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Synthesis of titanium(IV) ferrocenylaminate complexes

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Abstract

Attempts to prepare ferrocenylaminate(1-) complexes of titanium(IV) from a range of ferrocenylaminates are described. These often foundered due to problems of preparing pure samples of the 2-lithiated ferrocenylamines. However, [TiCp$_2$(Fc′CH$_2$CH$_2$NMe$_2$)Cl], [TiCp$_2$(Fc′CH$_2$NEt$_2$)Cl] and [TiCp(Fc′CH$_2$NMe$_2$)$_2$Cl], where Fc′ = Fe(C$_5$H$_5$)(2-C$_5$H$_3$), were isolated, and the last two were characterised structurally. In the second of these complexes, ferrocenylaminate is unexpectedly monodentate, possibly as a result of steric pressure. The last complex also contains monodentate ferrocenylaminates, and fills in a gap in the structures of the series of complexes [TiCp(Fc′CH$_2$NMe$_2$)$_n$Cl$_{3-n}$] ($n = 1$–3).

Keywords: Titanium(IV) complexes; Ferrocenylaminate ligands; Preparations X-ray structures; Denticity

1. Introduction

The ligand *N*,*N*-dimethylaminomethylferrocenyl ([Fe(C$_5$H$_5$)(C$_5$H$_3$CH$_2$NMe$_2$)] or Fc′CH$_2$NMe$_2^-$) has been used with several transition metal ions [1] since 1970 when the first mercury–Fc′CH$_2$NMe$_2$ [2] and palladium–Fc′CH$_2$NMe$_2$ [3] complexes were described. However, crystalline complexes have often not been isolated and structural data are sometimes lacking. The ligand Fc′CH$_2$NMe$_2^-$ is often assumed to be bidentate, with a ring carbon atom and the amine nitrogen acting as donors to a transition metal ion. The splitting of the C*H*$_2$NMe$_2$ [4] resonances in ^{1}H-NMR spectra and various ^{1}H chemical shifts attest that co-ordination has occurred.

For bis(cyclopentadienyl)titanium complexes specifically, [TiCp$^*_2$(Fc′CH$_2$NMe$_2$)Cl] [5] (Cp* = C$_5$Me$_5$), [TiCp$_2$(Fc′CH$_2$NMe$_2$)] [6,7] and [TiCp(Fc′CH$_2$NMe$_2$)$_2$] [7] have been described but not structurally characterised. It was suggested that ferrocenylaminate is monodentate in [TiCp$^*_2$(Fc′CH$_2$NMe$_2$)Cl] [5], but bidentate in [TiCp$_2$(Fc′CH$_2$NMe$_2$)] [6,7] and [TiCp(Fc′CH$_2$NMe$_2$)$_2$] [7], based on spectroscopic data and the relative thermal stabilities of these compounds. The single-crystal X-ray structures of [TiCp$_2$(Fc′CH$_2$NMe$_2$)$_2$] [5,6] and [TiCp$_2$(Fc′CH$_2$NMe$_2$)Cl] [8] show monodentate Fc′CH$_2$NMe$_2^-$ ligands. [Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCH$_2$Ph)(Fc′CH$_2$NMe$_2$)Cl] also has monodentate Fc′CH$_2$NMe$_2^-$ in which the *N*,*N*-dimethylamino group is directed away from the titanium atom [9], but the phenylaminate analogue [Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCH$_2$Ph)(C$_6$H$_4$CH$_2$NMe$_2$)Cl] has an unequivocal Ti–NMe$_2$ interaction [9].

The reaction of mono(cyclopentadienyl) complex [TiCpCl$_3$] with LiFc′-2-CH$_2$NMe$_2$ yields at least four products depending on the reaction conditions [8]. The deep blue diamagnetic complex [TiCp(Fc′CH$_2$NMe$_2$)Cl$_2$] from a reaction of one equivalent of LiFc′-2-CH$_2$NMe$_2$ contains bidentate Fc′CH$_2$NMe$_2^-$. Two or three equivalents of LiFc′-2-CH$_2$NMe$_2$ yielded the complexes [TiCp(Fc′CH$_2$NMe$_2$)$_2$Cl] and [TiCp(Fc′CH$_2$NMe$_2$)$_3$], respectively, both of undetermined structure. The last [TiCp(Fc′CH$_2$NMe$_2$)$_3$] is unstable at room temperature and above, changing to [TiCp(Fc′CH$_2$NMe$_2$)(Fc′CH$_2$NMeCH$_2$)–*C*,*N*,*C*]. It was postulated that hydrogen abstraction from a methyl group releases Fc′CH$_2$NMe$_2$ and the final product is further stabilised by the formation of a chelate ring which involves the Ti^{IV} ion.

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This paper describes attempts to prepare Fc′CH_2R (R = NEt_2, CH_2NMe_2, NC_4H_8O or $NMeCH_2Ph$) complexes of titanium(IV), analogous to the titanium Fc′CH_2NMe_2 complexes that were previously reported [8]. One aim was to see whether we could establish spectral criteria for the mode of attachment (monodentate or bidentate) of a ferrocenylaminate to a metal ion.

2. Results and discussion

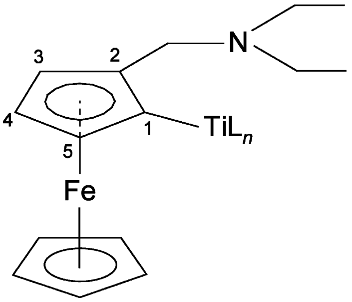
The ring metallation of Fc′CH_2R (R = NEt_2, CH_2NMe_2, NC_4H_8O or $NMeCH_2Ph$) was carried out with $LiBu^n$, followed by the direct addition of metallation mixture to the Ti starting material ([$TiCp_2Cl_2$] or [$TiCpCl_3$]). The major difficulty associated with this direct reaction without isolation of LiFc′-2-CH_2R was the achievement of a definite Ti/LiFc′-2-CH_2R stoichiometric proportion, as the lithiation processes are accompanied by the side reactions [10]. A “one-pot” technique was successfully used for metallation and subsequent aromatic electrophilic substitution reactions involving the addition of a large excess of organic electrophiles (ketones, aldehydes, esters, epoxyalkanes, etc.) to generate the desired products [11]. The preparation of specific organobimetallic complexes cannot follow this pattern. Reactions with [$TiCpCl_3$] and LiFc′CH_2NMe_2 are especially more complex. Solutions obtained from ferrocenylamine and butyllithium used after what seemed an optimum reaction time (between 1 and 16 h depending on the ferrocenylamine) were always contaminated with unreacted butyllithium and this could be removed only with resultant contamination due to polylithiation [10]. The butyllithium can reduce Ti^{IV} to Ti^{III} [12], and [{$TiCp_2Cl$}$_2$] was isolated in a number of occasions from mixtures involving [$TiCp_2Cl_2$].

In order to obviate these problems, a slight excess of Ti starting material was used and unreacted Ti starting material was frequently isolated during the work-up. We were finally able to isolate and characterise the two complexes by reaction of the appropriate lithium ferrocenylaminate with the bis(cyclopentadienyl) complex [$TiCp_2Cl_2$], [$TiCp_2$(Fc′CH_2NEt_2)Cl] (**I**) and [$TiCp_2$(Fc′$CH_2CH_2NMe_2$)Cl] (**II**). No further complexes of this type could be obtained in characterisable form. However, we were able to characterise structurally the complex [TiCp(Fc′CH_2NMe_2)$_2$Cl] (**III**). This contains two monodentate ferrocenylaminates, and fills in a gap in the series of complexes [TiCp(Fc′CH_2NMe_2)$_n$-Cl_{3-n}] ($n = 1$, 2 or 3) [8].

The diamagnetic complex (**I**) [$TiCp_2$(Fc′CH_2NEt_2)Cl] was characterised by IR, mass (EI), ^{1}H- and ^{13}C-NMR spectroscopies (Table 1). It is soluble in THF, Et_2O and aromatic hydrocarbons and is sparingly soluble in hexane. When recrystallised from saturated hexane solutions at room temperature, the product gave deep green crystals suitable for X-ray crystallographic analysis. It is moderately air-sensitive and its solutions change to reddish-brown after being exposed to air for ca. 10 min.

Table 1
H^1- and $^{13}C\{^1H\}$-NMR data for [$TiCp_2$(Fc′CH_2NEt_2)Cl] (**I**) in C_6D_6 δ-scale at room temperature

Proton or carbon	Chemical shifts	
	^{1}H-NMR	$^{13}C\{^1H\}$-NMR
NCH_2CH_3	0.95 (t, 6H, $^3J = 7.1$ Hz)	10.68
NCH_2CH_3	2.37–2.43 (m, 2H) 2.62–2.69 (m, 2H)	45.30
$C_5H_3CH_2N$	3.02 (d, 1H, $^2J = 12.7$ Hz) 3.47 (d, 1H, $^2J = 12.7$ Hz)	55.50
FeCp	4.18 (s, 5H)	70.07
Position 3	4.20 (m, 1H)	73.08
Position 4	4.06 (t, 1H)	67.31
Position 5	3.68 (s, br, 1H)	78.06
TiCp	6.02 (s, 5H) 6.32 (s, 5H)	116.88 116.43
Position 2	–	88.79
Position 1	–	136.93



Mass spectroscopy data for **I** are consistent with the structural formulation, and the isotopic pattern obtained for the molecular ion (m/z 483) corresponded exactly to the theoretical pattern. Compounds **I** and **II** obey the IR “1000, 1100 rule” [13] and show two strong absorptions, one near 1000 cm^{-1} due to C–H bending parallel to the C_5H_5 ring and another near 1100 cm^{-1} assigned to an asymmetric C_5H_5 ring deformation mode.

The crystal structure of the 16-electron compound **I** is shown in Fig. 1 and the selected bond lengths and angles are listed in Tables 2 and 3. Fc′CH_2NEt_2 is monodentate in the solid state, although there are vacant orbitals on titanium that would allow bidentate bonding to occur. Presumably, as in other bis(cyclopentadienyl) compounds [$TiCp_2$(Fc′CH_2NMe_2)Cl] [8] and [$TiCp_2$(Fc′-CH_2NMe_2)$_2$] [6], the two Cp rings force the ferrocenylaminate to be monodentate.

The two cyclopentadienyl rings are planar within the experimental error, almost eclipsed, parallel, with a

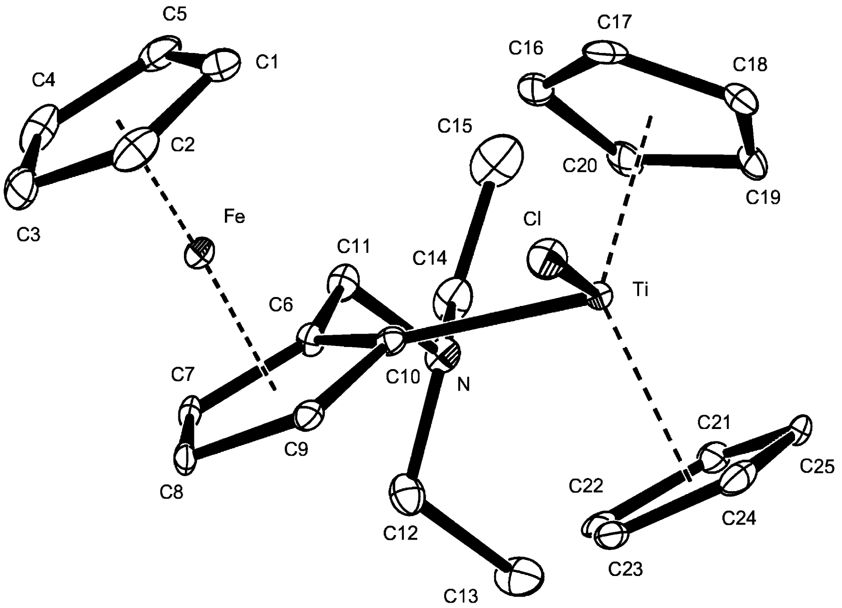


Fig. 1. Plot of the molecular structure of [TiCp$_2$(Fc′CH$_2$NEt$_2$)Cl] (**I**) showing the atom labelling scheme; the diagram was drawn with the use of the ORTEP package; thermal ellipsoids are drawn at 25% probability level; hydrogen atoms are omitted.

Table 2
Selected interatomic distances for the complex [TiCp$_2$(Fc′CH$_2$NEt$_2$)Cl] (**I**)

Atoms	Bond length (Å)
Fe–M(1) [a]	1.652 (5)
Fe–M(2) [a]	1.646 (5)
Fe–C(10)	2.092 (5)
Ti–M(3) [b]	2.057 (5)
Ti–M(4) [b]	2.079 (5)
Ti–C(10)	2.179 (5)
Ti–Cl	2.354 (2)
N–C(11)	1.480 (6)
N–C(12)	1.474 (6)
N–C(14)	1.454 (6)
C(6)–C(11)	1.502 (7)

Estimated S.D.s are in parentheses.

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

[b] M(3) and M(4) are the centroids of the C(16) to C(20) and C(21) to C(25) rings.

nearly linear M(1)–Fe–M(2) angle of 176.1(2)° (‘M’ denotes the centroid of a Cp ring). All this is not unusual. Complex **I** is structurally very similar to [TiCp$_2$(Fc′CH$_2$NMe$_2$)Cl] [8]. There are no significant intermolecular interactions, and the tertiary amino group does not play any significant role in the structure. Using the method of Marquarding et al. [14], we found that the deep green crystals of **I** embody the *R*-configuration. This seems to be a spontaneous resolution, as the starting material was racemic. In contrast, in the unit cell of [TiCp$_2$(Fc′CH$_2$NMe$_2$)Cl] [8], the *S*-isomer was observed.

Table 3
Selected bond angles for the complex [TiCp$_2$(Fc′CH$_2$NEt$_2$)Cl] (**I**)

Atoms	Bond angle (°)
M(1)–Fe–M(2) [a]	176.1 (2)
M(3)–Ti–M(4) [b]	130.1 (2)
M(3)–Ti–C(10) [b]	108.6 (2)
M(4)–Ti–C(10) [b]	102.3 (2)
C(10)–Ti–Cl	94.71 (13)
C(11)–N–C(12)	110.8 (4)
C(11)–N–C(14)	110.2 (4)
C(12)–N–C(14)	109.1 (4)
C(7)–C(6)–C(11)	121.2 (5)
N–C(11)–C(6)	115.7 (4)
N–C(12)–C(13)	112.5 (4)

Estimated S.D.s are in parentheses.

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

[b] M(3) and M(4) are the centroids of the C(16) to C(20) and C(21) to C(25) rings.

In ^{1}H- and ^{13}C{^{1}H}-NMR spectra (Table 1), the asymmetry of the molecule is evident from the diastereotopic resonances. The assignments made for complex **I** in Table 1 were supported by ^{13}C{^{1}H} DEPT-90 and DEPT-135 measurements. For the ferrocenyl moiety, assignments were supported by selective decoupling and NOE experiments. The splitting of the TiCp$_2$ signal is a feature of both ^{1}H- and ^{13}C-NMR spectra. Similar splittings have been reported for [TiCp$_2$(Fc′CH$_2$NMe$_2$)Cl] [8] but have not been observed for [TiCp$_2$(Fc′CH$_2$NMe$_2$)$_2$] [5] or for [TiCp$_2$Fc$_2$] [15]. The chemical non-equivalence of the titanium Cp protons is due to the prochiral ferrocenylaminate ligand and is not evidence for monodentate or bidentate binding. Additionally, the (^{13}C,^{1}H)-HETCOR NMR spectrum revealed that the protons of the TiCp group resonating at lower frequency ($\delta = 6.02$ ppm) are directly bonded to the TiCp carbons of highest frequency ($\delta = 116.88$ ppm).

The methylene protons of the ferrocenylaminate moiety ($C_5H_3CH_2N$) of **I** are also chemically non-equivalent and the geminal CH_2 protons of the $N(CH_2CH_3)_2$ group give rise to individual resonances which are split into multiplets in the regions $\delta = 2.37$–2.43 and 2.62–2.69 ppm, by coupling to each other and to the vicinal methyl protons [4,16] so that each is a typical doublet of quartets of an ABX_3 system. These assignments were confirmed by the (^{13}C,^{1}H)-HETCOR NMR experiment, which showed that the CH_2 carbons at $\delta = 45.30$ ppm gave two responses in the ^{1}H-NMR spectrum corresponding to two different hydrogen environments. However, the protons of the methyl groups give rise to a triplet at $\delta = 0.95$ ppm ($^{3}J = 7.1$ Hz). A single resonance is also observed for the methyl groups in the $^{13}C\{^{1}H\}$-NMR spectrum ($\delta = 10.68$ ppm), excluding a rigid (though not a fluxional) co-ordination of the *N*,*N*-diethylamino group to the titanium centre in solution.

In $^{13}C\{^{1}H\}$-NMR spectrum, the resonance of *C*1 (carbon–metal) appears at $\delta = 136.93$ ppm, which is very similar to those observed for the related complexes [TiCp$_2$(Fc′CH$_2$NMe$_2$)Cl] and [TiCp$^*_2$(Fc′CH$_2$NMe$_2$)Cl] ($\delta = 136.8$ [8] and 136.4 ppm [5], respectively). These resonances are of higher frequency than that observed for [TiCp$_2$(Fc′CH$_2$NMe$_2$)$_2$] ($\delta = 128.1$ ppm) [5]. This is probably due to the electron-withdrawing effect of the chlorine atom bound to Ti.

Two-dimensional NMR experiments (^{13}C,^{1}H-HETCOR) support the assignments of *C*3, *C*4 and *C*5. The $^{13}C\{^{1}H\}$-NMR signals at $\delta = 67.31$, 73.08 and 78.06 ppm were shown to be related to the *H*4, *H*3 and *H*5 signals, respectively, in ^{1}H-NMR spectrum. The inversion of the order of chemical shifts for carbon and proton signals ($H3 > H4 > H5$, while $C5 > C3 > C4$) has been previously observed in other ferrocene derivatives [16]. Furthermore, the order of chemical shifts $C5 > C3 > C4$ has been observed in LiFc′-2-CH$_2$NMe$_2$ [8], [TiCp$_2$(Fc′CH$_2$NMe$_2$)Cl] [8], [TiCp$^*_2$(Fc′CH$_2$NMe$_2$)Cl] [5], [TiCp$_2$(Fc′CH$_2$NMe$_2$)$_2$] [5], [TiCp(Fc′CH$_2$NMe$_2$)Cl$_2$] [8], [TiCp(Fc′CH$_2$NMe$_2$)$_2$Cl] [8], [TiCp(Fc′CH$_2$NMe$_2$)$_3$] [8] and [Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCH$_2$Ph)(Fc′CH$_2$NMe$_2$)Cl] [9], among others.

The deep green diamagnetic solid [TiCp$_2$(Fc′CH$_2$CH$_2$NMe$_2$)Cl] (**II**) is fairly soluble in non-polar solvents such as hexane and is air-sensitive. Mass spectroscopic data are consistent with the formulation proposed for **II**, as the spectrum contains the molecular ion (*m/z* 469) with its expected isotopic pattern. The ^{1}H- and $^{13}C\{^{1}H\}$-NMR data are presented in Table 4. The assignments of the carbon resonances were supported by $^{13}C\{^{1}H\}$ DEPT-135 measurements.

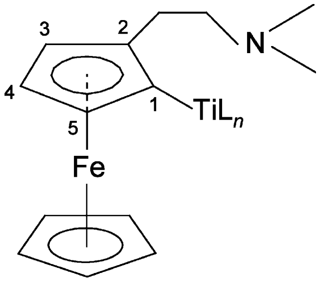
Table 4
H^{1}- and $^{13}C\{^{1}H\}$-NMR data for [TiCp$_2$(Fc′CH$_2$CH$_2$NMe$_2$)Cl] (**II**) in C_6D_6, δ-scale

Proton or carbon	Chemical shifts	
	^{1}H-NMR	$^{13}C\{^{1}H\}$-NMR
$C_5H_3CH_2$	[a]	29.71
	2.38–2.46 (m) [b]	
NCH_3	2.20 (s) [c]	45.89
NCH_2	2.38–2.46 (m) [b]	61.46
FeCp	4.20 (s, 5H)	70.25
Position 3	4.15 (m, 1H)	68.77
Position 4	4.02 (t, 1H)	67.19
Position 5	3.68 (m, br, 1H)	77.13
TiCp	5.86 (s, 5H)	116.68
	6.18 (s, 5H)	116.57
Position 2	–	91.60
Position 1	–	137.80

[a] Signal is hidden by the singlet at 2.20 ppm, but its presence was confirmed by (^{13}C,^{1}H)-HETCOR.

[b] Block of 3H.

[c] Block of 7H.



Again, the resonances assigned to the cyclopentadienyl ligands bound to titanium are split in both ^{1}H- and $^{13}C\{^{1}H\}$-NMR spectra due to the planar chiral ferrocenylaminate ligand. In $^{13}C\{^{1}H\}$-NMR spectrum, the N*C*H$_2$ carbon ($\delta = 61.46$ ppm) resonates at a much higher frequency than the C$_5$H$_3$*C*H$_2$ carbon ($\delta = 29.71$ ppm) due to the increased deshielding of carbon adjacent to the electron-withdrawing nitrogen atom. Only one signal for the *N*,*N*-dimethylamino group is recorded in ^{1}H- and $^{13}C\{^{1}H\}$-NMR spectra, indicating

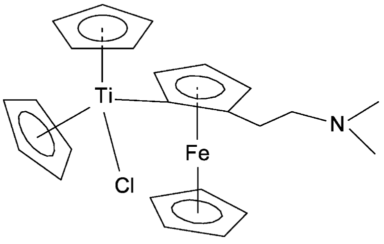


Fig. 2. A schematic representation of the proposed structure of [TiCp$_2$(Fc′CH$_2$CH$_2$NMe$_2$)Cl] (**II**).

Table 5
Selected interatomic distances for the complex [TiCp(Fc′CH_2N-$NMe_2)_2Cl$] (**III**)

Atoms	Bond length (Å)
Fe(1)–M(2) [a]	1.652 (4)
Fe(1)–M(3) [a]	1.643 (4)
Fe(1)–C(11)	2.036 (4)
Fe(1)–C(12)	2.051 (4)
Fe(2)–M(4) [b]	1.662 (4)
Fe(2)–M(5) [b]	1.651 (4)
Fe(2)–C(24)	2.039 (3)
Fe(2)–C(28)	2.083 (4)
Ti–M(1) [c]	2.055 (4)
Ti–C(15)	2.063 (4)
Ti–C(28)	2.098 (4)
Ti–Cl	2.270 (1)
N(1)–C(16)	1.472 (5)
N(2)–C(29)	1.469 (5)
C(11)–C(16)	1.500 (5)
C(24)–C(29)	1.500 (5)

Estimated S.D.s are in parentheses.

[a] M(2) and M(3) are the centroids of the C(6) to C(10) and C(11) to C(15) rings.

[b] M(4) and M(5) are the centroids of the C(19) to C(23) and C(24) to C(28) rings.

[c] M(1) is the centroid of the C(1) to C(5) ring.

the presence of monodentate or fluxional bidentate ferrocenylaminate in solution. Additionally, inversion of the order of chemical shifts for the carbon and proton signals of the disubstituted Cp ring was observed ($H3 > H4 > H5$, while $C5 > C3 > C4$), as in complex **I**.

A balance between steric pressures and electronic requirements probably determines the solid-state structure of this complex. On the basis of the structural evidence accumulated for the related **I**, [$TiCp_2$(Fc′CH_2NMe_2)Cl] [8] and [$TiCp_2$(Fc′$CH_2NMe_2)_2$] [6], it seems likely that Fc′$CH_2CH_2NMe_2$ is monodentate, as sketched in Fig. 2. ^{1}H- and ^{13}C-NMR data spectra of **II** indicate the absence of a rigid chelating interaction between the tertiary amino group and the titanium atom in solution.

Table 6
Selected bond angles for the complex [TiCp(Fc′$CH_2NMe_2)_2Cl$] (**III**)

Atoms	Bond angle (°)
M(3)–Fe(1)–M(2) [a]	177.0 (2)
M(5)–Fe(2)–M(4) [b]	176.6 (2)
M(1)–Ti–C(15) [c]	105.2 (2)
M(1)–Ti–C(28) [c]	113.0 (2)
M(1)–Ti–Cl [c]	120.7 (1)
C(15)–Ti–Cl	112.1 (1)
C(28)–Ti–Cl	105.4 (1)
C(17)–N(1)–C(16)	111.4 (3)
C(30)–N(2)–C(29)	111.9 (3)
N(1)–C(16)–C(11)	114.2 (3)
N(2)–C(29)–C(24)	114.1 (3)

Estimated S.D.s are in parentheses.

[a] M(2) and M(3) are the centroids of the C(6) to C(10) and C(11) to C(15) rings.

[b] M(4) and M(5) are the centroids of the C(19) to C(23) and C(24) to C(28) rings.

[c] M(1) is the centroid of the C(1) to C(5) ring.

Complex **III**, [TiCp(Fc′$CH_2NMe_2)_2Cl$], was prepared according to the literature procedure [8]. It can be reproducibly crystallised from saturated hexane solutions at room temperature over 3–7 days to give thin blue needles suitable for X-ray crystal structure determination. The crystals were kept in the mother liquor and the selection and mounting of a single crystal were done quickly. Principal molecular dimensions are summarised in Tables 5 and 6 while a diagram of the molecular structure is shown in Fig. 3. Fc′CH_2NMe_2 ligands are monodentate, generating a highly electron-deficient 12e$^-$ species, but with minimised steric strain involving the ferrocenyls. The alternative bidentate Fc′CH_2NMe_2 ligands would provide a highly strained 16e$^-$ complex.

In the mono(Fc′CH_2NMe_2) analogue [TiCp(Fc′CH_2-$NMe_2)Cl_2$], the ferrocenylaminate moiety is bidentate [8], whereas in [TiCp(Fc′$CH_2NMe_2)_3$] they are believed to be monodentate. The complex [Ti^{III}Cp(Fc′CH_2-$NMe_2)_2$] contains bidentate ferrocenylaminate ligands [7]. In this case, chelation seems to be necessary to provide minimal complex stabilisation. There are no significant intermolecular interactions.

The average Fe(1)–C(Cp), Fe(2)–C(Cp), Ti–Cl and Ti–C(Cp) Ti–M(1) distances in **III** are typical [6,8,13] and the planar cyclopentadienyl rings in the ferrocene units are nearly eclipsed.

The deep blue crystals of **III** contain a mixture of diastereomers so that the overall effect is meso, as also observed in the centrosymmetric unit cells of the closely analogous complexes [$TiCp_2$(Fc′$CH_2NMe_2)_2$] [6] and [TiCp(Fc′CH_2NMe_2)(Fc′CH_2NMeCH_2)] [8]. The starting amine was probably racemic.

3. Conclusions

Substitution of one chloride ion in [$TiCpCl_3$] by Fc′$CH_2NMe_2^-$ gives [TiCp(Fc′$CH_2NMe_2)Cl_2$], in which the ferrocenylaminate moiety is *C*,*N*-bidentate. Substitution of two chloride ions gives [TiCp(Fc′CH_2N-$NMe_2)_2Cl$], which contains monodentate ferrocenylaminate ligands. Finally, complete halide substitution produces [TiCp(Fc′$CH_2NMe_2)_3$]. This compound changes spontaneously at room temperature into the complex [TiCp(Fc′CH_2NMe_2)(Fc′CH_2NMeCH_2)], which contains a monodentate and a “tridentate” ferrocenylaminate moiety. In contrast, the ferrocenylaminate ligand in the half-sandwich compound [Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2Ph$)(Fc′CH_2NMe_2)Cl] [13] is monodentate. In this case, the size of the bidentate C_5Me_4Si-

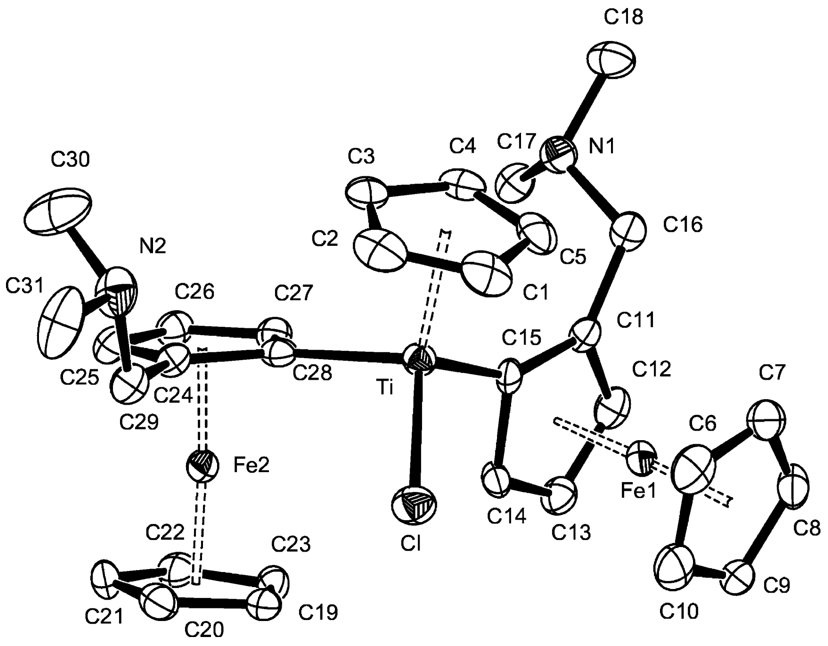


Fig. 3. Plot of the molecular structure of [TiCp(Fc′CH$_2$NMe$_2$)$_2$Cl] (**III**) showing the atom labelling scheme; the diagram was drawn with the use of the ORTEP package; thermal ellipsoids are drawn at 30% probability level; hydrogen atoms are omitted.

Me$_2$NCH$_2$Ph ligand apparently forces the Fc′CH$_2$NMe$_2$ to adopt monodentate bonding.

There are still no reliable spectral criteria to indicate whether the ferrocenyl residue is monodentate or bidentate in any given compound. A single resonance is observed for the methyl groups in both ^{1}H- and ^{13}C{^{1}H}-NMR spectra of these complexes, excluding a rigid co-ordination of the tertiary amino group at the titanium centre. Nevertheless, a bidentate fluxional co-ordination of the amine function in solution cannot be excluded. In addition, the benzyl methylene protons are chemically non-equivalent. However, this phenomenon is a consequence of the asymmetry of the disubstituted Cp ring and is not evidence either of bidentate or of monodentate binding.

4. Experimental

All operations were carried out under an inert atmosphere in an argon-filled dry box or with the use of standard Schlenk techniques. Solvents were dried by standard procedures and distilled under N$_2$ prior to use. The commercial products *N*-bromosuccinimide, *n*-butyllithium (1.6 M solution in hexane), titanocene dichloride (Aldrich) and *N*,*N*-dimethylaminomethylferrocene (Lancaster) were dried and, where appropriate, distilled prior to use. [TiCpCl$_3$] was prepared by the literature methods [17]. *N*,*N*-Diethylaminoferrocene and the related aminoferrocenes were prepared as described in [10].

Microanalyses were carried out at the University of Surrey using Leenan CE 440 CHN elemental analyser or at MEDAC, Brunel Science Centre, Surrey. 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 deuterated solvents using a Bruker 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 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. 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]. Details of the analyses are shown in Table 7.

4.1. Synthesis of [TiCp$_2$(Fc′CH$_2$NEt$_2$)Cl] (*I*)

4.1.1. Preparation of LiFc′-2-CH$_2$NEt$_2$

N,*N*-Diethylaminomethylferrocene (1.12 g, 4.13 mmol) was dissolved in diethyl ether (30 cm^3) and treated drop-wise with a 1.6 M solution of butyllithium in hexane (2.6 cm^3, 4.16 mmol). Stirring was continued for 16 h at room temperature (r.t.). This mixture was

Table 7
Details of X-ray crystal structure determinations

Formula	$C_{25}H_{30}ClFeNTi$	$C_{31}H_{37}ClFe_2N_2Ti$
M (g mol^{-1})	483.70	632.68
Crystal system	Orthorhombic	Triclinic
Crystal size (mm^3)	$0.35 \times 0.10 \times 0.05$	$0.25 \times 0.20 \times 0.15$
Space group	$P2_12_12_1$ (No. 19)	$P\bar{1}$(No. 2)
Unit cell dimensions		
a (Å)	7.796 (3)	8.187 (4), $\alpha = 82.44$ (3)°
b (Å)	14.399 (10)	11.757 (8), $\beta = 79.28$ (3)°
c (Å)	19.561 (13)	15.126 (8), $\gamma = 82.65$ (3)°
Cell volume, V (Å^3)	2196 (2)	1410.1 (1)
Formula units per cell, Z	4	2
Density, D_c (g cm^{-3})	1.46	1.49
Absorption coefficient, μ (mm^{-1})	1.16	1.41
Radiation wavelength, λ (Å)	Mo–K$_\alpha$ (mean) 0.71073	Mo–K$_\alpha$ (mean) 0.71073
F(000)	1008	656
Range for data collection, θ (°)	$3.8 \leq \theta \leq 23.0$	$3.9 \leq \theta \leq 25.1$
Index ranges	$-8 \leq h \leq 8$, $-15 \leq k \leq 15$, $-21 \leq l \leq 21$	$-9 \leq h \leq 9$, $-14 \leq k \leq 14$, $-18 \leq l \leq 17$
Number of unique reflections collected	3039	4932
Number of observed reflections ($I > 2\sigma(I)$)	2499	3588
Number of parameters refined	263	334
Goodness-of-fit on F^2	1.048	1.018
Transmission factor	Maximum 0.876; minimum 0.822	Maximum 0.763; minimum 0.736
Final R_1, wR_2 ($I > 2\sigma(I)$)	0.043; 0.072	0.047; 0.089
R_1, wR_2 (all data)	0.061; 0.078	0.078; 0.100
Largest difference peak and hole (e Å^{-3})	0.24 and −0.23	0.35 and −0.42

used directly for the next step without isolation of the Li salt.

4.1.2. Reaction of [$TiCp_2Cl_2$] with LiFc′-2-CH_2NEt_2

To a stirred suspension of [$TiCp_2Cl_2$] (1.03 g, 4.14 mmol) in diethyl ether (30 cm^3), an ethereal solution of LiFc′-2-CH_2NEt_2 (30 cm^3) was added drop-wise. The reaction mixture changed immediately from red to dark green. After stirring for 3 h at r.t., the resulting mixture was filtered. The residue on the sinter (LiCl and unreacted [$TiCp_2Cl_2$]) was discarded. The filtrate was concentrated to ca. 10 cm^3 under vacuum and then layered with hexane (20 cm^3). Deep green crystals (0.72 g, 1.49 mmol and 36% yield based on titanium) were separated upon standing at −20 °C for 72 h. Recrystallisation from a concentrated hexane solution at r.t. afforded deep green needles suitable for X-ray analysis (Found: C, 62.5; H, 6.45; N, 2.80. $C_{25}H_{30}ClFeNTi$ requires: C, 62.08; H, 6.25; N, 2.89%).

IR: 624 (m), 721 (m), 754 (w), 809 (s), 950 (w), 1012 (shoulder), 1023 (s), 1037 (m), 1104 (s), 1261 (m), 1413 (w), 1707 (w), 2478 (w), 2566 (w), 3089 (w).

4.2. Synthesis of [$TiCp_2(Fc'CH_2CH_2NMe_2)Cl$] (**II**)

4.2.1. Preparation of LiFc′-2-$CH_2CH_2NMe_2$

To an amber solution of N,N-dimethylaminoethylferrocene (1.01 g, 3.93 mmol) in diethyl ether (30 cm^3), a 1.6 M solution of butyllithium in hexane (2.4 cm^3, 3.84 mmol) was added drop-wise. Stirring was continued for 16 h at r.t. This mixture was used directly for the next step without isolation of the Li salt.

4.2.2. Reaction of [$TiCp_2Cl_2$] with LiFc′$CH_2CH_2NMe_2$

To a stirred suspension of [$TiCp_2Cl_2$] (0.98 g, 3.94 mmol) in diethyl ether (30 cm^3), an ethereal solution of LiFc′-2-$CH_2CH_2NMe_2$ (30 cm^3) was added drop-wise. The reaction mixture changed immediately from red to dark green. After stirring for 3 h at r.t., the resulting mixture was filtered. The residue on the sinter (LiCl and unreacted [$TiCp_2Cl_2$]) was discarded. The filtrate was then evaporated to dryness and the oily residue was extracted with hexane (20 cm^3) and stored at −20 °C for 1 week. The product, [$TiCp_2(Fc'CH_2CH_2NMe_2)Cl$], was isolated as a dark green powder (0.44 g, 0.94 mmol, and yield 24% based on titanium). The product is very soluble in low polarity solvents, even in hexane, and this is an obstacle to isolation and purification (Found: C, 60.07; H, 5.86; N, 2.99. $C_{24}H_{28}ClFeNTi$ requires: C, 61.38; H, 6.01; N, 2.98%).

IR: 622 (m), 724 (m), 754 (w), 796 (s), 965 (w), 1013 (s), 1024 (shoulder), 1103 (s), 1261 (m), 1410 (w), 2448 (w), 2564 (w), 3077 (w).

4.3. Synthesis of [$TiCp(Fc'CH_2NMe_2)_2Cl$] (**III**) [8]

To a yellow solution of [$TiCpCl_3$] (1.22 g, 5.56 mmol) in diethyl ether (130 cm^3), two portions of the freshly prepared solid LiFc′-2-CH_2NMe_2 (1.36 g, 5.46 mmol and 1.38 g, 5.54 mmol) were added sequentially. The additions were made as slowly as possible, under vigorous stirring, producing a gradual change (yellow → deep green → deep blue). The reaction mixture was stirred for a further 5 h. The mixture was then filtered, giving a small amount of a grey powder, which was discarded. The filtrate was then evaporated to dryness and the solid residue was suspended in 30 cm^3 of Et_2O–hexane, 1:2, cooled to −20 °C for 72 h, filtered and washed with 10 cm^3 of cold hexane. After drying for 3 h under vacuum, 1.54 g of the product was isolated. Yield: 2.43 mmol, 44% (Found: C, 58.01; H, 5.96; N, 4.18. $C_{31}H_{37}ClFe_2N_2Ti$ requires: C, 58.85; H, 5.89; N, 4.43%). Thin deep blue needles were obtained by recrystallisation from saturated hexane solutions at r.t. The product is very soluble in diethyl ether, even at low temperature. It is highly hydroscopic and changes to brownish-red and then to orange when exposed to air.

^{1}H-NMR (C_6D_6, ppm): δ 2.10 (s, NCH_3, 12H), 2.61 (d, NCH_2, 2H, $^2J = 12.3$), 3.78 (d, NCH_2, 2H, $^2J = 12.3$), 3.97 (m, *H*5, 2H), 4.08 (t, *H*4, 2H), 4.17 (s, FeCp, 10H), 4.86 (m, *H*3, 2H), 6.79 (s, TiCp, 5H).

$^{13}C\{^1H\}$-NMR (C_6D_6, ppm): δ 45.34 (NCH_3), 61.60 (NCH_2), 68.41 (*C*4), 71.18 (FeCp), 73.55 (*C*3), 78.43 (*C*5), 89.22 (*C*2), 116.80 (TiCp), 151.65 (*C*1).

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