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1,1′-BIS(*N*,*N*-DIMETHYLAMINO)FERROCENE, 1,1′-BIS(*N*,*N*-DIMETHYLAMINO)COBALTOCENIUM HEXAFLUOROPHOSPHATE AND 1,1′-BIS(*N*,*N*-DIMETHYLAMINO)TITANOCENE DICHLORIDE. CRYSTAL STRUCTURE OF 1,1′-BIS(*N*,*N*-DIMETHYLAMINO)TITANOCENE DICHLORIDE

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Summary

A general method for the preparation of 1,1′-bis(*N*,*N*-dimethylamino)metallocenes is described, involving the reaction of *N*,*N*-dimethylamino-cyclopentadienyllithium (**1**-Li) with metal chlorides. 1,1′-Bis(*N*,*N*-dimethylamino)ferrocene (**2**), 1,1′-bis(*N*,*N*-dimethylamino)cobaltocenium hexafluorophosphate ($\mathbf{3}^+$ PF_6^-) and 1,1′-bis(*N*,*N*-dimethylamino)titanocene dichloride (**4**) have been synthesized in this way. The influence of the dimethylamino donor substituent has been studied by means of cyclic voltammetry. 1,1′-Bis(*N*,*N*-dimethylamino)ferrocene (**2**), e.g., has the most negative redox potential ($E°$ -0.23 V (SCE)) so far reported for a ferrocene derivative.

The structure of 1,1-bis(*N*,*N*-dimethylamino)titanocene dichloride (**4**) has been determined by X-ray crystallography. It crystallizes in hexagonal plates with the space group $C2/c$ ($Z = 4$, a 1301.4, b 647.2, c 1828.5 pm, β 98.81°). The titanium atom does not lie exactly above the centres of the cyclopentadienyl rings, and the C–N bond from the cyclopentadienyl ring carbon atom C(1) to the nitrogen atom of the dimethylamino group is very short (134.7 pm).

Introduction

There have been only a few reports of the preparation of bis(amino)metallocenes. 1,1′-Bis(amino)ferrocene has been synthesized by hydration of 1,1′-bis(azido)ferrocene or 1,1′-bis(phenylazo)ferrocene [1]. 1,1′-Bis(diphenylamino)ferrocene has been prepared recently [2], and the 1,1′-bis(amino)cobaltocenium cation is accessible via a multistep synthesis [3]. In all these cases the amino group was formed from other substituents already present at the metallocene in a more or less tedious manner. Introduction of a required substituent already attached to the cyclopentadienyl ring

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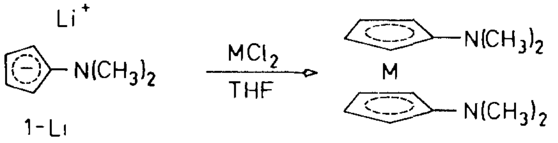
is the more general method [4]. We thus describe below the use of *N*,*N*-dimethylamino-cyclopentadienyllithium (**1**-Li) for the preparation of 1,1′-bis(*N*,*N*-dimethylamino)metallocenes, and consider some of the properties of the latter.

Preparation of the 1,1′-bis(*N*,*N*-dimethylamino)metallocenes 2, 3^+ PF_6^-, 4, 5^+ I^- and 5^{2+} $2I^-$

Reaction of the easily accessible *N*,*N*-dimethylamino-cyclopentadienyllithium (**1**-Li) [5] with two molar equivalents of iron(II) chloride, cobalt(II) chloride or titanium(IV) chloride in tetrahydrofuran (THF) led to the metallocenes **2**, $\mathbf{3}^+$ PF_6^- and **4**, respectively.

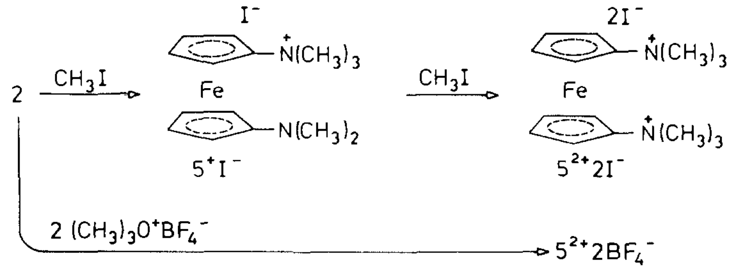


compound	M	yield [%]
2	Fe	33
$3^+PF_6^-$	Co	29^a
4	$TiCl_2$	30

a: the Co^{II}—species has not been isolated

The diaminoferrocene **2** forms red, air-sensitive, crystalline needles, and is easily oxidized to the corresponding Fe^{III} compound (see the electrochemical studies).

Methylation of **2** gives the 1,1′-bis(*N*,*N*-dimethylamino)ferrocene methyl iodide $\mathbf{5}^+$ I^- and the corresponding dimethyl iodide $\mathbf{5}^{2+}$ $2I^-$, depending on the amount of methyl iodide used.



If trimethyloxonium tetrafluoroborate is used instead of methyl iodide only $\mathbf{5}^{2+}$ $2BF_4^-$ is isolated.

In the reaction of cobalt(II) chloride with **1**-Li the initially formed **1**,**1**′-bis(*N*,*N*-dimethylamino)cobaltocene is readily oxidized in acid solution to give the cobaltocenium cation, which was isolated as its PF_6^- salt $\mathbf{3}^+$ PF_6^-, a red-brown powder.

1,1′-Bis(*N*,*N*-dimethylamino)titanocene dichloride (**4**) is the first known aminotitanocene species. Its black-green colour is noteworthy, the titanocene dihalides usually being red [6].

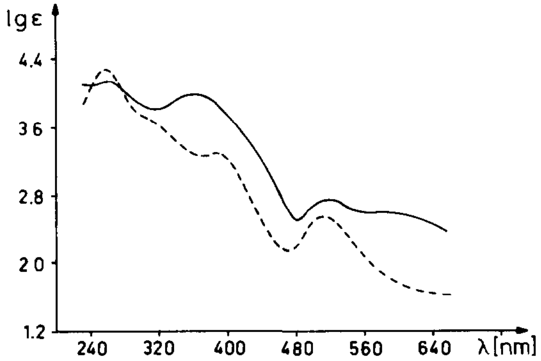


Fig. 1. UV/VIS absorption spectrum of the bis(amino)titanocene dichloride **4** (———) and of Cp_2TiCl_2 (— — —) in acetonitrile.

Figure 1 shows the UV/VIS absorption spectrum of **4** in acetonitrile together with the spectrum of the unsubstituted titanocene dichloride. In the spectrum of **4**, the absorption band at 360 nm in particular, which is very intense (log ϵ 4.03) and shifted towards shorter wavelengths compared with the same band of titanocene dichloride (log ϵ 3.29; λ 390 nm). The strong absorption band of **4** must correspond to a charge transfer from the cyclopentadienyl ligands into the titanium *d*-orbitals [7]. In the case of alkyl substituted titanocene dihalides this band shows a red shift [8]. In contrast to the dimethylamino groups in the ferrocene **2**, the dimethylamino groups in the titanocene **4** are not methylated either by methyl iodide (no reaction takes place) or by trimethyloxonium tetrafluoroborate (the starting material **4** is slowly decomposed). Apparently the free electron pair at the dimethylamino substituents is less available for a nucleophilic substitution in **4** than in **2**. This is nicely supported by the X-ray structural data of **4** (see below) which show a very short C–N bond from the cyclopentadienyl carbon atom to the nitrogen atom, reflecting the strong acceptor qualities of the d^{16}-electron configuration of the titanocene dichloride complex.

The reaction of cyclopentadienyltitanium trichloride (**6**) with **1**-Li does not give 1-(*N*,*N*-dimethylamino)titanocene dichloride (**7**) [9].

$$\underset{(\mathbf{7})}{C_5H_4\text{–}N(CH_3)_2(Cp)TiCl_2} \nleftarrow \underset{(\mathbf{6})}{CpTiCl_3} + \mathbf{1}\text{-Li} \rightarrow \underset{(1/1)}{Cp_2TiCl_2 + \mathbf{4}}$$

Instead, a 1/1 mixture of the unsubstituted titanocene dichloride and the diaminotitanocene **4** is formed. Similar observations have been made for comparable reactions of other mono-substituted titanocenes [10].

Redox potentials

The electrochemical behaviour of **2**, $\mathbf{3}^+$ PF_6^-, **4** and $\mathbf{5}^{2+}$ $2BF_4^-$ was studied by cyclic voltammetry.

The diaminoferrocene **2** has a reversible potential at $E°$ -0.23 V (SCE). This is by far the most negative potential ever measured for a ferrocene derivative [11], and is the result of the powerful π-donating character of the two dimethylamino substituents, which strongly stabilize the positive charge in the ferrocenium cation [12]. The other oxidation steps at +0.53 and +1.25 V (SCE) are irreversible under the experimental conditions (acetonitrile with 0.1 *M* $(n\text{-Bu})_4N^+$ ClO_4^- as supporting electrolyte at room temperature) (see Fig. 2).

$$\underset{(\mathbf{2})}{(C_5H_4\text{-}N(CH_3)_2)_2Fe} \rightleftharpoons \underset{(\mathbf{2}^{+\cdot})}{(C_5H_4\text{-}N(CH_3)_2)_2Fe^{+\cdot}} + e^-$$

The electrochemically formed 1,1′-bis(*N*,*N*-dimethylamino)ferrocenium radical cation ($\mathbf{2}^{+\cdot}$) is stable in the electrochemical cell for at least 24 h. The bis(ammonium)ferrocene $\mathbf{5}^{2+}$ $2BF_4^-$ has a reversible (sweep rate > 500 mV s^{-1}) redox potential at $E°$ +1.25 V (SCE).

The redox potentials of substituted ferrocenes correlate linearly with the Hammett substituent constant σ_p of the substituent [13]. As shown by the extrapolated data for $N(CH_3)_2$ (in **2**) and $\overset{+}{N}(CH_3)_3$ (in $\mathbf{5}^{2+}$ $2BF_4^-$), this also applies for these two substituents:

$$\sigma_p(N(CH_3)_2) = -0.72 \text{ (lit. data: } -0.83\ [14])$$

$$\sigma_p\left(\overset{+}{N}(CH_3)_3\right) = +0.82 \text{ (lit. data: } +0.82\ [14])$$

In the case of the 1,1′-bis(*N*,*N*-dimethylamino)cobaltocenium hexafluorophosphate ($\mathbf{3}^+$ PF_6^-) a reversible redox potential was at $E°$ −1.35 V (SCE), corresponding to reduction of the cation $\mathbf{3}^+$ PF_6^- to the cobaltocene **3**.

$$\underset{(\mathbf{3}^+PF_6^-)}{(C_5H_4\text{-}N(CH_3)_2)_2Co^+} + e^- \rightleftharpoons \underset{(\mathbf{3})}{(C_5H_4\text{-}N(CH_3)_2)_2Co}$$

The reduction potential of $\mathbf{3}^+$ PF_6^- is markedly more negative than that of the unsubstituted cobaltocenium cation ($E°$ −0.98 V (SCE)) [15], again because of the π-donating properties of the dimethylamino substituents. An irreversible oxidation of $\mathbf{3}^+$ PF_6^- was also observed. The potential depends on the sweep rate v: at $v = 100$ mV s^{-1} $E = 1.105$ V, at $v = 1000$ mV s^{-1} $E = +1.120$ V.

Normally, a tenfold increase of v is related to a $\Delta E \sim 30$ mV. The experimental

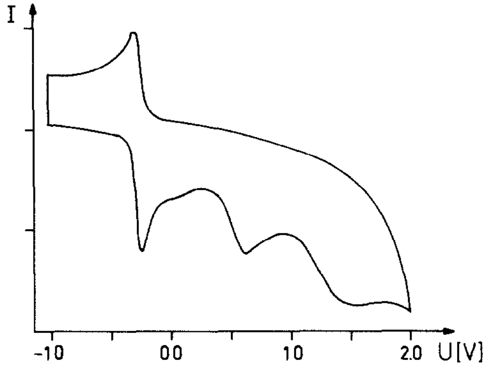


Fig. 2. Voltammogram of the bis(amino)ferrocene **2** in acetonitrile with 0.1 *M* $(n\text{-Bu})_4N^+$ ClO_4^- at room temperature vs the standard calomel electrode (SCE).

value of ΔE, however, is exactly half of that (15 mV). This could mean, that a two-electron oxidation of $3^+PF_6^-$ takes place irreversibly [16].

In the case of 1,1′-bis(*N*,*N*-dimethylamino)titanocene dichloride (**4**) the potential for the reduction of the Ti^{IV} to the Ti^{III} compound amounts to $E°$ −1.11 V (SCE). A further reduction takes place irreversibly at −1.84 V (SCE). The potentials of the unsubstituted titanocene dichloride are found at $E°$ −0.64 and −2.06 V (SCE) [17]. As in the case of **2** and 3^+ PF_6^-, the dimethylamino substituents in **4** also stabilize the higher oxidation state of titanium relative to the lower one.

4 is irreversibly oxidized at $E°$ +0.64 V (SCE).

Crystal structure of $(C_5H_4(NMe_2))_2TiCl_2$ (4)

A green-black metallic reflecting hexagonal plate was examined at room temperature (293 K) on a 4-circle X-ray diffractometer. The most important crystal and experimental data are given in Tab. 1.

A resonable density is derived by assuming the asymmetric unit to contain half a molecule. The solution of the structure by direct methods showed that the Ti atom lies on a twofold axis, the complex thus having C_2 symmetry. Full matrix refinement using anisotropic temperature factors for the non-hydrogen atoms and a common one for each group of similar H atoms converged at reliability factors of

$R_w = \Sigma\sqrt{w}\,\Delta/\Sigma\sqrt{w}\,|F_0| = 0.042$ and

TABLE 1

EXPERIMENTAL DETAILS OF THE X-RAY STRUCTURAL ANALYSIS OF BIS(*N*,*N*-DIMETHYLAMINO)TITANOCENE DICHLORIDE ($TiCl_2N_2C_{14}H_{20}$) (4)

Crystal data	
Crystal shape	hexagonal plate, 0.3×0.3×0.12 mm^3
Space group	$C2/c$, $Z = 4$
Lattice constants	a 1301.4(1) pm b 647.2(1) pm c 1828.5(3) pm β 98.81(1)°
Density	d_c 1.463 g cm^{-3}
Data collection	
Diffractometer	4-circle (CAD4, Enraf-Nonius)
Radiation	Mo-K_α, graphite-monochromated
Scan mode	ω-scan
Scan angle	$(1.0+0.35\ \mathrm{tg}\theta)°$ and 25% before and after each reflection for background measuring
Measuring time	variable, max. 15 s/reflection
Measuring range	$2° < \theta < 28°$ h: −16 to 16, k: 0 to 8, l: 0 to 23
Number of reflections measured	total: 1637; independent with $F_0 > 5\sigma$: 1175
Calculations	TR440-Computer at the Rechenzentrum der Universität Marburg
Programs	System STRUX [18] with programs CADLP [19], MULTAN [20], SHELX [21] and ORTEP [22]
Scattering factors	for neutral atoms [23], anomalous dispersion correction [24]

TABLE 2

ATOM COORDINATES FOR BIS(DIMETHYLAMINOCYCLOPENTADIENYL)TITANIUM(IV) DICHLORIDE (4) WITH E.S.D.'S IN PARENTHESES

Atom	x	y	z
Ti	0.0	0.4440(2)	0.2500
Cl	−0.1304(1)	0.2023(2)	0.2691(1)
C(1)	−0.0234(3)	0.4963(6)	0.3855(2)
C(2)	−0.0299(4)	0.6815(6)	0.3436(2)
H(2)	−0.083(4)	0.755(7)	0.334(2)
C(3)	0.0680(5)	0.7189(8)	0.3231(2)
H(3)	0.085(4)	0.823(7)	0.302(2)
C(4)	0.1308(4)	0.5516(9)	0.3436(2)
H(4)	0.194(4)	0.513(7)	0.334(2)
C(5)	0.0744(3)	0.4070(7)	0.3791(2)
H(5)	0.095(3)	0.277(7)	0.396(2)
N	−0.0957(3)	0.4225(6)	0.4241(2)
C(6)	−0.0830(5)	0.2229(9)	0.4588(3)
H(61)	−0.112(5)	0.218(11)	0.502(4)
H(62)	−0.017(5)	0.203(11)	0.485(4)
H(63)	−0.100(6)	0.121(11)	0.430(4)
C(7)	−0.1968(4)	0.5223(10)	0.4181(4)
H(71)	−0.227(5)	0.490(11)	0.459(3)
H(72)	−0.190(5)	0.675(11)	0.422(4)
H(73)	−0.234(5)	0.508(10)	0.363(4)

$$R_g = \left\{ \Sigma w\Delta^2 / \Sigma w F_0^2 \right\}^{1/2} = 0.043 \;*$$

with $\Delta = ||F_0| - |F_c||$ and weights $w = 1.65/\sigma^2(F_0)$ (σ = e.s.d.'s from counting statistics). The maximal parameter shift in the last refinement cycle was 0.4% of the e.s.d., and the maximal and minimal peak heights on a final difference Fourier map were 0.41 and 0.28 e Å^{-3}, respectively.

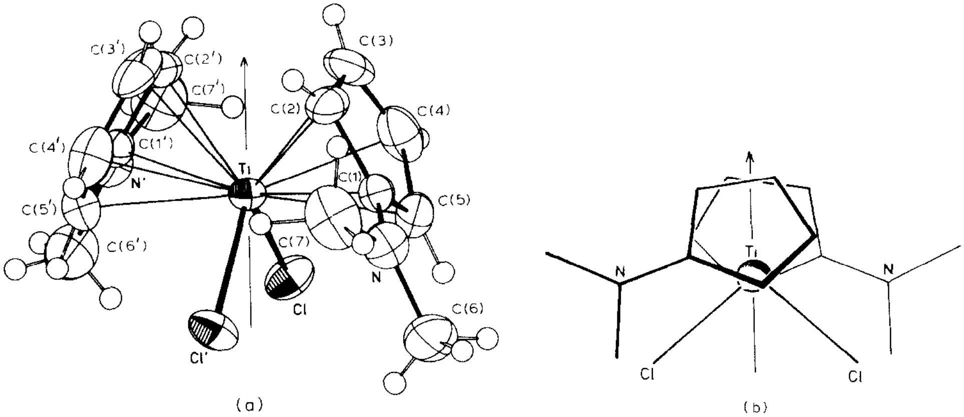


Fig. 3(a) ORTEP drawing of the structure of **4** in the crystal (50% probability plots for thermal ellipsoids). H atoms with artificially small radii. C_2 axis in the drawing plane. (b) Projection on the $TiCl_2$ plane.

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* Lists of structure factors and thermal parameters may be obtained from the authors.

TABLE 3

BOND LENGTHS (pm) AND BOND ANGLES (°) IN **4** WITH E.S.D.'S IN PARENTHESES

Ti-Cl	237.3(1)	Cl-Ti-Cl′	97.5(1)
Ti-C(1)	256.4(4)	C(2)-C(1)-C(5)	106.3(4)
Ti-C(2)	237.6(4)	N-C(1)-C(2)	126.5(4)
Ti-C(3)	231.8(4)	N-C(1)-C(5)	127.2(4)
Ti-C(4)	232.9(4)	C(1)-C(2)-C(3)	108.0(4)
Ti-C(5)	242.3(4)	C(2)-C(3)-C(4)	108.6(4)
average Ti-C	240.2	C(3)-C(4)-C(5)	108.6(4)
		C(4)-C(5)-C(1)	107.7(4)
C(1)-C(2)	141.8(5)	average in the ring	107.8
C(1)-C(5)	141.9(6)		
C(2)-C(3)	140.3(7)	C(1)-N-C(6)	120.5(4)
C(3)-C(4)	137.4(7)	C(1)-N-C(7)	119.9(5)
C(4)-C(5)	140.8(6)	C(6)-N-C(7)	118.3(5)
average C-C	140.4	*short intramolecular contacts*	
N-C(1)	134.7(5)	Ti ··· N	359.3
N-C(6)	143.8(6)	Cl ··· N	314.2
N-C(7)	145.5(6)	H(2) ··· H(3′)	253
		C(2) ··· C(3′)	302.2
		C(3) ··· C(3′)	297.2

The resulting atomic coordinates are given in Tab. 2. The bond lengths and angles are shown in Tab. 3 (values including H atoms are omitted). The molecular structure is shown from two perspectives in Figs. 3a and 3b.

TABLE 4

DISTANCES (pm) FROM "BEST PLANES" THROUGH THE ATOMS MARKED BY AN *, AND DIHEDRAL ANGLES

Plane **1** (Cyclopentadienyl)		Plane **2** (TiCl$_2$)	
C(1)*	−5.3	Ti*	0
C(2)*	4.8	Cl*	0
C(3)*	−2.4	Cl′*	0
C(4)*	−1.0		
C(5)*	3.9	Plane **3** (C-(N)Me$_2$)	
N	−21.6	C(1)*	0
C(6)	−18.4	C(6)*	0
C(7)	−14.5	C(7)*	0
Ti	207.4	N	−9.2
		C(2)	3.7
		C(5)	6.3
Dihedral angles (°)			
1-1′[a]	125.7	**1-2**	27.3
1-3	176.8	**1′-2**	27.3

[a] Equivalent plane generated by the 2-fold axis.

TABLE 5

COMPARISON OF SOME GEOMETRIC DATA OF $(C_5H_5)_2TiCl_2$ [25], $(C_5H_4CH_3)_2TiCl_2$ [26] AND $(C_5H_4N(CH_3)_2)_2TiCl_2$ (averaged, in pm and °)

	$(C_5H_5)_2TiCl_2$	$(C_5H_4CH_3)_2TiCl_2$	$(C_5H_4N(CH_3)_2)_2TiCl_2$
Ti-Cp[a]	205.9	206.7	207.4[b] 217.9[c]
Ti-C	237.0	231.7	240.2
Ti-Cl	236.4	236.1	237.3
Cl-Ti-Cl	94.5	93.2	97.5
Cp-Ti-Cp	131.0	130.2	125.7[b] 135.7[c]

[a] Center of the C_5H_5 ring. [b] Normal to the ring (foot not in the center). [c] Distance to the ring center.

Discussion of the structure of 4

The titanium atom in **4**, as in $(C_5H_5)_2TiCl_2$ [25] and $(C_5H_4CH_3)_2TiCl_2$ [26], is quasi-tetrahedrally surrounded by the two (substituted) cyclopentadienyl rings and the two chlorine atoms. The dihedral angle of the two $C_5H_4N(CH_3)_2$ rings is 125.7°, and the Cl–Ti–Cl angle is 97.5° (Fig. 3(a)). In contrast to the situation in $(C_5H_5)_2TiCl_2$ and $(C_5H_4CH_3)_2TiCl_2$, however, the metal atom is not situated exactly above the center of the five carbon atoms of the $C_5H_4N(CH_3)_2$ ring. The distances of the ring carbon atoms C(1)–C(5) to the titanium atom clearly show the shorter distances to C(3) and C(4) (Tab. 3). This effect is also demonstrated by the rather short distance of Ti from the ring plane (207.4 pm) (Tab. 4) compared with its distance from the center of the ring (217.9 pm) (Tab. 5).

The $C_5H_4N(CH_3)_2$ rings are slightly distorted from planarity (Tab. 4), and the dimethylamino groups are slightly bent out of the plane of the ring carbon atoms, away from Ti: the nitrogen atom is 9.2 pm above the plane of C(1)–C(6)–C(7). The distance from a nitrogen to a chlorine atom (314.2 pm) is less than the sum of the relevant Van der Waals radii (330 pm).

The C(1)–N distance (134.7 pm) is remarkably short, and in fact, is as short as the CN ("double") bond in amides. This indicates that the free electron pair at the nitrogen atom is strongly engaged in stabilizing the 16 electron Ti complex. This observation is in accord with the resistance of **4** towards alkylation. As in amides [27], therefore, the rotation around the C(1)–N bond in **4** must be hindered because of its considerable double bond character. The donor–acceptor relationship in the bis(dimethylamino)titanocene **4** thus is "umgepolt" compared to that in an α-ferrocenylcarbenium ion [28]. In the latter case the d^{18}-electron metallocene, which is a powerful electron donor, strongly stabilizes the exocyclic positive charge. As a result of that, the rotation around the C–C bond to the α-carbon atom is hindered [28]. It thus seems likely that α-titanocenyl carbanions are also stabilized species, with a hindered rotation around the exocyclic C–C bond.

Herberhold [29] has recently described triferrocenylamine, which has also a nearly planar nitrogen atom (N is 6 pm out of the plane). The N–C distances are 141.4 pm, slightly shorter than in trimethylamine (145.1 pm) [30] but much longer than in **4**. This clearly shows the difference between the C(1)–N bond in the titanocene **4** compared with the same bond in an amino substituted d^{18}-electron ferrocene.

Experimental

^{1}H and ^{13}C NMR spectra: JEOL FX-100; IR spectra: Perkin-Elmer 437, UV/VIS spectra: Beckmann Acta III; Mass spectra: Varian Match 7; melting points are uncorrected.

All reactions with metallorganic reagents were performed under nitrogen or argon. *N,N*-Dimethylamino-cyclopentadienyllithium (**1**-Li) was prepared according to a published method [5]; the colourless crystals are stable under argon in the refrigerator. NMR data are listed in Tab. 6.

1,1'-Bis(N,N-dimethylamino)ferrocene (2)

To 0.66 g (5.21 mmol) of water-free iron(II) chloride suspended in 30 ml THF, a solution of 1.50 g (13.0 mmol) **1**-Li in 30 ml THF was added at −30 °C during 1 h, forming a brown solution. After being allowed to warm to room temperature overnight, the solution was evaporated, finally at 10^{-3} Torr. The dark brown residue was extracted with pentane until the solvent remained colourles, then the pentane solution was concentrated and kept at −75 °C to give orange red crystals of **2**. **2** is rather air sensitive (the colour changes to brown); 0.46 g (33%). M.p. 66 °C.

IR (KBr): ν(cm^{-1}) 3120 und 2900 (ν(C–H)); 1560, 1440, 1420 and (ω(C–H)); 1080; 1050; 980 (δ(C–H)); 860; 810 (γ(C–H)); 780; 650. UV (MeOH): λ_{max} (nm) (ϵ) 214 (18130), 285 (6280), 322 (6950), 433 (2560) MS: $m/e = 272$ (100%, M^+), 229 (86%, $M^+ - C_2H_5N$).

Found: C, 61.80; H, 7.35; N, 10.15. $C_{14}H_{20}FeN_2$ (272.2) calcd.: C, 61.78; H, 7.41; N, 10.29%.

1,1'-Bis(N,N-dimethylamino)ferrocene methyl iodide (5^+ I^-)

A solution of 0.50 g (1.84 mmol) of **2** in 20 ml diethyl ether was treated with 1.02 g (3.60 mmol) of methyl iodide at room temperature. The orange crystals obtained were recrystallized from ethanol/ether, to gave the red $\mathbf{5}^+$ I$^-$. (0.54 g, 72%), m.p. 180 °C (decomp.).

UV (MeOH): λ_{max}(nm) (ϵ) 221 (30220), 304 (4630). MS: $m/e = M^+$ (0%), 272 (100%, $(C_5H_4N(CH_3)_2)_2Fe^+$) 141 (40%, CH_3I^+).

Found: C, 43.37; H, 5.65; N, 6.76. $C_{15}H_{23}FeIN_2$ (414.1) calcd.: C, 43.51; H, 5.60; N, 6.76%.

1,1'-Bis(N,N-dimethylamino)ferrocene dimethyl diiodide (5^{2+} $2I^-$)

A solution of 0.11 g (0.40 mmol) **2** in 15 ml diethyl ether was heated under reflux for 4 h with 1.25 g (4.40 mmol) methyl iodide. The light brown crystals were washed with ether to give 0.21 g (95%) of $\mathbf{5}^{2+}$ 2I$^-$. M.p. 170 °C (decomp.).

UV (CH$_3$CN): λ_{max} (nm) (ϵ) 208 (24500), 233 (sh, 5250), 268 (sh, 2520). MS: $m/e = M^+$ (0%), 272 (98%, $(C_5H_4N(CH_3)_2)_2Fe^+$), 142 (100%, CH_3I^+), 108 (42%, $C_5H_4N(CH_3)_2{}^+$).

Found: C, 34.77; H, 4.76; N, 5.03. $C_{16}H_{26}FeN_2$ (555.5) calcd.: C, 34.56; H, 4.71; N, 5.05%.

1,1'-Bis(N,N,N-trimethylammonium)ferrocene bis(tetrafluoroborate) (5^{2+} $2BF_4^-$)

A solution of 0.50 g (3.40 mmol) trimethyloxonium tetrafluoroborate in 8 ml nitromethane was added at room temperature with stirring to 0.46 g (1.70 mmol) of

TABLE 6

^{1}H AND ^{13}C NMR SPECTROSCOPIC DATA FOR SOME METALLOCENES (chemical shifts δ in ppm relative to internal tetramethylsilane))

Compound	^{1}H NMR					^{13}C NMR					Solvent
	H(2,5)	H(3,4)	H(ring)	N–CH$_3$	Ref.	C(1)	C(2,5)	C(3,4)	N–CH$_3$	Ref.	
$(C_5H_5)_2Fe$	–	–	4.05	–	31	67.9	67.9	67.9	–	32	$CDCl_3$
Aminoferrocene	3.80	3.70	3.95	–	31	104.4	59.0	63.2	–	32	$CDCl_3$
2	4.07	3.77	–	2.33		115.2	54.7	62.3	42.4		$CDCl_3$
5$^+$ I$^-$	4.48	4.06	–	2.50		117.7	55.8	65.3	42.0		DMSO-d_6
	4.71	4.18	–	3.41		–[a]	59.3	65.5	57.0		
5^{2+} 2I$^-$	5.20	4.92	–	3.62		112.6	62.6	69.2	56.9		DMSO-d_6
Cp_2Co^+ PF_6^-	–	–	5.96	–	33						$CDCl_3/CF_3COOH$
Aminocobaltocenium hexafluorophosphate	5.46	5.38	5.48	–	33						$CDCl_3/CF_3COOH$
1,1′-Bis-aminocobaltocenium hexafluorophosphate	5.22	5.06	–	–	33						$CDCl_3/CF_3COOH$
3$^+$ PF_6^-	5.59	5.37	–	3.03		124.7	69.3	81.2	44.5		$CDCl_3/CF_3COOH$
Cp_2TiCl_2	–	–	6.58	–	34	120.0	120.0	120.0	–	35	$CDCl_3$
4	6.12	5.46	–	3.00		157.8	95.0	114.1	39.8		$CDCl_3$
1-Li	5.33	5.15	–	2.55		139.2	90.5	99.3	44.1		THF-d_8

[a] No signal found.

2 in 30 ml diethyl ether. An orange-coloured precipitation was immediately formed. This was washed with ether and dried, to give 0.73 g (90%) of crude $\mathbf{5}^{2+}$ $2BF_4^-$. Recrystallization from acetonitril/ethyl acetate gave 0.64 (79%) of orange crystals. M.p. 155 °C (decomp.).

Found: C, 40.64; H, 5.44; N, 6.02. $C_{16}H_{26}B_2F_8FeN_2$ (475.8) calcd.: C, 40.39; H, 5.51; N, 5.89%.

Use of 1/1 ratio of **2** and $(CH_3)_3O^+$ BF_4^- did not give the monomethylated product; instead $\mathbf{5}^{2+}$ $2BF_4^-$ was isolated in lower yield (20%).

1,1′-Bis(N,N-dimethylamino)cobaltocenium hexafluorophosphate (3^+ PF_6^-)

To a solution of 2.10 g (18.2 mmol) of **1**-Li in 40 ml THF, 1.56 g (12.0 mmol) of cobalt(II) chloride was added with stirring at −30 °C. The mixture was allowed to warm to room temperature overnight then treated with 2 *N* HCl. Extraction with diethyl ether followed by filtration of the aqueous phase through charcoal and addition of 3.00 g (16.3 mmol) of potassium hexafluorophosphate gave 1.43 g (38%) $\mathbf{3}^+$ PF_6^- (which crystallized from 30 ml of the solution). Recrystallization (chloroform/acetone) yielded 1.10 (29%) of the red $\mathbf{3}^+$ PF_6^- as a red-brown powder, m.p. 145 °C (decomp.).

IR (KBr): $\nu(\mathrm{cm}^{-1})$ 3150, 3000, 2910 (ν(C–H)); 1540; 1420 (ω(C–H)); 1180; 1140; 1060 (δ(C–H)); 810 (γ(C–H)). UV(MeOH): $\lambda_{\max}$(nm) (ϵ) = 208 (17710), 241 (sh, 7350), 269 (sh, 4730), 342 (14160), 415 (sh, 3700). MS: $m/e = 275$ (100%, M^+), 108 (55%, $C_5H_4N(CH_3)_2^+$)

Found: C, 40.33; H, 4.84; N, 6.34. $C_{14}H_{20}CoF_6N_2P$ (420.2) calcd.: C, 40.02; H, 4.80; N, 6.67%.

1,1′-Bis(N,N-dimethylamino)titanocene dichloride (4)

A solution of 2.46 g (13.0 mmol) of titanium tetrachloride in 15 ml pentane was added at −30 °C with stirring to 2.97 g (25.8 mmol) of **1**-Li in 60 ml THF. The brown solution was kept at −30 °C for 1 h then allowed to warm to room temperature overnight. After removal of the solvent the residue was extracted with 250 ml chloroform in a Soxlet apparatus. Compound **4** crystallized from 20 ml of chloroform solution at −78 °C as green-black crystals (1.30 g (30%)). Mp. 225 °C (decomp.).

IR (KBr): $\nu(\mathrm{cm}^{-1})$ 3080, 2950, 2850 and 2790 (ν(C–H)); 1510; 1430 (ω(C–H)); 1390; 1190; 1140; 1050 and 1030 (δ(C–H)); 960; 800(ν(C–H)); 600.

UV(CH_3CN): $\lambda_{\max}$ (nm) (ϵ) 206 (24520), 259(14880) 360 (10790), 550 (270). MS: $m/e = 338$ (6%, $M^+ + 4$), 336 (29%, $M^+ + 2$), 334 (42%, M^+), 108 (100%, $C_5H_4N(CH_3)_2{}^+$)

Found: C, 50.32; H, 6.14; N, 8.28. $C_{14}H_{20}Cl_2N_2Ti$ (335.1) calcd.: C, 50.18; H, 6.02; N, 8.34%.

The reaction of 4 with methylating agents

Methyl iodide (14.2 g, 0.10 mol) was added with stirring at room temperature to 1.49 mmol of **4** in 40 ml chloroform. After 3 h the solvent and methyl iodide were removed, leaving only unchanged **4** (^{1}H NMR). (When the procedure was repeated at the reflux temperature an unidentified red brown product was formed.) Similar results were obtained with one molar equivalent of trimethyloxonium fluoroborate and methyl trifluoromethylsulfonate at room temperature.

The reaction of 1-Li with cyclopentadienyltitanium trichloride

To 1.80 g (15.6 mmol) of **1**-Li in 40 ml THF a solution of 3.43 g (15.6 mmol) cyclopentadienyltitanium trichloride in 25 ml THF was added at −30 °C. After 12 h room temperature the solvent was removed and the dark brown residue extracted 7 times with 60 ml chloroform. After removal of most of the solvent some pentane was added, and this gave 1.43 g of a precipitate. Recrystallization from chloroform yielded 0.7 g (14%) of **4**. The chloroform solution contained 0.7 g (19%) of titanocene dichloride.

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