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Synthesis of titanium(IV) (cyclopentadienylalkyl)aminate complexes

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Abstract

We describe the synthesis of hydrochlorides of [TiCp{$(C_5H_4(CH_2)_nNMe_2$}Cl_2] ($n = 2$ or 3) via [$TiCpCl_3$] and the lithiated (cyclopentadienylalky)lamine. The $-NHMe_2$ groups in these complexes are not coordinated to the titanium, and probably not in the parent amines either, the metal stereochemistry being the same in each group of compounds. The structure of [TiCp(η^5-$C_5H_4CH_2CH_2CH_2NHMe_2$)Cl_2]Cl is described in detail.

Keywords: Titanium; Cyclopentadienyl; Aminate complexes

1. Introduction

Our particular interest in the dimethylaminoethylcyclopentadienyl ligand, is as an extension of our work on (dialkylaminoethyl)aryl ligands [1] and (dialkylaminoethyl)ferrocenyl ligands [2], both of which potentiate vanadium(II) to dinitrogen uptake.

Several titanium complexes containing dialkylaminoethylferrocenyl have been reported. A titanium dichloride containing an unfunctionalised cyclopentadienyl ligand as well as a dimethylaminoethylcyclopentadienyl ligand was obtained [3,4] in the reaction of $Me_3Si(C_5H_4CH_2CH_2NMe_2)$ with [$TiCpCl_3$] and was characterised as its hydrochloride [TiCp($C_5H_4CH_2CH_2NHMe_2$)Cl_2]Cl [3]. [TiCp($C_5Me_4CH_2CH_2NMe_2$)Cl_2] has an uncoordinated NMe_2 group, whereas in the Ti^{III} analogue [TiCp($C_5Me_4CH_2CH_2NMe_2$)Cl], a chelating bonding mode for the cyclopentadienylaminate ligand was observed [5]. The synthesis of [TiCp($C_5H_4CH_2CH_2CH_2NMe_2$)Cl_2] was also described [6].

2. Results and discussion

In an attempt to prepare unsymmetrical ferrocenes analogous to the ferrocenylaminates described by us recently [2], the lithium salts of the (cyclopentadienylalkyl)amines $C_5H_5CH_2CH_2NMe_2$ and $C_5H_5CH_2CH_2CH_2NMe_2$ were employed with [Fe(C_5H_5)$(CO)_2$I]. We isolated no tractable products, although some likely ones are known [7]. Although the aryls and ferrocenyl analogues of these (cylopentadienylalkyl)amines, react with [$VCl_2(tmen)_2$] with uptake of dinitrogen, probably to form bridging dinitrogen complexes, during the reaction of [$VCl_2(tmen)_2$] with two equivalents of Li($C_5H_4CH_2CH_2NMe_2$) or Li($C_5H_4CH_2CH_2CH_2NMe_2$) no dinitrogen uptake was observed, and no products were characterised. However, we achieved success in the reactions with titanium compounds.

The reaction of [$TiCpCl_3$] with one equivalent of Li($C_5H_4CH_2CH_2NMe_2$) in toluene afforded the orange solid [TiCp(η^5-$C_5H_4CH_2CH_2NMe_2$)Cl_2] (**I**) which is extremely air- and moisture-sensitive. Complex **I** has been previously prepared from [$TiCpCl_3$] and $Me_3Si(C_5H_4CH_2CH_2NMe_2)$ in thf [6], but our synthesis is more straightforward. The complex **I** reacts with one equivalent of HCl dissolved in methanol with protonation of the amino group to give the air- and moisture-

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stable diamagnetic solid [TiCp(η^5-$\mathrm{C_5H_4CH_2CH_2NHMe_2}$)$\mathrm{Cl_2}$]Cl (**II**) [8]. Compound **II** is very soluble in polar solvents such as MeOH and only slightly soluble in chlorinated solvents such as $\mathrm{CH_2Cl_2}$ and $\mathrm{CHCl_3}$ and insoluble in non-polar solvents such as toluene.

In the IR spectrum of **II**, a broad strong band at 2560 $\mathrm{cm^{-1}}$ assigned to ν(N–H) was observed. Bands characteristic of the cyclopentadienyl rings were also observed, at 1016, 2960 and 3108 $\mathrm{cm^{-1}}$. The EI-MS data obtained for the hydrochloride **II** are consistent with the proposed formulation and ^{1}H- and ^{13}C{^{1}H}-NMR data, hitherto unrecorded, are presented in Table 1

Due to protonation, both the N$\mathit{CH_2}$ and the N$\mathit{CH_3}$ signals are shifted slightly more downfield than in the unprotonated species. The fact that the N$\mathit{CH_3}$ signal is not split into a doublet by the NH proton, and also that the signal due to the NH proton is not observed, is a consequence of an exchange process between the N*H* proton and the O*D* deuterium from the solvent. Thus, in $\mathrm{CDCl_3}$ rather than in methanol an additional broad singlet is observed at low field ($\delta = 12.66$ ppm) assigned to the protonated amino group, whereas the signal due to the N$\mathit{CH_3}$ protons is observed as a doublet ($J_{\mathrm{HN-CH}} = 4.6$ Hz).

Compound **II** can be reproducibly crystallised from $\mathrm{CH_2Cl_2}$–MeOH solutions at 0 °C as red plates. Preliminary X-ray crystallographic data showed the compound to have the expected tetrahedral structure with the $\mathrm{NMe_2}$ group not coordinated. Unfortunately, the *R* factor was too high ($R > 16\%$) for detailed presentation. For this reason, the structure of this compound will not be discussed in detail.

The reaction of [$\mathrm{TiCpCl_3}$] with one equivalent of Li($\mathrm{C_5H_4CH_2CH_2CH_2NMe_2}$) in toluene afforded the orange solid [TiCp(η^5-$\mathrm{C_5H_4CH_2CH_2CH_2NMe_2}$)$\mathrm{Cl_2}$] (**III**). This has been previously prepared by a reaction of [$\mathrm{TiCpCl_3}$] with $\mathrm{Me_3Si(C_5H_4CH_2CH_2CH_2NMe_2)}$ [6]. It is highly moisture sensitive and reacts with one equivalent of HCl dissolved in methanol with protonation of the amino group to give the air- and moisture-stable red diamagnetic solid [TiCp(η^5-$\mathrm{C_5H_4CH_2CH_2CH_2NHMe_2}$)$\mathrm{Cl_2}$]Cl (**IV**). This compound shows excellent solubility in polar solvents such as methanol and acetonitrile. Red crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a saturated methanolic solution.

Table 1
$\mathrm{H^1}$- and ^{13}C{^{1}H}-NMR data for [TiCp($\mathrm{C_5H_4CH_2CH_2NHMe_2}$)$\mathrm{Cl_2}$]Cl (**II**) in $\mathrm{CD_3OD}$ (in ppm, δ-scale, room temperature)

Proton or carbon	Chemical shifts	
	^{1}H-NMR	^{13}C{^{1}H}-NMR
$\mathrm{C_5H_4}\mathit{CH_2}$	3.25 (m, 2H)	26.8
N$\mathit{CH_3}$	2.93 (s, 6H)	43.7
N$\mathit{CH_2}$	3.52 (m, 2H)	57.9
$\mathit{C_5H_4}$	6.39 (m, 2H)	115.9
$\mathit{C_5H_5}$	6.66 (s, 5H)	121.8
$\mathit{C_5H_4}$	6.69 (m, 2H)	125.7
C_{ipso} of $\mathrm{C_5H_4}$	–	132.4

Mass spectroscopy (EI technique) data are consistent with the proposed formulation, as the molecular ion $\mathrm{M^+}$ (*m*/*z* 334) and many expected fragments were detected. In the IR spectrum, a broad strong band at 2627 $\mathrm{cm^{-1}}$ assigned to ν(N–H) was observed. ^{1}H- and ^{13}C{^{1}H}-NMR data obtained for **IV** are presented in Table 2. The assignments are straightforward.

A single-crystal X-ray diffraction study of **IV** established the expected monomeric bent-metallocene type structure (Fig. 1). The dimethylaminopropyl group is on the open side of the sandwich. Selected bond lengths and angles are included in Table 3. Two chlorine atoms together with the centroids of the cyclopentadienyl rings form a considerably distorted tetrahedral coordination geometry around the titanium with angles ranging from 92.83(6)° (Cl(1)–Ti–Cl(2)) to 131.6(2)° (M(2)–Ti–M(1)). These values are similar to those reported for [$\mathrm{TiCp_2Cl_2}$] [9], [Ti($\mathrm{C_5H_4CH_2CH_2NPr^i_2}$)$_2$$\mathrm{Cl_2}$] [1] and [Ti($\mathrm{C_5H_4SiMe_3}$)($\mathrm{C_5H_4CH_2CH_2NHPr^i_2}$)$\mathrm{Cl_2}$]Cl [8].

The Ti–Cl bond lengths are close to those reported for [$\mathrm{TiCp_2Cl_2}$] (2.364 Å) [9] and related compounds [5,8]. Furthermore, the Ti–M distances (‘M’ denotes the centroid of a Cp ring) are very similar in a range of complexes analogous to **IV** [7,8,10–12]. The different substitution pattern of the Cp rings do not significantly affect the basic molecular structure.

The N–H separation is 0.930 Å, not very different from that found in [Ti($\mathrm{C_5H_4SiMe_3}$)($\mathrm{C_5H_4CH_2CH_2NHPr^i_2}$)$\mathrm{Cl_2}$]Cl [8]. There are MeOH solvate molecules in the crystal lattice of **IV**. Hydrogen bonds N–H···Cl (2.146 Å) and O–H···Cl (2.341 Å) are present, involving all the active hydrogen atoms. Complex **IV** loses solvent of crystallisation upon drying.

Table 2
$\mathrm{H^1}$- and ^{13}C{^{1}H}-NMR data for [TiCp($\mathrm{C_5H_4CH_2CH_2CH_2NHMe_2}$)$\mathrm{Cl_2}$]Cl (**IV**) in $\mathrm{CD_3OD}$ (in ppm, δ-scale, room temperature)

Proton or carbon	Chemical shifts	
	^{1}H-NMR	^{13}C{^{1}H}-NMR
$\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2}$	2.24 (m, 2H)	25.3
$\mathrm{C_5H_4}\mathit{CH_2}$	3.01 (m, in block of 8H)	28.2
N$\mathit{CH_3}$	3.03 (s, in block of 8H)	43.6
N$\mathit{CH_2}$	3.46 (m, 2H)	58.4
$\mathit{C_5H_4}$	6.42 (m, 2H)	117.1
$\mathit{C_5H_5}$	6.69 (s, in block of 7H)	121.2
$\mathit{C_5H_4}$	6.71 (m, in block of 7H)	124.1
C_{ipso} of $\mathrm{C_5H_4}$	–	137.4

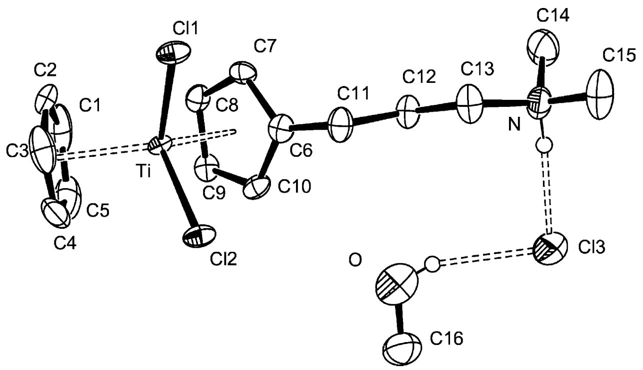

Fig. 1. The molecular structure of $[TiCp(C_5H_4CH_2CH_2CH_2NHMe_2)Cl_2]Cl\cdot MeOH$ (**IV**), showing the numbering scheme.

Table 3
Selected interatomic distances and bond angles for $[TiCp(C_5H_4CH_2CH_2CH_2NHMe_2)Cl_2]Cl\cdot MeOH$ (**IV**)

Bond lengths			
Ti–M(2) [a]	2.056(5)	Ti–Cl(1)	2.365(15)
Ti–M(1) [a]	2.058(5)	Ti–C(3)	2.368(5)
Ti–C(8)	2.332(5)	Ti–C(4)	2.383(6)
Ti–C(9)	2.338(4)	Ti–C(10)	2.393(5)
Ti–C(2)	2.351(5)	O–C(16)	1.341(9)
Ti–C(1)	2.358(5)	N–C(15)	1.484(7)
Ti–Cl(2)	2.360(4)	N–C(13)	1.484(6)
Ti–C(5)	2.364(6)	N–C(14)	1.490(7)
Bond angles			
M(2)–Ti–M(1) [a]	131.6(2)	C(13)–N–C(14)	112.9(4)
M(2)–Ti–Cl(2) [a]	106.1(2)	C(10)–C(6)–C(11)	126.9(4)
M(1)–Ti–Cl(2) [a]	107.2(2)	C(7)–C(6)–C(11)	126.4(4)
Cl(1)–Ti–Cl(2)	92.83(6)	C(6)–C(11)–C(12)	110.9(4)
C(15)–N–C(13)	110.7(4)	C(13)–C(12)–C(11)	108.9(4)
C(15)–N–C(14)	109.5(5)	N–C(13)–C(12)	114.8(4)

[a] M(1) and M(2) are the centroids of the C(1)-to-C(5) and C(6)-to-C(10) rings.

3. Conclusions

This short paper completes a series of studies on selected N,C-donors, namely ferrocenylaminates [2], (arylalkyl)aminates [1] and (cyclopentadienylalkyl)aminates These were all obtained by lithiation of the corresponding neutral compounds, and although lithiation always occurred at the 2-position of an aromatic ring the lithiation was rarely clean and poly-lithiation was always a problem. Nevertheless, we have shown that the first two classes of ligand form complexes with titanium(IV) in which the aminate is monodentate unless packing problems about the titanium are minimal. In addition, both ligand types potentiate vanadium(II) to dinitrogen uptake, probably bridging, though this needs to pursued further. However, the (cyclopentadienylalkyl) aminates of the present study do not potentiate vanadium(II) to dinitrogen uptake. The differences between the various aminates are worthy of a more thorough investigation.

In this final study the complexes $[TiCp(C_5H_4CH_2CH_2NHMe_2)Cl_2]Cl\cdot MeOH$ (**II**) and $[TiCp(C_5H_4CH_2CH_2CH_2NHMe_2)Cl_2]Cl\cdot MeOH$ (**IV**) were synthesised by a simplified route fully characterised. Complex **IV** was analysed by X-ray crystallography. Attempts to prepare mixed ferrocenes by reacting the Li salts $Li(C_5H_4CH_2CH_2NMe_2)$ or $Li(C_5H_4CH_2CH_2CH_2NMe_2)$ with $[Fe(C_5H_5)(CO)_2I]$ were not successful (Table 4).

4. Experimental

All operations were carried out under an inert atmosphere in an argon-filled drybox or with use of standard Schlenk techniques. Solvents were dried by standard procedures and distilled under N_2 prior to use [13]. $[TiCpCl_3]$ [14] and $[VCl_2(tmen)_2]$ [15] were prepared by literature methods. The compounds $C_5H_5CH_2CH_2NMe_2$ and $C_5H_5CH_2CH_2CH_2NMe_2$ were prepared according to literature methods [16,17]. They are colourless, light-sensitive liquids and are only briefly stable under ambient conditions. They were stored at low temperatures.

IR spectra were recorded on a Perkin–Elmer Spectrum One model FT-IR spectrometer, from Nujol mulls prepared under dinitrogen and spread on KBr plates. NMR spectra were obtained in the appropriate deuter-

Table 4
Crystallographic data for $[TiCp(C_5H_4CH_2CH_2CH_2NHMe_2)Cl_2]Cl\cdot MeOH$ (**IV**)

Formula	$C_{15}H_{22}Cl_3NTi\cdot CH_3OH$
M (g mol^{-1})	402.6
Crystal system	Monoclinic
Crystal size (mm^3)	0.40 × 0.40 × 0.05
Space group	$P2_1/c$ (no. 14)
Unit cell dimensions	
a (Å)	25.170(17)
b (Å)	6.600(10)
c (Å)	11.695(4)
β (°)	100.75(4)
V ($Å^3$)	1909(3)
Z	4
D_{calc} (g cm^{-3})	1.40
$F(000)$	840
Range for data collection θ (°)	$2 \leq \theta \leq 25$
Index ranges	$0 \leq h \leq 29$, $0 \leq k \leq 7$, $-13 \leq l \leq 13$
Number of unique reflections collected	3319
Number of observed reflections ($I > 2\sigma(I)$)	2680
Number of parameters refined	203
Final R (all data)	0.082
R_w	0.192

ated solvents using a Brüker 300 or 500 MHz instrument. (^{13}C, ^{1}H)-HETCOR NMR, ^{1}H{^{1}H}-NOE and variable temperature ^{1}H-NMR experiments were carried out by Dr. Tony Avent, University of Sussex. Mass spectra were taken by Dr. Ali Abdul-Sada, at the University of Sussex, using a Kratos M580RF instrument for FAB spectra (and 3-nitrobenzyl alcohol as a matrix material), and a Fisons VG Autospec for EI spectra. X-ray crystal structure data were collected by the $2\theta-\omega$ scan method at 173(2) K using an Enraf–Nonius CAD4 diffractometer with Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) radiation. During processing, the data were corrected for absorption by semi-empirical ψ-scan methods. The structures were solved by direct methods in SHELXS and refined by full-matrix least-square methods in SHELXN [18]. All non-hydrogen atoms were refined anisotropically. Diagrams of the molecular structure of complexes were drawn with the ORTEP package [19].

4.1. Preparation of [TiCp($C_5H_4CH_2CH_2NMe_2$)Cl_2] (**I**) [6]

The synthetic method for [Ti($C_5H_4SiMe_3$)($C_5H_4CH_2CH_2N^iPr_2$)Cl_2] [8] was adapted to synthesise of [TiCp($C_5H_4CH_2CH_2NMe_2$)Cl_2]. A solution of butyllithium in hexane (1.6 M, 4.7 cm^3, 7.52 mmol) was added slowly to a solution of $C_5H_5CH_2CH_2NMe_2$ (1.01 g, 7.37 mmol) in diethyl ether (50 cm^3) at 0 °C. The reaction mixture was allowed to stir for 1 h and the resulting suspension was added dropwise with stirring to a solution of [TiCpCl_3] (1.61 g, 7.33 mmol) in toluene (40 cm^3) at −30 °C. The solution changed immediately from yellow to deep red. The reaction mixture was allowed to warm to room temperature (r.t.) within 1 h and stirred for an additional 5 h. The solution was filtered and the solvent was removed under vacuum. The residue was washed with 2×20 cm^3 of cold pentane (−30 °C), leaving [TiCp($C_5H_4CH_2CH_2NMe_2$)Cl_2] as an orange red solid (1.71 g, 5.34 mmol, 73%).

^{1}H-NMR ($CDCl_3$, ppm): δ 2.71 (s, CH_3, 6H), 3.26 (m, CH_2, 4H), 6.37–6.46 (m, C_5H_4, 4H), 6.61 (s, C_5H_5, 5H).

4.2. Preparation of [TiCp($C_5H_4CH_2CH_2NHMe_2$)Cl_2]Cl (**II**) [3]

The compound [TiCp($C_5H_4CH_2CH_2NMe_2$)Cl_2] (0.81 g, 2.53 mmol) was dissolved in 15 cm^3 of MeOH (saturated with HCl gas) and then stirred for 30 min. The solution was concentrated under vacuum. The residue was recrystallised from a CH_2Cl_2–MeOH mixture at 0 °C as red crystals. The product is stable against air and moisture. It is very soluble in polar solvents such as methanol, dimethyl sulfoxide and acetonitrile; it is only slightly soluble in $CHCl_3$ and insoluble in non-polar solvents such as toluene.

4.3. Preparation of [TiCp($C_5H_4CH_2CH_2CH_2NMe_2$)Cl_2] (**III**) [6]

This was obtained by the method used to synthesise [TiCp($C_5H_4CH_2CH_2NMe_2$)Cl_2], from $C_5H_5CH_2CH_2CH_2NMe_2$ (0.70 g, 4.64 mmol), butyllithium (1.6 M solution in hexane, 3.0 cm^3, 4.8 mmol) and [TiCpCl_3] (1.01 g, 4.60 mmol). The product [TiCp($C_5H_4CH_2CH_2CH_2NMe_2$)Cl_2] was isolated as an orange red solid (1.16 g, 3.47 mmol, 75%).

^{1}H-NMR ($CDCl_3$, ppm): δ 2.23 (m, $CH_2CH_2CH_2$, 2H), 2.79 (s, CH_3, 3H), 2.81 (s, CH_3, 3H), 2.89 (m, $C_5H_4CH_2$, 2H), 3.03 (m, NCH_2, 2H), 6.39–6.45 (m, C_5H_4, 4H), 6.59 (s, C_5H_5, 5H).

4.4. Preparation of [TiCp($C_5H_4CH_2CH_2CH_2NHMe_2$)Cl_2]Cl (**IV**)

As for the synthesis of [TiCp($C_5H_4CH_2CH_2NHMe_2$)Cl_2]Cl but using [TiCp($C_5H_4CH_2CH_2CH_2NMe_2$)Cl_2] (0.58 g, 1.74 mmol). The compound [TiCp($C_5H_4CH_2CH_2CH_2NHMe_2$)Cl_2]Cl was recrystallised from layered MeOH/Et_2O as red crystals (0.52 g, 1.40 mmol, 81%). The product is stable to air and moisture. It is very soluble in polar solvents such as methanol, dimethyl sulfoxide and acetonitrile and insoluble in non-polar solvents.

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