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PREPARATION OF (η^5-C_5H_5)$_2$Ti ALKYL COMPOUNDS AND REACTIONS WITH UNSATURATED SUBSTRATES

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Summary

Reaction of Cp_2TiCl with RLi (R = $-CH_3$, $-C_2H_5$, —n-C_4H_9, —s-C_4H_9, —t-C_4H_9) yields the thermally instable Ti^{III} compounds Cp_2TiR. Reaction of these compounds with 2,6-xylylisocyanide, phenylisocyanate or carbon dioxide results in insertion of these ligands into the Ti—alkyl bond with formation of iminoacyl, amido and carboxylato derivatives, respectively. In the reaction with ketones a pinacol-type dimerisation is observed.

Introduction

In a previous paper we described the preparation of the thermally unstable Ti^{III}compound Cp_2TiCH_3 [1]. This compound shows interesting reactivity towards unsaturated substrates. Pyridines and quinolines, for instance, are metallated by Cp_2TiCH_3 at the α-C atom, which is quite unusual in transition metal chemistry [2]. In order to explore this reactivity in more detail we prepared several alkyl derivatives Cp_2TiR (R = $-CH_3$, $-C_2H_5$, —n-C_4H_9, —s-C_4H_9, —t-C_4H_9) and studied their reactions with a variety of organic substrates. In this report we describe reactions with 2,6-xylylisocyanide, phenylisocyanate, carbon dioxide and ketones, and some physical properties of the complexes formed.

Results and discussion

The compounds Cp_2Tialkyl

Reaction of Cp_2TiCl in toluene or diethylether with 1 mol of RLi (R = $-CH_3$, $-C_2H_5$, —n-C_4H_9, —s-C_4H_9, —t-C_4H_9) at −78°C gives green to brown solutions of Cp_2TiR in about 30 minutes, depending on R. These solutions are thermally unstable. The stability order, qualitatively determined on 0.1 *M* solutions

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TABLE 1

EPR g VALUES OF Cp_2TiR (—80°C) AND ITS DECOMPOSITION PRODUCT (20°C) IN TOLUENE (DPPH EXTERNAL REFERENCE)

R =	Colour	g-value of Cp_2TiR [a]	g-value of decomposition product [a]
$-CH_3$	green	1.980 [b]	1.981
$-C_2H_5$	brown—green	1.987	1.977
$-n\text{-}C_4H_9$	brown—green	1.986	1.977
$-s\text{-}C_4H_9$	brown—green	1.987	1.979
$-t\text{-}C_4H_9$	brown—green	1.976	1.976
$-CH_2C(CH_3)_3$ [c]	green	1.982	— [d]

[a] Singlets; line widths about 5 G. [b] In ether solution [1]. [c] Prepared according to ref. 11. [d] Stable at 20°C.

in toluene, is $-C_2H_5 < -CH_3 < -n\text{-}C_4H_9 < -s\text{-}C_4H_9 < -t\text{-}C_4H_9$ (the decomposition temperatures range from about —80°C to —30°C). In the decomposition RH is formed almost exclusively (for R = $-CH_3$: 0.93 mol CH_4/mol Ti) and a dark brown, moderately soluble product is formed. The latter is probably a mixture of compounds with mainly C_5H_4 bridged or fulvalene type structures, since in reaction with HCl in ether up to 60% of purple $[(Cp)_2C_{10}H_8Ti_2Cl_2]$ is formed [3]. As only traces of alkenes (<1%; GC) are formed and no coupling products RR, decomposition processes such as β-hydrogen elimination or homolysis are unlikely. Studies with deuterated Cp_2TiCH_3 show that the exclusive decomposition process is apparently intermolecular hydrogen abstraction by the alkyl group from the cyclopentadienyl ligands [1].

The formation and decomposition of the paramagnetic compounds Cp_2TiR can be followed by EPR spectroscopy (Table 1, Fig. 1). The EPR spectra of the compounds in toluene at —80°C show the singlets expected for Cp_2TiR with $g = 1.976$—1.987 (Table 1). This indicates that in toluene the compounds are, at least partly, monomeric, since dimers are expected to be EPR inactive because of Ti—Ti interaction. On warming to 20°C the original singlet signal decays rapidly and a new singlet signal ($g = 1.976$—1.981) appears, which is ascribed to (some of) the decomposition products (Table 1). Figure 1 shows the EPR spectrum of $Cp_2TiC_2H_5$ in toluene on warming from —80°C to 20°C. Addition of diethyl ether to toluene solutions of Cp_2TiR shifts the singlets to somewhat different g values. This indicates that the compounds form adducts $Cp_2TiR \cdot$ ether, as found previously for Cp_2TiCH_3 [1]. Similarly, addition of THF results in the formation of $Cp_2TiR \cdot THF$. For the THF adduct with R = $-CH_3$ and $-C_2H_5$ a quartet signal at $g = 1.981$ ($a = 4.4$ G) and a triplet signal at $g = 1.981$ ($a = 2.0$ G), respectively, are observed, due to interaction of the unpaired electron on Ti with α-hydrogens of the alkyl group. This is not observed for the other compounds Cp_2Tialkyl, which give singlets in THF.

A detailed characterisation of Cp_2TiR (by UV-vis, elemental analyses etc.) for the methyl derivative was reported before [1].

In the reactions of Cp_2Tialkyl with 2,6-xylylisocyanide, phenylisocyanate, CO_2 and ketones as described below solutions of Cp_2Tialkyl prepared "in situ" were used.

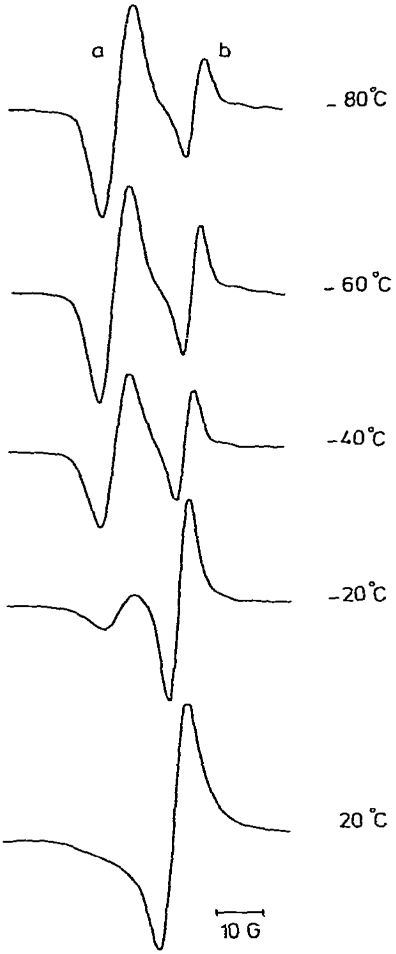
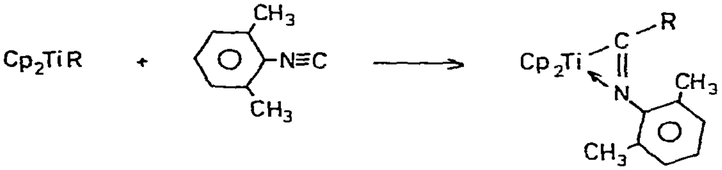


Fig. 1. EPR spectrum of $Cp_2TiC_2H_5$ (a; $g = 1.987$) in toluene on warming to 20°C: thermal decomposition (b; decomposition product $g = 1.977$); DPPH external reference.

Reactions with 2,6-xylylisocyanide

In reaction of Cp_2TiR (R = $-CH_3$, $-C_2H_5$, $-n\text{-}C_4H_9$, $-s\text{-}C_4H_9$, $-t\text{-}C_4H_9$) with 2,6-xylylisocyanide an insertion of the isocyanide ligand into the Ti—C bond is observed with formation of η^2-iminoacyl compounds $Cp_2TiC(R)=N\text{-}2,6\text{-}(CH_3)_2\text{-}C_6H_3$ (Scheme 1).



SCHEME 1

This reaction is similar to the insertion of isocyanides into the Ti—C bond of Cp_2Tiaryl complexes [4]. The red-brown, thermally stable compounds, ob-

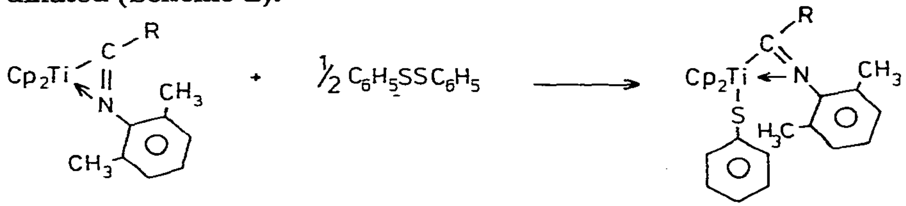
TABLE 2

ANALYTICAL AND PHYSICAL DATA FOR $Cp_2TiC(R)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$

R	Yield (%)	EPR [c] (g-value)	Analysis (found (calcd.) (%))			IR [d] ν(CN) (cm^{-1})
			C	H	Ti	
$-CH_3$ [a,b]	10	1.987	73.59 (74.07)	7.14 (6.83)	13.77 (14.77)	1578
$-C_2H_5$	25	—	73.72 (74.55)	7.54 (7.15)	14.20 (14.16)	1570
$-s\text{-}C_4H_9$	30	1.987	74.57 (75.40)	7.76 (7.70)	12.83 (13.07)	1572
$-t\text{-}C_4H_9$	35	1.988	73.85 (75.40)	7.85 (7.70)	12.49 (13.07)	1578

[a] Molecular weight (cryoscopically in benzene): found 304 (calcd. 324). [b] Melting point 88°C; decomposition temperature 142°C. [c] Ether, 30°C; DPPH external reference; all signals are singlets with line widths of about 4 G. [d] KBr; Nujol.

tained in yields of 10—35%, were characterized by elemental analyses (Table 2), IR (Table 2), and molecular weight determination (monomeric, Table 2). The EPR spectra of these Ti^{III} compounds show singlets with $g = 1.987$—1.988 (Table 2). The IR spectra show, in addition to the characteristic $\eta^5\text{-}C_5H_5$ and aryl absorptions, ν(CN) at 1572—1578 cm^{-1} (Table 2; ν(CN) for 2,6-xylylisocyanide 2115 cm^{-1}) which is comparable to ν(CN) at 1573 cm^{-1} of the phenyl analogue $Cp_2TiC(C_6H_5)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$, a value that was ascribed to η^2-coordination of the ligand [4]. As a typical example Fig. 2 shows the IR spectrum of $Cp_2TiC(CH_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$. These compounds of trivalent Ti can easily be oxidized by $C_6H_5SSC_6H_5$ (and I_2 [1]) to tetravalent Ti compounds $Cp_2Ti(SC_6H_5)C(R)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$ in which the iminoacyl ligand is still η^2-coordinated (Scheme 2).



SCHEME 2

The yellow diamagnetic compounds, obtained in yields of 70—85% were char-

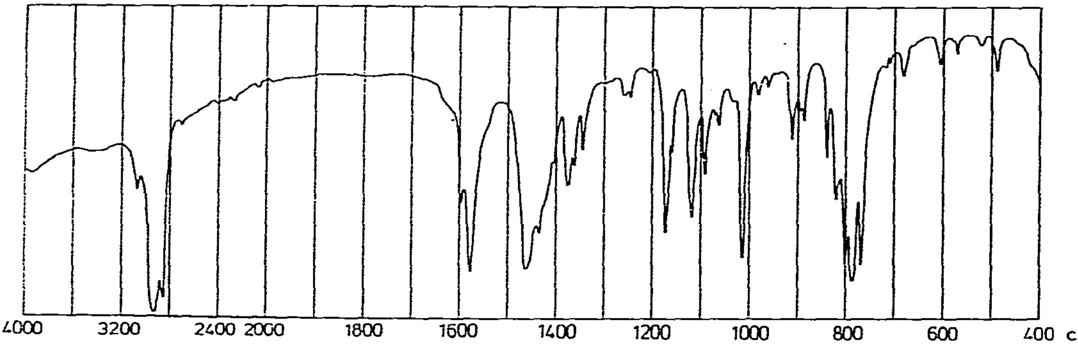
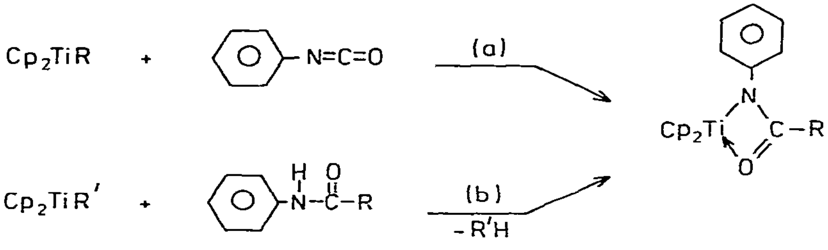


Fig. 2. IR spectrum of $Cp_2TiC(CH_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$ (KBr, Nujol).

acterized by IR (Table 3) and ^{1}H NMR (Table 3). The IR spectra show ν(CN) in the range 1654—1675 cm^{-1} which is comparable to the analogue with R = C_6H_5 [4]. The ^{1}H NMR spectra (Table 3) show singlets for the Cp ligands at δ 5.58—5.70 ppm. All resonances are in agreement with the proposed structure.

Reactions with phenylisocyanate

On reaction of Cp_2TiR (R = —CH_3, —n-C_4H_9) with phenylisocyanate, insertion of the ligand into the Ti—C bond is observed with formation of the amido derivatives $Cp_2TiN(C_6H_5)C(O)R$ according to Scheme 3 (reaction (a)).



SCHEME 3

The blue, thermally stable compounds, obtained in yields of 50—75%, were characterized by elemental analyses (Table 4), IR (Table 4) and molecular weight determinations (monomeric, Table 4). The EPR spectra of these trivalent Ti compounds show a singlet at g = 1.981 (Table 4). The IR spectra (Table 4) show, in addition to the characteristic η^5-C_5H_5 and phenyl absorptions, an absorption around 1550 cm^{-1} assigned to ν(CO, coordinated) (absorptions around 1650 cm^{-1} which would be expected for uncoordinated $\gt$C=O are absent). Similar values for ν(CO) were found for the corresponding amido derivatives obtained from $Ti[N(CH_3)_2]_4$ and C_6H_5NCO [5]. As an example, Fig. 3 shows the IR spectrum of $Cp_2TiN(C_6H_5)C(O)CH_3$.

The products obtained according to Scheme 3 (reaction (a)) can be also prepared from Cp_2TiR' and amides $C_6H_5NHC(O)R$ with elimination of R'H (Scheme 3; reaction (b)). For R = R' = —CH_3 the product is isolated in 45% yield. The amido derivatives can be easily hydrolysed with formation of the corresponding amides $C_6H_5NHC(O)R$ (for R = —CH_3 80% of acetanilide C_6H_5-$NHC(O)CH_3$, characterized by ^{1}H NMR, IR and mass spectrometry).

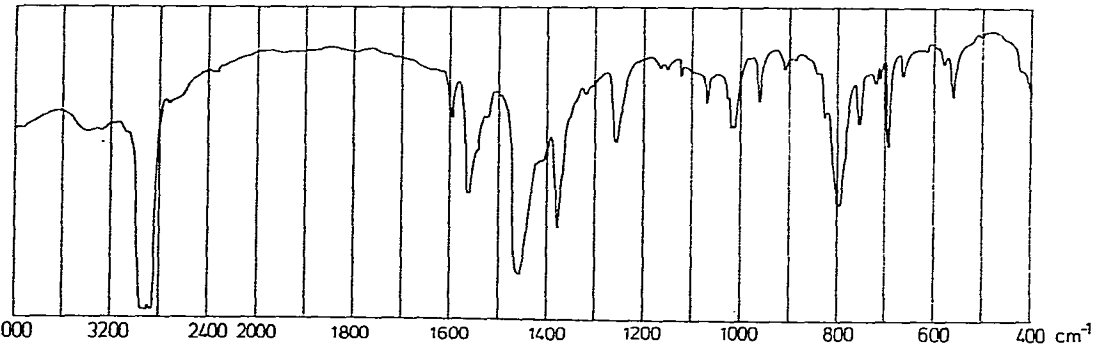


Fig. 3. IR spectrum of $Cp_2TiN(C_6H_5)C(O)CH_3$ (KBr, Nujol).

TABLE 3

SPECTROSCOPIC DATA FOR $Cp_2Ti(SC_6H_5)C(R)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$

R	Yield (%)	^1H NMR [d]				IR [e]
		δ(Cp) (ppm)	δ(CH_3) (ppm)	δ(aryl) (ppm)	δ(R) (ppm)	ν(CN) (cm^{-1})
$-CH_3$ [a,b]	70	5.58 (s, 10)	2.09 (s, 6)	6.8—7.2 (m, 8)	δ(CH_3) 2.44 (s, 3)	1662
$-C_2H_5$	75	5.62 (s, 10)	2.09 (s, 6)	6.8—7.2 (m, 8)	δ(CH_2) 2.69 (q, 2) δ(CH_3) 1.32 (t, 3)	1662
$-n\text{-}C_4H_9$	85	5.66 (s, 10)	2.10 (s, 6)	6.8—7.2 (m, 8)	0.8—2.9 (m, 9)	1670
$-s\text{-}C_4H_9$	85	5.63 (s, 10)	2.10 (s, 6)	6.8—7.2 (m, 8)	0.7—1.4 (m, 9)	1675
$-t\text{-}C_4H_9$ [c]	80	5.70 (s, 10)	2.02 (s, 6)	6.8—7.2 (m, 8)	δ(CH_3) 1.28 (s, 9)	1654

[a] Elemental analysis found: C, 71.85; H, 6.48; Ti, 11.13. $C_{26}H_{27}NSTi$ calcd.: C, 72.04; H, 6.28; Ti, 11.05%. [b] ^{13}C NMR; see ref. 1. [c] Elemental analysis found: C, 72.63; H, 6.96; Ti, 11.00. $C_{29}H_{33}NSTi$ calcd.: C, 73.25; H, 6.99; Ti, 10.07%. [d] $CDCl_3$, TMS, 35°C. [e] KBr, Nujol.

TABLE 4

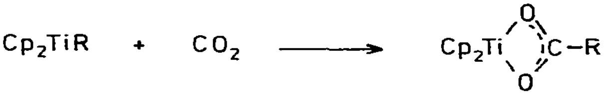
ANALYTICAL AND PHYSICAL DATA FOR $Cp_2TiN(C_6H_5)C(O)R$

R	Yield (%)	EPR [a] (g-value)	Mol. weight [b] found (calcd.)	Melting point (°C)	Decomposition temperature (°C)	Analysis (found (calcd.) (%))			IR [e]
						C	H	Ti	ν(CO) (cm^{-1})
$-CH_3$	75	1.981	277 (312)	94 [c]	150 [c]	68.83 (69.24)	5.99 (5.81)	15.24 (15.34)	1560
$-n\text{-}C_4H_9$	50	1.981	—	11—13 [d]	—	—	—	—	1533

[a] Ether, 30°C, DPPH external reference; both signals are singlets with line widths of about 4 G. [b] Cryoscopically in benzene. [c] From DTA measurements. [d] Determined visually. [e] KBr, Nujol.

Reactions with carbon dioxide

On reaction of Cp_2TiR ($R = —CH_3$, $—t\text{-}C_4H_9$) with CO_2 carboxylato-type insertion products $Cp_2TiOOCR$ are formed according to Scheme 4.



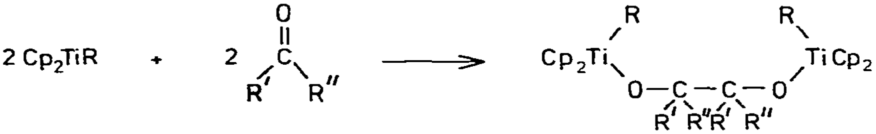
SCHEME 4

The blue compounds, isolated in yields of 40% ($R = —t\text{-}C_4H_9$) to 65% ($R = —CH_3$) are identical with those obtained by reaction of Cp_2TiCl with $RCOONa$ [6]. The compounds prepared according to Scheme 4 were characterized by comparing their physical properties with those of authentic samples prepared according to ref. [6].

Hydrolysis of the carboxylato derivatives yields the corresponding carboxylic acids $RCOOH$ (for $R = —t\text{-}C_4H_9$ 85% of trimethyl acetic acid, identified by ^1H NMR, IR and mass spectrometry).

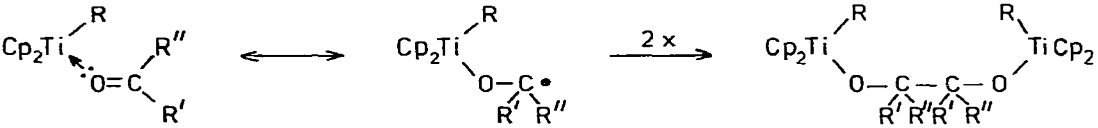
Reactions with ketones

Reaction of Cp_2TiR ($R = —CH_3, —C_2H_5, —n\text{-}C_4H_9, —s\text{-}C_4H_9, —t\text{-}C_4H_9$) with ketones $R'R''C{=}O$ ($R', R'' = —CH_3, —CH_3$); ($R', R'' = —CH_3, —C_2H_5$) results in a dimerisation with formation of $[Cp_2Ti(R)OC(R'R'')]_2$, according to Scheme 5.



SCHEME 5

This pinacol-type dimerisation, which is also known in the chemistry of $CpTiCl_2$ [7], strongly resembles the dimerisation of cyanides by compounds Cp_2Ti-aryl [8]. By analogy to that reaction we assume that the unpaired electron on Ti in Cp_2Tialkyl is transferred to the ketone ligand by back-donation from Ti to the antibonding π orbital of the ligand which induces some radical character at the ketone carbon atom. Coupling of two of these radicals gives the observed dimerisation product (Scheme 6).



SCHEME 6

The coupling reaction proceeds most readily for Cp_2TiR and $R'R''C{=}O$ with small R, R', R'': it takes place at —80°C for Cp_2TiCH_3 and acetone; at —30°C for $Cp_2Ti(t\text{-}C_4H_9)$ and acetone; at —30°C for Cp_2TiCH_3 and methyl ethyl ketone and it does not proceed at all with methyl tert-butyl ketone. Obviously back-donation and, therefore the dimerisation, is less effective in adducts $Cp_2TiR \cdot O{=}CR'R''$ with bulky groups R, R' and R''. This suggests that the orientation of the ketone ligand in the adduct stage, which, especially for bulky ketones, is more or less fixed by the Cp ligands, determines its π-acceptor

TABLE 5

ANALYTICAL AND PHYSICAL DATA FOR $[Cp_2Ti(R)OC(R'R'')]_2$

R	R′	R″	Yield (%)	Mass spectrum [a] M^+ (*m/e*)	Decomposition [b] temperature (°C)	Analysis (found (calcd.) (%))		
						C	H	Ti
$-CH_3$	$-CH_3$	$-CH_3$	35	502	98	66.27 (66.94)	7.75 (7.62)	18.84 (19.07)
$-n\text{-}C_4H_9$	$-CH_3$	$-CH_3$	60	—	107	69.48 (69.62)	8.85 (8.59)	16.19 (16.33)
$-s\text{-}C_4H_9$	$-CH_3$	$-CH_3$	15	586	125	68.56 (69.62)	8.42 (8.59)	16.50 (16.33)
$-CH_3$	$-CH_3$	$-C_2H_5$	15	—	—	68.07 (67.93)	8.05 (7.98)	—

[a] 100° C. [b] From DTA measurements.

TABLE 6

^1H NMR data for $[Cp_2Ti(R)OC(R'R'')]_2$

R	R′	R″	^1H NMR [a]			
			δ(Cp) (ppm)	δ(R) (ppm)	δ(R′) (ppm)	δ(R″) (ppm)
$-CH_3$	$-CH_3$	$-CH_3$	5.67 (s, 20)	0.83 (s, 6)	1.12 (s, 6)	1.12 (s, 6)
$-C_2H_5$	$-CH_3$	$-CH_3$	5.71 (s, 20)	1.42–1.72 (m, 10)	1.12 (s, 6)	1.12 (s, 6)
$-n\text{-}C_4H_9$	$-CH_3$	$-CH_3$	5.70 (s, 20)	0.80–1.90 (m, 18)	1.12 (s, 6)	1.12 (s, 6)
$-s\text{-}C_4H_9$	$-CH_3$	$-CH_3$	5.75 (s, 20)	0.73–1.90 (m, 18)	1.16 (s, 6)	1.16 (s, 6)
$-t\text{-}C_4H_9$	$-CH_3$	$-CH_3$	5.73 (s, 20)	1.68 (s, 6), 1.63 (s, 6), 1.07 (s, 6) [b]	1.11 (s, 6)	1.11 (s, 6)
$-CH_3$	$-CH_3$	$-C_2H_5$	5.62 (s, 20)	0.76 (s, 6)		[c]

[a] C_6D_6, TMS, 35° C. [b] No coalescence up to 85° C. [c] This part of the spectrum is not well resolved.

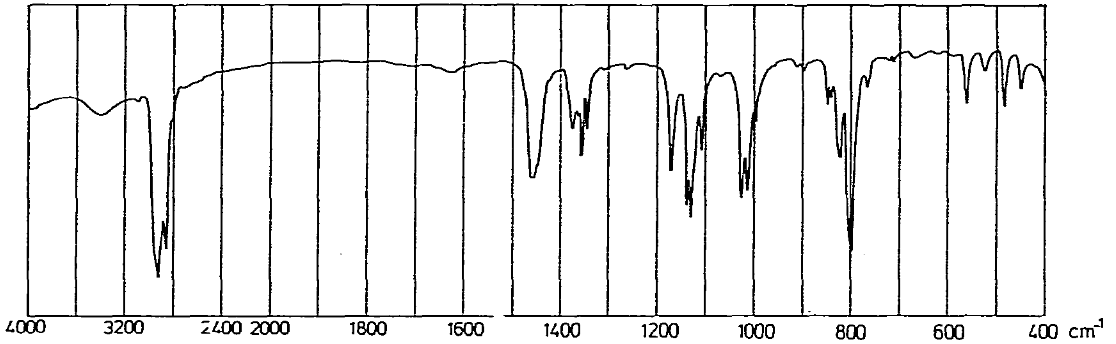


Fig. 4. IR spectrum of $[Cp_2Ti(s\text{-}C_4H_9)OC(CH_3)_2]_2$ (KBr, Nujol).

properties. More detailed studies of this aspect are in progress.

The yellow dimeric products prepared according to Scheme 5 are isolated in yields of 15—60% (Table 5). They are diamagnetic and characterized by elemental analyses (Table 5), IR, mass spectrometry (Table 5) and ^1H NMR (Table 6). The compounds are thermally quite stable and decompose without melting around 110°C (Table 5). The IR spectra all show, in addition to the characteristic η^5-C_5H_5 absorptions around 800 cm^{-1} and 1010 cm^{-1}, very characteristic absorptions in the range 1120—1170 cm^{-1} associated with C—O—Ti frequencies [7]. As an example, Fig. 4 shows the IR spectrum of $[Cp_2Ti(s\text{-}C_4H_9)\text{-}OC(CH_3)_2]_2$. The mass spectra (Table 5) are in agreement with the proposed structure. They show low-intensity M^+ peaks but very abundant $[M - 2\ R]^+$ peaks (R = alkyl).

The ^1H NMR spectra of the compounds (Table 6), which show the Cp resonances around δ 5.70 ppm, are in agreement with the proposed structure. The tert-butyl group in the spectrum of $[Cp_2Ti(t\text{-}C_4H_9)OC(CH_3)_2]_2$ gives rise to three NMR singlets (at δ 1.68, 1.63 and 1.07 ppm), which indicates a hindered rotation of the tert-butyl group in this compound.

Experimental

All experiments were carried out under argon unless otherwise stated. Solvents were distilled from benzophenoneketylsodium under nitrogen. Commercially available CH_3Li (in ether), n-C_4H_9Li (in hexane) and t-C_4H_9Li (in hexane) were used; C_2H_5Li and s-C_4H_9Li were prepared in pentane according to ref. 9. Phenylisocyanate and ketones were distilled before use and stored under Ar; CO_2 was purchased from Gardner Cryogenics. 2,6-Xylylisocyanide was prepared according to ref. 10. Elemental analyses were performed in the Microanalytical Department of this University under supervision of Mr. A.F. Hamminga. IR spectra were measured on a JASCO-IRA-2 spectrophotometer (KBr/Nujol), ^1H NMR spectra on a Perkin-Elmer R-24B spectrometer and on a Varian XL-100 spectrometer. The EPR spectra were recorded on a Varian E3X-band EPR spectrometer. Melting points and decomposition temperatures of solids were determined by differential thermal analysis (heating rate 1.5°C/min). Mass spectra were taken by Mr. A. Kiewiet on an AEI-MS902 spectrometer using an ionizing voltage of 70 eV. GC experiments were performed on a Hewlett-Packard 428 GLC apparatus on a Porapak Q column at 100° C.

Preparation of Cp_2TiR

To a suspension of 1.00 g of Cp_2TiCl_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 one hour the resulting green suspension of Cp_2TiCl * was cooled to —78° C and 4.0 mmol of RLi in ether, pentane or hexane were added in 15 minutes. After 30 minutes at —78° C the reaction was complete, and green to brown coloured solutions of Cp_2TiR had formed. This solution was filtered at —78° C and then used in the experiments described below. In the thermal decomposition studies the solutions were warmed to room temperature and the gas and liquid phases were analysed by GC.

Preparation of $Cp_2TiC(CH_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$

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 allowed to warm slowly to room temperature (two hours) and subsequently stirred for 15 hours. The resulting brown-purple solution was evaporated to dryness and extracted with 20 ml of n-pentane. Cooling of the n-pentane extract to —78° C gave a purple oil. The red-brown mother liquor was decanted, concentrated to about the half of the original volume and cooled to —78° C to give red-brown crystals of $Cp_2TiC(CH_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$ (0.40 mmol; 10%). The product is very air-sensitive and readily soluble in the common organic solvents. The other $Cp_2TiC(R)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$ compounds were prepared in the same way.

Preparation of $Cp_2Ti(SC_6H_5)C(CH_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$

To a solution of 0.70 mmol of $Cp_2TiC(CH_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$ 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 (two hours) a yellow precipitate of $Cp_2Ti(SC_6H_5)C(CH_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$ formed. After several washings with n-pentane, 0.49 mmol (70%) of the crude product was isolated. The compound can be purified by recrystallization from ether. It is moderately air-sensitive, insoluble in aliphatic hydrocarbons but soluble in ether, THF and benzene. The other $Cp_2Ti(SC_6H_5)C(R)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$ compounds were prepared in the same way.

Preparation of $Cp_2TiOOCCH_3$

A solution of 4.00 mmol of Cp_2TiCH_3 in 30 ml of toluene at —78° C was connected to a gas burette filled with CO_2. The take-up of CO_2 started immediately and was complete after 30 minutes. The resulting blueish-green solution was warmed to room temperature (two hours), evaporated to dryness and extracted with 50 ml of n-pentane. On cooling the n-pentane extract to —78° C blue crystals of $Cp_2TiOOCCH_3$ separated (2.60 mmol; 65%). The product is

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* Pure Cp_2TiCl in toluene can also be used.

very air-sensitive and readily soluble in the common organic solvents. The other $Cp_2TiOOCR$ compounds were prepared in the same way.

Preparation of $Cp_2TiN(C_6H_5)C(O)CH_3$

a. From Cp_2TiCH_3 *and phenylisocyanate.* To a solution of 4.00 mmol of Cp_2TiCH_3 in 30 ml of ether at —78° C 4.00 mmol of phenylisocyanate were added. The blue mixture was warmed to room temperature (two hours), evaporated to dryness and extracted with 40 ml of n-pentane. On cooling the n-pentane extract to —78° C light blue crystals of $Cp_2TiN(C_6H_5)C(O)CH_3$ separated (3.00 mmol; 75%). The product is very air-sensitive and readily soluble in the common organic solvents. The other $Cp_2TiN(C_6H_5)C(O)R$ compounds were prepared in the same way.

b. From Cp_2TiCH_3 *and acetanilide.* To a solution of 4.00 mmol of Cp_2TiCH_3 in 30 ml of ether at —78° C 4.00 mmol of acetanilide were added. The brown mixture was warmed to room temperature (two hours) upon which the colour changed to blue and methane was evolved (from about 0° C; GC). After subsequent stirring for one hour at room temperature the mixture was evaporated to dryness and extracted with 40 ml of n-pentane. On cooling the n-pentane extract to —78° C light blue crystals of $Cp_2TiN(C_6H_5)C(O)CH_3$ separated (1.80 mmol; 45%).

Preparation of $[Cp_2Ti(CH_3)OC(CH_3)_2]_2$

To a solution of 4.00 mmol of Cp_2TiCH_3 in 30 ml of ether at —78° C 4.00 mmol of acetone were added. A yellow precipitate of $[Cp_2Ti(CH_3)OC(CH_3)_2]_2$ formed immediately. After warming to room temperature (two hours) the crude product was isolated and extracted with 150 ml of ether. On cooling the ether extract to —78° C yellow crystals of $[Cp_2Ti(CH_3)OC(CH_3)_2]_2$ separated (0.70 mmol; 35%). The product is somewhat air-sensitive, insoluble in aliphatic hydrocarbons, moderately soluble in ethers and readily soluble in aromatic solvents. The other $[Cp_2Ti(R)OC(R'R'')]_2$ compounds were prepared in the same way.

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