

MONOALKYL- AND MONOARYL-AMIDOTITANIUM COMPLEXES

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Summary

A series of new monoalkyl- and monoaryl-amido complexes, $\text{CpTiCl}_2\text{NHR}$ ($\text{R} = \text{Et, i-Pr, t-Bu, Ph}$), has been synthesized and characterized. They were made in essentially quantitative yields by a very convenient reaction of CpTiCl_3 with Me_3SiNHR . The new complexes yield NMR and IR spectroscopic data for monoalkylamido complexes, such data being previously scarce. The compounds have very reactive amido hydrogen atoms, as is demonstrated by their thermal decomposition and their reaction with (Lewis) bases such as amines or organoalkali compounds. The products are the new bridged imido complexes, $(\text{CpTiCl})_2(\mu\text{-NR})_2$.

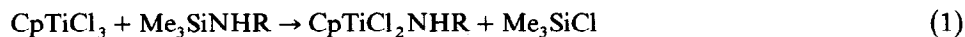
Introduction

In contrast to dialkyl- and diaryl-amido complexes [1], monoalkyl- and monoaryl-amido compounds, M-NHR , have been little mentioned in the literature. Their number has increased during the last few years, however, and complexes of Hf, Ta, Mo, W, Re and Ni are known [2]. Some investigations on titanium complexes have been carried out; early attempts to prepare $\text{CpTiCl}_2\text{NH}_2$ and $\text{CpTiCl}_2\text{NHMe}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) were unsuccessful [3], but the related dicyclopentadienyl compounds $\text{Cp}_2\text{TiClNHR}$ ($\text{R} = \text{Et, Ph, C}_6\text{H}_4\text{NO}_2$) and $\text{Cp}_2\text{Ti}(\text{NHR})_2$ ($\text{R} = \text{Ph, C}_6\text{H}_4\text{NO}_2$) have been reported, though they were poorly characterized [4]. In this paper the syntheses and spectroscopic properties of the series $\text{CpTiCl}_2\text{NHR}$ ($\text{R} = \text{Et, i-Pr, t-Bu, Ph}$) are described, and the reactivity of the hydrogen atom in the amido ligand is considered.

Results and discussion

Synthesis

Reaction of CpTiCl_3 with silylamines Me_3SiNHR ($\text{R} = \text{Et, i-Pr, t-Bu, Ph}$) gives the amido complexes $\text{CpTiCl}_2\text{NHR}$ (eq. 1).



Replacement of only one chlorine atom per titanium is observed in all cases even if a large excess of amine is used. The reaction rates seem to depend on the size of R, since the *t*-butyl and phenyl derivatives are formed most slowly. With R = Ph the reaction can be accelerated to an acceptable rate by using a large excess of amine. The yields are virtually quantitative (Table 1). For $\text{CpTiCl}_2\text{NH-t-Bu}$ the product still contains some CpTiCl_3 (< 10%) even after stirring of the reaction mixture with excess of amine for 3 d.

$\text{CpTiCl}_2\text{NHMe}$ could not be made by this route; complex mixtures of presumably dimeric or polymeric amido compounds were formed, and these were not studied further.

Spectroscopic properties

The mass spectra of all the compounds show similar fragmentation patterns. The absence of the molecular ion peak in the spectra of the alkylamides is striking; instead peaks with mass $M^+ - 15$ are found. High resolution mass measurements proved that the missing fragment is a methyl group and not NH. This observation is in keeping with the well-known α -cleavage of α -substituted primary organic amines [5]. The α -cleavage occurs because of the high stability of the imminium ion which is formed (eq. 2). In the case of $\text{CpTiCl}_2\text{NHPH}$ elimination of a methyl group is impossible, and the molecular ion peak is observed. Common fragments in all the mass spectra are: $m/e = 36$ (HCl^+), 65 (Cp^+), 66 (CpH^+), 83 (TiCl^+), 113 (CpTi^+), 118 (TiCl_2^+), 148 (CpTiCl^+), 153 (TiCl_3^+), 183 (CpTiCl_2^+) and 218 (CpTiCl_3^+).



The IR spectra show the characteristic frequencies of the Cp groups at 3100, 1435, 1010–1020 and 825–830 cm^{-1} . The spectra give little information about the presence of the alkyl groups (Fig. 1a,b,c). In the spectrum of $\text{CpTiCl}_2\text{NHPH}$ (Fig. 1d) the characteristic phenyl group frequencies are found at the expected positions (1590, 1580, 1490, 755 and 680 cm^{-1}). The presence of the amido ligands is evident from the strong N–H stretching bands at 3300 cm^{-1} in all cases. The CN stretching vibration mode is found at 1190 and 1235 cm^{-1} for R = *t*-Bu and Ph, respectively;

TABLE 1
PHYSICAL AND ANALYTICAL DATA FOR $\text{CpTiCl}_2\text{NHR}$

R	Colour	Yield (%)	DTA (°C)	Elemental analysis (Found (calcd.) (%))				
				Ti	Cl	C	H	N
Et	yellow	94	82	20.77 (21.01)	30.98 (31.10)	36.51 (36.88)	4.95 (4.86)	6.65 (6.15)
<i>i</i> -Pr	yellow	99	139	19.96 (19.79)	29.14 (29.30)	39.78 (39.70)	5.43 (5.41)	5.84 (5.79)
<i>t</i> -Bu	orange	86	156	18.59 (18.71)	27.68 (27.69)	42.24 (42.22)	5.93 (5.91)	5.42 (5.47)
Ph	brown	95	116	17.27 (17.35)	25.73 (25.69)	48.01 (47.86)	4.10 (4.02)	5.11 (5.08)

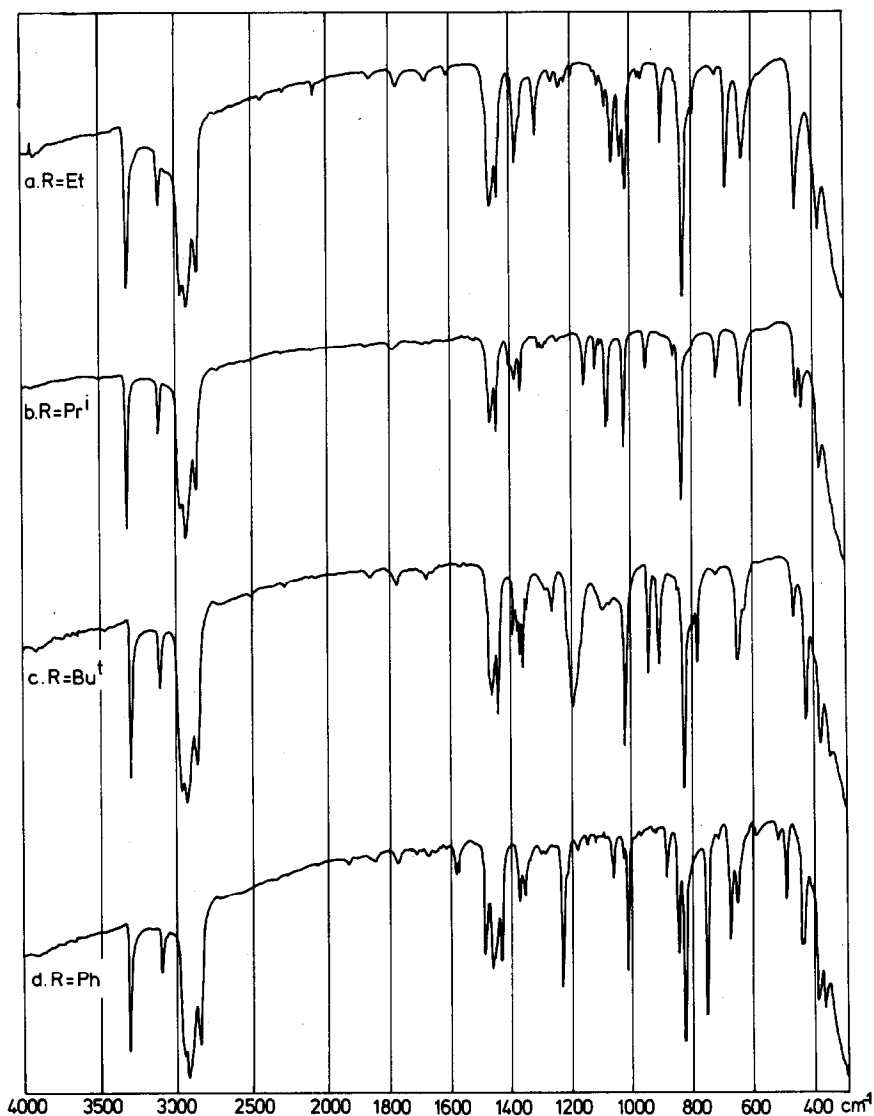


Fig. 1. IR spectra of $\text{CpTiCl}_2\text{NHR}$.

the corresponding bands positions in the spectra of the ethyl and *i*-propyl derivatives could not be clearly identified.

No Ti–N stretching vibrations of monoalkyl- or monoaryl-amido complexes have yet been assigned. A series of dialkylamido complexes, $\text{Ti}(\text{NR}_2)_n\text{X}_{4-n}$ (X = halogen, $n = 1-4$), however, has been investigated, and vibrational modes assigned [6]. These show $\nu(\text{Ti}-\text{N})$ vibrations in the range 570–616 ($\text{R} = \text{Me}$) and 600–622 cm^{-1} ($\text{R} = \text{Et}$), independent of the number of amido ligands n . By analogy we may expect the $\nu(\text{Ti}-\text{N})$ of the complexes $\text{CpTiCl}_2\text{NHR}$ in the range 500–700 cm^{-1} . The spectra are rather simple in this region, and so we tentatively assign $\nu(\text{Ti}-\text{N})$ as follows: 630 ($\text{R} = \text{Et}$ and *i*-Pr), 650 ($\text{R} = \text{t-Bu}$) and 655 cm^{-1} ($\text{R} = \text{Ph}$). The

frequencies show little dependence on R, especially for the ethyl and i-propyl derivatives. A similar effect was found for the compounds $\text{Ti}(\text{NEt}_2)\text{Cl}_3$ and $\text{Ti}(\text{N-i-Pr}_2)\text{Cl}_3$, which also show Ti-N stretching vibrations at essentially constant frequency (604 cm^{-1}).

The ^1H NMR spectra show single Cp resonances at positions which are almost independent of the group R on nitrogen if R = alkyl (Table 2). The chemical shifts are closer to those of the aryloxy complexes $\text{CpTiCl}_2\text{OAr}$ ($\delta(\text{Cp})$ 6.6–6.7 ppm) [7] than to that of CpTiCl_3 ($\delta(\text{Cp})$ 7.16 ppm), and it seems that the inductive effect of the amido ligand is comparable to that of an aryloxy group. The exceptional value for the phenyl complex indicates that the phenylamido ligand is electron-withdrawing with respect to the alkylamido ligands, which is consistent with the known electronic nature of the phenyl group. The H_α resonances of the ethyl and i-propyl groups are considerably shifted to low field compared to the corresponding free amines (EtNH_2 : $\delta(\text{H}_\alpha)$ 2.76 ppm; i-PrNH_2 : $\delta(\text{H}_\alpha)$ 3.05 ppm). The shielding effect of the nitrogen lone pair in sp^3 -hybridized amines is clearly substantially decreased in the amido complexes. As in most known structures of amido complexes, $\text{CpTiCl}_2\text{NHR}$ probably has an amido ligand of planar geometry with sp^2 -hybridized nitrogen and with the nitrogen lone pair involved in $p_\pi \rightarrow d_\pi$ interaction with the metal. The chemical shifts of the NH protons are found at very low field, comparable to organic carboxylic acid protons (δ 10–13 ppm). This indicates that the protons are rather acidic.

The ^{13}C NMR spectra show features similar to those in the ^1H NMR spectra. The Cp resonances lie upfield with respect to CpTiCl_3 ($\delta(\text{Cp})$ 122.6 ppm). Also the C_α resonances of the alkyl groups lie at lower field than those of the free amines (EtNH_2 : $\delta(\text{C}_\alpha)$ 36.5 ppm; i-PrNH_2 : $\delta(\text{C}_\alpha)$ 43.1 ppm; t-BuNH_2 : $\delta(\text{C}_\alpha)$ 47.9 ppm [8]), and this can again be attributed to the sp^2 -hybridization of nitrogen in the amido complex. The ^{13}C spectrum of $\text{CpTiCl}_2\text{NHPH}$ could not be obtained because of the instability of this complex in solution (vide infra). $\text{CpTiCl}_2\text{NHEt}$ also decomposed in solution, but at a slightly lower rate, so that the main ^{13}C resonances could be located.

Chemical and thermal stability

The amido complexes are very air sensitive. In moist air the amine hydrochloric

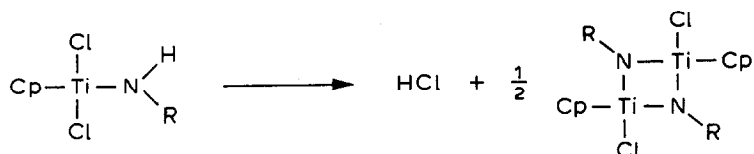
TABLE 2

NMR SPECTROSCOPIC DATA FOR $\text{CpTiCl}_2\text{NHR}^a$

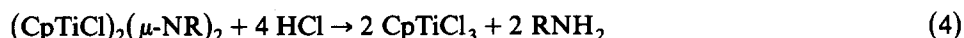
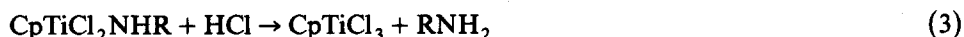
R	^1H NMR			^{13}C NMR	
	Cp	R	NH ^b	Cp	R
Et	6.75 (s, 5H)	4.38 (q, 2H) 1.15 (t, 3H)	10.0	117.9 (–)	51.8 (–) 16.6 (–)
i-Pr	6.75 (s, 5H)	5.38 (h, 1H) 1.18 (d, 6H)	9.7	117.7 (d, <i>J</i> 177)	56.9 (d, <i>J</i> 134) 23.4 (q, <i>J</i> 127)
t-Bu	6.77 (s, 5H)	1.49 (s, 9H)	10.7	118.3 (d, <i>J</i> 177)	64.1 (s) 31.4 (q, <i>J</i> 126)
Ph	6.93 (s, 5H)	6.7–7.5 (m, 5H)	11.9	–	–

^a In CD_2Cl_2 (room temperature); values given in $\delta(\text{ppm})$ relative to the solvent = 5.43 ppm (^1H NMR) and 53.61 ppm (^{13}C NMR). Multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet. *J*(CH) in Hz. ^b Broad singlets, dependent on concentration.

salt is formed as well as polymeric, oxygen-bridged CpTi compounds, which were not further characterized. In reaction with dry HCl/ether CpTiCl₃ and RNH₂ · HCl are formed. The presence of the acidic proton on nitrogen and the chloride ligands on titanium makes the complexes quite reactive. In several experiments it was shown that HCl is easily eliminated and that new binuclear imido complexes are formed [9].



This reaction occurs even in the solid state upon heating the complex in vacuum (R = Et, i-Pr, Ph). However, the hydrochloric acid thus formed reacts with starting material and the product, to cleave the Ti-N bonds, giving CpTiCl₃ and the free amine RNH₂ (eqs. 3 and 4).



Decomposition temperatures for the amido complexes were determined by Differential Thermal Analysis (DTA). Endothermic effects were observed in all cases (Table 1), and were shown in separate experiments to correspond to the elimination of hydrochloric acid (R = Et, i-Pr, Ph). The stability order was qualitatively established as t-Bu > i-Pr > Et, Ph.

The same reaction as in the solid state was observed in solution at room temperature (R = Et, Ph), and could be followed by NMR spectroscopy. Resonances at 7.16 and at 6.52 (R = Et) or 6.33 ppm (R = Ph), due to Cp ligands in CpTiCl₃ and in (CpTiCl)₂(μ-NR)₂, respectively, appeared immediately in the NMR spectra, while the Cp resonances of CpTiCl₂NHR at 6.75 (R = Et) and 6.93 ppm (R = Ph) decreased in intensity. The i-propyl derivative also decomposed, but much more slowly, and higher temperatures were required for complete decomposition.

The undesired side reaction of HCl with the amido and imido complexes (eqs. 3 and 4) can be avoided by adding a (Lewis) base to the solution. t-Butylamine is excellent in this respect and, when the reaction is carried out in CH₂Cl₂, t-BuNH₂ · HCl can be readily separated from the product.

The behaviour of the amido complex CpTiCl₂NH-t-Bu is anomalous. There is no elimination of HCl when the solid is heated in vacuum, instead the compound sublimes without decomposition. Similarly there is no elimination in solution, even in the presence of a moderately strong base. Imido formation could only be achieved with stronger Lewis bases, such as MeLi or PhNa, used at room temperature in ether or THF (Scheme 1). Two mechanisms are possible for these reactions: the first

SCHEME 1

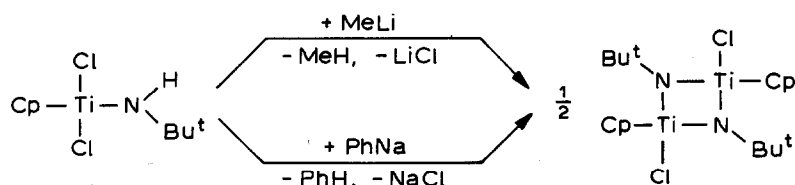


TABLE 3

AMOUNTS AND REACTION TIMES FOR SYNTHESIS OF $\text{CpTiCl}_2\text{NHR}$

R	CpTiCl_3 (mmol)	Me_3SiNHR (mmol)	Solvent (ml)	Reaction time
Et	18	18	Ether, 4	4 h
i-Pr	47	48	THF, 6	24 h
t-Bu	40	44	THF, 4	3 d
Ph	35	70	Ether, 5	3 d

reaction step may be replacement of Cl by Me or Ph, or substitution of the proton on nitrogen by Li or Na. In the case of MeLi it seems probable that methylation of titanium occurs first. The subsequent step, elimination of methane, involves a reaction of a type previously observed by Mayer et al. [10]; they found that reaction of $\text{Cp}^*\text{TaMe}_3\text{Cl}$ with LiNHR did not yield the expected amido complex $\text{Cp}^*\text{TaMe}_3\text{NHR}$, but instead the imido complex $\text{Cp}^*\text{TaMe}_2\text{NR}$. In the amido complex both a methyl ligand and a reactive proton would be present on nitrogen as in our case, and obviously, elimination of methane is very favourable.

Experimental

General

All experiments were carried out under purified nitrogen. Solvents were purified by distillation under nitrogen from sodium or from molten sodium-potassium alloy in the presence of a small amount of benzophenone. CH_2Cl_2 was dried over Molecular Sieve 4 Å.

Elemental analyses were performed by the Microanalytical Department of this University under the supervision of Mr. A.F. Hamminga. Mass spectra were recorded by Mr. A. Kiewiet on an AEI MS-902 instrument at an ionizing voltage of 70 eV. IR spectra were measured on a Pye Unicam SP3-300 spectrophotometer using Nujol mulls between KBr disks. ^1H and ^{13}C NMR spectra were recorded by Drs. R.J. Bouma at 200 and 50.3 MHz, respectively, on a Nicolet NT 200 spectrometer equipped with a Nicolet model 1180 data system.

Decomposition temperatures were determined with a low temperature DTA apparatus at a heating rate of $2\text{--}3^\circ\text{C min}^{-1}$. Thermal decomposition experiments were carried out with a Homef infrared heat source, type LB-03, equipped with a Philips IR lamp (220 V/375 W) and connected to a variable transformer. This method of heating has advantages over the commonly used oil bath because under vacuum conditions radiation is the most efficient heat transfer. A disadvantage can be that the temperature inside the vessel is difficult to measure and control. Therefore no temperatures are given for the experiments.

The starting materials Me_3SiNHR ($R = \text{Et, i-Pr, t-Bu, Ph}$) were prepared from the corresponding primary amines by reaction with Me_3SiCl [11].

Preparation of $\text{CpTiCl}_2\text{NHR}$ ($R = \text{Et, i-Pr, t-Bu, Ph}$)

The preparations of the amido complexes from CpTiCl_3 and Me_3SiNHR were carried out at room temperature in ether or THF. Because the thermal decomposition of the amido compounds was fast in THF and slower in ether, the ethyl and

phenyl derivatives were prepared in ether. The best results were obtained when very small amounts of solvent were used. The specific amounts and the reaction times are given in Table 3. The same procedure was followed in all cases. The preparation of $\text{CpTiCl}_2\text{NH-i-Pr}$ is given as an example. The products thus obtained were analytically pure, except for $\text{CpTiCl}_2\text{NH-t-Bu}$, which was recrystallized from THF.

Preparation of $\text{CpTiCl}_2\text{NH-i-Pr}$

CpTiCl_3 (10.3 g, 47 mmol) was suspended in 6 ml of THF and 48 mmol of $\text{Me}_3\text{SiNH-i-Pr}$ were added. The suspension was stirred for 24 h. Subsequently, the mother liquor was decanted off, and the solid $\text{CpTiCl}_2\text{NH-i-Pr}$ was washed with pentane until the washings were colourless then dried in vacuo. Yield 11.3 g (99%).

Thermal decomposition of $\text{CpTiCl}_2\text{NHR}$ in the solid state

The thermal decompositions of the amido complexes all proceed fairly similarly. The course of the reaction is demonstrated most clearly by thermolysis of $\text{CpTiCl}_2\text{NHPh}$, which is given as an example.

Finely powdered $\text{CpTiCl}_2\text{NHPh}$ (27.6 g, 100 mmol) was heated at 0.02 mmHg. Volatile products were collected in a cold trap (-196°C) and identified as aniline and the aniline hydrochloric salt (IR). A yellow, nicely crystalline product, which subsequently sublimed out was identified as CpTiCl_3 (IR). The remaining brown solid material was the imido complex $(\text{CpTiCl})_2(\mu\text{-NPh})_2$, which was later sublimed (0.001 mmHg). The yield of $(\text{CpTiCl})_2(\mu\text{-NPh})_2$ (35 mmol, 70%) indicates that HCl, which is eliminated during the thermolysis, only partly reacts with the Ti-N compounds (giving CpTiCl_3 and aniline) and partly condenses in the cold trap (giving $\text{PhNH}_2 \cdot \text{HCl}$).

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