olefins and acetylenes.

If the dark brown decomposition residue of Cp_2TiCH_3 is treated with an excess of HCl/ether at —78°C three compounds are formed: $CpTiCl_3$, Cp_2TiCl_2 and "$C_{10}H_9TiCl_2$" [18], whereas 0.92 moles of H_2/Ti are evolved. The formation of "$C_{10}H_9TiCl_2$" indicates that $(\eta^1—\eta^5)$ bridging Cp groups or fulvalene type ligands are present in the original residue. Table 5 shows the yields of the compounds formed under various conditions. If the decomposition is carried out under Ar, "$C_{10}H_9TiCl_2$" is formed as the major product (52%). Addition of THF to the original reaction mixture under Ar (which has a stabilizing effect) does not affect the product formation to a great extent. However, if the decomposition is carried out in ether under N_2 (at —80°C a dark blue colour characteristic of a binuclear Ti dinitrogen complex is observed) Cp_2TiCl_2 (63%) is formed as the major product after HCl/ether reaction. Moreover, 0.20 moles of NH_3/Ti and 0.02 moles of N_2H_4/Ti are obtained after acidolysis. For this nitrogen reduction 0.68 electrons are necessary. Addition of THF to the original reaction mixture under N_2 yields even more Cp_2TiCl_2 (85%), and reversed amounts of reduced nitrogen compounds. viz. 0.06 moles NH_3/Ti and 0.11 moles N_2H_4/Ti, amounts which correspond to 0.62 electrons/Ti. Studies of the mechanism of this nitrogen-reducing reaction are in progress.

Catalytic aspects

Cp$_2$TiCH$_3$ is a very interesting compound in relation to Ziegler-Natta catalysis and also homogeneous isomerisation and hydrogenation catalysis. It proves to be a good precursor of active catalysts in both homogeneous isomerisation and hydrogenation of olefins and acetylenes. Two systems derived from Cp$_2$TiCH$_3$ were investigated. The first is obtained by reaction of Cp$_2$TiCH$_3$ with H$_2$. It is active in *cis-trans* isomerisation of olefins, conversion of terminal olefins into internal olefins and conversion of non-conjugated dienes into conjugated dienes. At a substrate-to-catalyst ratio of 200, 1,5 cyclooctandiene for instance is completely converted into 1,3 cyclooctadiene in 25 minutes at 20°C. The system is also active in hydrogenation of terminal and internal olefins, dienes and internal acetylenes. At a substrate-to-catalyst ratio of 200, 1-hexene is hydrogenated to hexane completely in 8 minutes, at 20°C and a hydrogen pressure of 1 atm. The other system studied is that obtained from thermal decomposition of Cp$_2$TiCH$_3$. This system, however, is less active than the first. Details of mechanistic aspects of these catalysed processes will be reported elsewhere.

Experimental Part

All experiments were carried out under argon unless otherwise stated. Solvents were distilled from benzophenoneketylsodium under nitrogen; 2,6 xylylisocyanide was prepared according to ref. 19.

CD$_3$Li was prepared according to ref. 20, and (C$_5$D$_5$)$_2$TiCl$_2$ according to ref. 21. Elemental analyses were performed in the Microanalytical Department of this University under the supervision of Mr. A.F. Hamminga. IR spectra were measured on a JASCO-IRA-2 spectrophotometer (KBr/Nujol). ^{1}H NMR spectra were recorded on a Perkin-Elmer R-24B spectrometer; ^{13}C NMR spectra were recorded by Dr. P.B.J. Driessen on a Varian XL-100 spectrometer. The EPR spectra were recorded on a Varian E3X-band EPR spectrometer. The melting points and decomposition temperatures of solids were determined by differential thermal analysis (heating rate 1.5°C/min). Mass spectra were obtained on an AEI-902 spectrometer normally using an ionizing voltage of 70 eV; they were taken by Mr. A. Kiewiet. For methane characterization an ionizing voltage of 15.5 eV was used in order to minimize fragmentation. A pure sample of CD$_3$H run at 15.5 eV (100°C) gives ion ratios for m/e 19 : 18 : 17 : 16 of 10 : 1 : 0 : 0 in comparison with 10 : 3 : 4 : 1 obtained at 70 eV.

Synthesis of (C$_5$H$_5$)$_2$TiCH$_3$

To a suspension of 1.00 g of Cp$_2$TiCl$_2$ (4.0 mmol) in 30 ml of ether a solution of 4.0 mmol of i-PrMgCl in ether was added dropwise at room temperature during 15 minutes. After 1 hour the resulting green suspension of (Cp$_2$TiCl)$_2$ was cooled to −78°C and 4.0 mmol of CH$_3$Li in ether were added during 10 minutes. After 15 minutes at −78°C the reaction was complete, and a green solution of (C$_5$H$_5$)$_2$TiCH$_3$ had formed. This solution was used in the experiments described below. In the decomposition studies the solution was warmed to room temperature, and this finally yielded a dark brown solution with evolution of methane.

Synthesis of $(C_5H_5)_2TiCD_3$ and $(C_5D_5)_2TiCD_3$

These products were prepared in essentially the way described for $(C_5H_5)_2Ti$-CH_3 above starting from $(C_5H_5)_2TiCl_2$ or $(C_5D_5)_2TiCl_2$; reduction with i-PrMgCl in ether and reaction with CD_3Li in ether.

HCl and DCl/ether reactions

The mixture to be oxidized was cooled to $-78°C$ and a threefold excess of HCl/ether was added. After slowly warming to room temperature, the solvent (ether) was decanted and the residue extracted with n-pentane. Evaporation of the ether-pentane layers yielded $CpTiCl_3$ which was identified by IR. The total yield was estimated from the total Ti content of the ether-pentane layers. Cp_2TiCl_2 was extracted from the residue with dichloromethane and determined spectrophotochemically. After washing with 1.0 M HCl the green compound "$C_{10}H_9TiCl_2$" was left. If applicable, the HCl solutions were analyzed for NH_3 and N_2H_4.

Preparation of $Cp_2TiC(CH_3)=N-2,6-(CH_3)_2C_6H_3$

To a solution of 4.00 mmol of Cp_2TiCH_3 in 30 ml of ether at $-78°C$ 4.00 mmol of 2,6 xylylisocyanide in 10 ml of ether were added during 10 minutes. The purple mixture was slowly warmed to room temperature (2 h) and subsequently stirred for 15 hours. The resulting brown-purple solution was evaporated to dryness and extracted with 20 ml of n-pentane. On cooling the n-pentane extract to $-78°C$ a purple oily product separated (possibly polymeric). The red-brown mother liquor was decanted, concentrated to about the half of the original volume and cooled to $-78°C$, which gave red-brown crystals of $Cp_2TiC(CH_3)=N-2,6(CH_3)_2C_6H_3$ (0.40 mmol; 10%). The product is very air-sensitive and readily soluble in the common organic solvents.

Preparation of $Cp_2Ti(CS_6H_5)C(CH_3)=N-2,6-(CH_3)_2C_6H_3$

To a solution of 0.70 mmol of $Cp_2TiC(CH_3)=N-2,6-(CH_3)_2C_6H_3$ in 10 ml of n-pentane a solution of 0.35 mmol of $C_6H_5SSC_6H_5$ in 10 ml of n-pentane was added during 10 minutes at $-78°C$. On warming to room temperature (2 h) a yellow precipitate of $Cp_2Ti(SC_6H_5)C(CH_3)=N-2,6-(CH_3)_2C_6H_3$ formed. After several washings with n-pentane and recrystallization from ether the pure compound was isolated (0.25 mmol; 36%).

Preparation of $Cp_2Ti(I)C(CH_3)=N-2,6-(CH_3)_2C_6H_3$

To a solution of 0.70 mmol of $Cp_2TiC(CH_3)=N-2,6-(CH_3)_2C_6H_3$ in 10 ml of n-pentane a solution of 0.35 mmol of I_2 in 15 ml of n-pentane was added during 10 minutes at $-78°C$. On warming to room temperature (2 h) a yellow precipitate of $Cp_2Ti(I)C(CH_3)=N-2,6-(CH_3)_2C_6H_3$ formed. After several washings with n-pentane the compound was isolated (0.57 mmol; 81%), but it could not be obtained sufficiently pure. The compound is insoluble in aliphatic/hydrocarbons, ether, THF and benzene, but readily soluble in acetone or acetonitrile.

Reaction of Cp_2TiCH_3 with CS_2

To a solution of 4.00 mmol of Cp_2TiCH_3 in 30 ml of ether at $-78°C$ 4.00 mmol of CS_2 were added. The resulting dark green solution was warmed to

room temperature (2 h), during which the colour slowly changed to light brown. After 3 hours at room temperature the mixture was evaporated to dryness and extracted with 30 ml of n-pentane. Upon cooling the yellow n-pentane extract to $-78°C$, yellow needles of $Cp_2Ti(CH_3)_2$ separated (yield 1.68 mmol, 84%; identification by IR and ^1H NMR). Except for Mg and Li salts the residue contains only pale red Cp_2TiCS_2 (IR [4]). Because of its very low solubility in the common organic solvents this compound could not be purified.

Acknowledgements

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