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Synthesis and structural features of [$(C_5H_4–CMe_2NMe_2)_2TiCl$], a bis(cyclopentadienyl)Ti(III) complex with internal dimethylamino coordination

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Abstract

Treatment of 6-dimethylamino-6-methylfulvene (**1**) with methyllithium gave the [$C_5H_4–CMe_2–NMe_2$]Li product (**2**) that was characterized by X-ray diffraction. Compound **2** features an oligomeric chain structure with the [$C_5H_4–CMe_2–NMe_2$] unit serving as a bridging ligand using its Cp anion moiety and the –NMe_2 donor functionality. Treatment of **2** with $FeCl_2$ yielded the substituted ferrocene **3**. The corresponding reaction of **2** with $TiCl_4(THF)_2$ gave the titanocene complex $(C_5H_4–CMe_2–NMe_2)_2TiCl_2$ (**4**) that exhibits an ordinary bent metallocene structure in the solid state without involvement of the pendant –$CMe_2–NMe_2$ donor ligands. In contrast, the titanium(III) complex $(C_5H_4–CMe_2–NMe_2)_2TiCl$ (**5**), obtained from the reaction of **2** with $TiCl_3(THF)_3$, has one of the two nitrogen donors strongly coordinated to the metal center. In the crystal, complex **5** thus attains a typical pseudotetrahedral Group 4 bent metallocene structure, as shown by an X-ray crystal structure analysis.

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Keywords: Functionalized cyclopentadienides; Bent metallocenes; Ferrocenes; Intramolecular coordination

1. Introduction

The (dimethylaminomethyl)cyclopentadienyl ligand family [$C_5H_4–CR^1R^2–NMe_2$]$^-$ shows some very special structural and chemical properties. When coordinated to a sufficiently Lewis acidic metal center, it tends to have the pendant –NMe_2 functional group involved in the coordination. The oligomeric chain structures of some [$C_5H_4–CHR–NMe_2$]Li compounds represent such examples [1]. In the respective zirconocene chloride cations [$(C_5H_4–CMe_2–NMe_2)_2ZrCl$]$^+$, we have found a symmetrical twofold intramolecular –NMe_2 coordination by X-ray diffraction [2,3]. The corresponding [$(C_5H_4–CMe_2–NMe_2)_2ZrCH_3$]$^+$ cation and related examples are even unstable due to a rapid CH_4 extrusion by means of CH activation at the α-position to nitrogen [4]. In contrast, the 16-electron $(C_5H_4–CR_2–NMe_2)_2ZrCl_2$ complexes show normal bent metallocene structures that have the pendant dimethylamino group not involved in the ligand interaction with the mildly electrophilic Group 4 metal [2–4]. We have now characterized a series of $(C_5H_4–CMe_2–NMe_2)$M complexes, involving M = Li, Fe, Ti(IV) and Ti(III), by X-ray diffraction and found some remarkable principal differences in the coordinative features of the bifunctional [$C_5H_4–CMe_2–NMe_2$]$^-$ ligand in these examples.

2. Results and discussion

2.1. Syntheses

The [$C_5H_4–CMe_2–NMe_2$]$^-$ ligand system was prepared as previously described by us [4]. 6-Dimethylamino-6-methylfulvene (**1**) [5] was treated with methyllithium in ether to yield the ([$C_5H_4–CMe_2–NMe_2$]Li)$_n$ system (**2**). Crystals of **2** that were suited for the X-ray crystal structure analysis (see below) were obtained by slow solvent evaporation from a saturated diethylether solution. Treatment of **2** with $FeCl_2$ gave 1,1′-bis(dimethylamino-1-methylethyl)ferrocene (**3**, 50%

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[1] X-ray crystal structure analyses.

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isolated) [6]. Complex **3** shows very typical NMR features [^{1}H: δ 3.61 (s, 12H, CMe_2), 4.10 (s, 12H, NMe_2), 6.15 (m, 8H, C_5H_4); ^{13}C: δ 69.5, 70.0, 93.6 (C_5H_4), 57.9, 27.5 (CMe_2) and 40.5 (NMe_2)]. Single crystals for the X-ray crystal structure determination of **3** were obtained from a pentane–toluene solution at −30 °C.

The titanium complex $[C_5H_4–CMe_2–NMe_2]_2TiCl_2$ (**4**) was prepared by treatment of **2** with $TiCl_4(THF)_2$ [7]. Recrystallization from pentane gave suitable crystals for the X-ray crystal structure analysis of this Ti(IV) bent metallocene complex. Similarly, the reaction of **2** with $TiCl_3(THF)_3$ furnished the corresponding Ti(III) complex **5** as a very air- and moisture-sensitive green solid (75% isolated) that was also characterized by X-ray diffraction (single crystals obtained by slow diffusion of pentane into saturated toluene solution of **5**) [8] (Scheme 1).

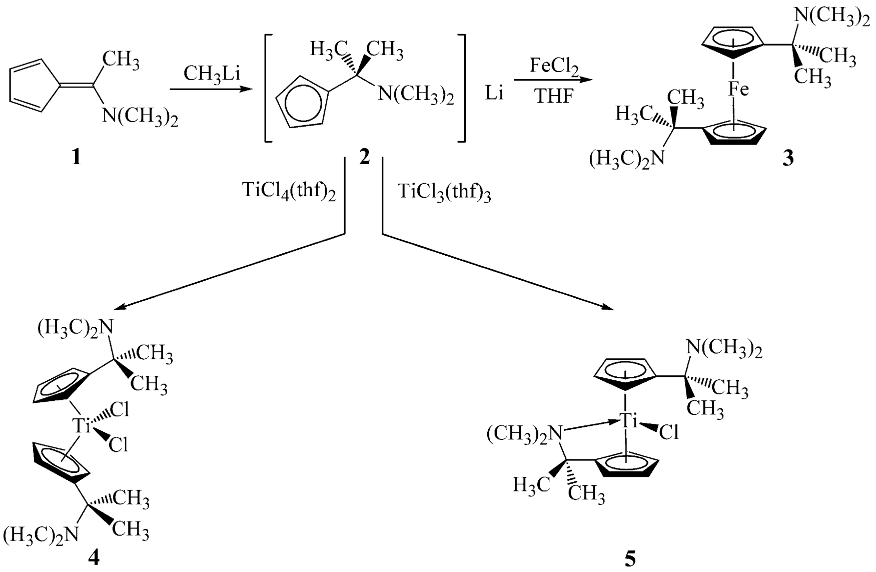
2.2. X-ray crystal structure analyses

^{R}CpLi complexes (R = alkyl or functionalized alkyl) can attain a variety of structures ranging from ligand-stabilized mononuclear half-sandwiches through mixed intermediate types all the way to polymeric super-sandwich structures [9,10]. Lithium salt **2** is oligomeric in the crystal. It adopts an unsymmetrical "$(Cp–Li)_n$" structural-type, similarly as it was recently described by us for differently substituted examples [1]. The superstructure of **2** can be thought as constructed of superimposed inverse lithiocene cation moieties (i.e. $[Li–(^RCp)–Li]^+$) with strongly distorted bent lithiocene anions (i.e. $[^RCp–Li–^RCp]^-$) under involvement of a strongly coordinating $–NMe_2$ group (see Fig. 1).

The lithium atom in **2** is (electrostatically [11]) uniformly η^5-coordinated to the Cp-ring of an adjacent $[C_5H_4–CMe_2–NMe_2]$ ligand [with Li–C(1–5) distances ranging from 2.227(3) to 2.261(3) Å]. The lithium atom is also coordinated to the NMe_2 nitrogen atom of the next $[C_5H_4–CMe_2–NMe_2]$ ligand. In addition, there is a short contact between Li and one of the Cp-carbon atoms of that ligand [Li–C2*: 2.667(3) Å] that complements the coordination environment around the lithium atom. The Li–Cp*(centroid)–Li* angle is 124.1°. The Cp(centroid)–Li–Cp*(centroid) moiety is also bent (144.5°). The Li–N* distance in **2** amounts to 2.045(3) Å, the C6*–N*–Li angle is 108.4(1)°.

The substituted ferrocene **3** shows two slightly unsymmetrically bound substituted Cp-ligands in the crystal (two independent molecules are present). The Fe–C1 and Fe–C11 bonds to the substituted C(Cp) atom are slightly longer at 2.080(2) and 2.078(2) Å than the remaining Fe–C(Cp) distances, which are in a range between 2.042(2) and 2.058(2) Å. The $Cp–CMe_2$ vectors are oriented antiperiplanar at the ferrocene moiety [12]. The adjacent $–CMe_2–NMe_2$ vectors both point away from the central metal atom (see Fig. 2). The nitrogen atoms are pyramidal (sum of the C–N bonding angles at N1 and N2: 337.0° and 337.1°).

The structure of the Ti(IV) bent metallocene **4** will serve as a reference for a comparison with the new Ti(III) complex (**5**, see below). The structure of the titanocene dichloride derivative bears some principal relationship with that of the ferrocene complex **3** despite the fact that the Cp(centroid)–Ti–Cp(centroid) unit (131.3°) is, of course, bent. As in **3** the metal to Cp(C1–C11) distances in **4** (Ti–C1: 2.528(2) Å; Ti–C11: 2.493(2) Å) are slightly longer than the remaining



Scheme 1.

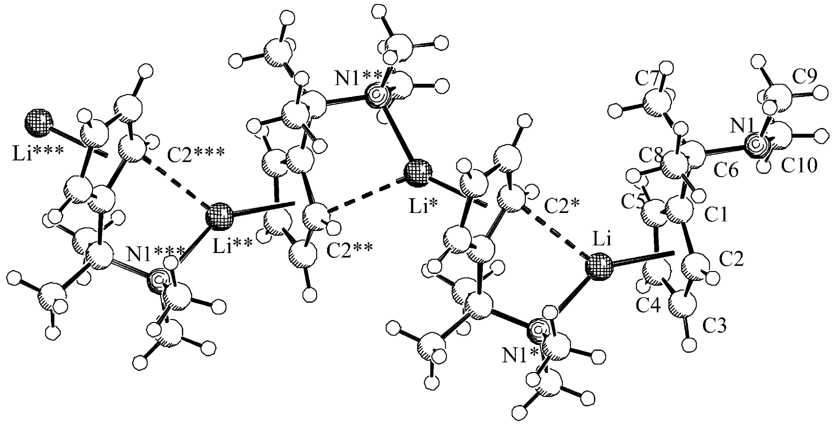


Fig. 1. A view of the oligomeric chain structure of **2**. Selected bond lengths (Å): Li–N1*, 2.045(3); Li–C1, 2.261(3); Li–C2, 2.230(3); Li–C3, 2.227(3); Li–C4, 2.230(4); Li–C5, 2.251(4); Li–C2*, 2.667(3); C1–C6, 1.512(2); C6–N1, 1.517(2). Selected bond angles (°): C2*–Li–N1*, 82.3(1); Li–N1*–C6*, 108.4(1); N1–C6–C1, 106.5(1).

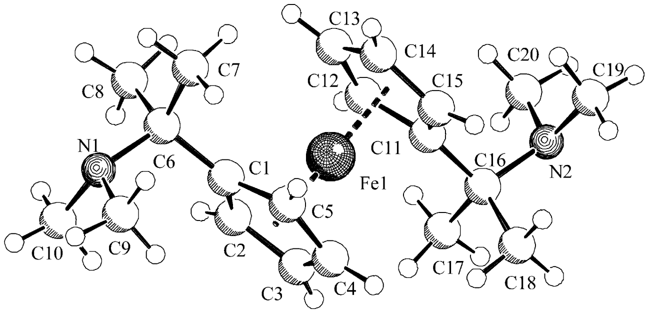


Fig. 2. Projection of the molecular structure of **3** in the crystal. Selected bond lengths (Å) (values from molecule A): Fe–C1, 2.080(2); Fe–C11, 2.078(2); Fe–C2, 2.058(2); Fe–C12, 2.052(2); Fe–C3, 2.047(2); Fe–C13, 2.042(2); Fe–C4, 2.045(2); Fe–C14, 2.049(2); Fe–C5, 2.048(2); Fe–C15, 2.053(2); Fe–Cp(centroid)1, 1.661; Fe–Cp(centroid)2, 1.663; C1–C6, 1.516(3); C11–C16, 1.524(3); C6–N1, 1.504(3); C16–N2, 1.498(3); N1–C9, 1.455(3); N2–C19, 1.455(3); N1–C10, 1.468(3); N2–C20, 1.465(3). Selected bond angles (°) (values from molecule A): Cp(centroid)1–Fe–Cp(centroid)2, 178.5; C1–C6–N1, 111.4(2); C11–C16–N2, 111.5(2); C6–N1–C9, 114.7(2); C16–N2–C19, 114.4(2); C6–N1–C10, 114.0(2); C16–N2–C20, 114.4(2); C9–N1–C10, 108.3(2); C19–N2–C20, 108.3(2).

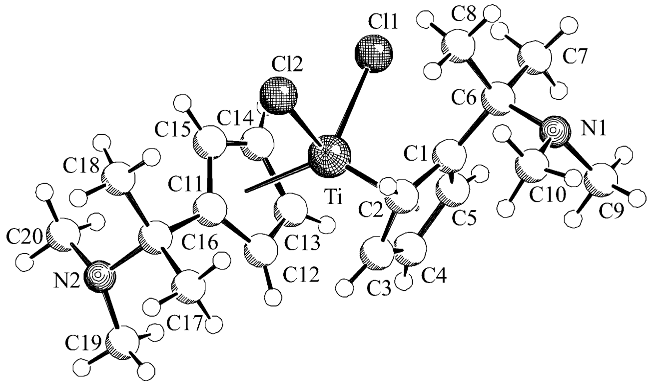


Fig. 3. Molecular structure of **4**. Selected bond lengths (Å): Ti–Cl1, 2.372(1); Ti–Cl2, 2.357(1); Ti–C1, 2.528(2); Ti–C11, 2.493(2); Ti–C2, 2.431(2); Ti–C12, 2.393(2); Ti–C3, 2.326(2); Ti–C13, 2.327(2); Ti–C4, 2.342(2); Ti–C14, 2.394(2); Ti–C5, 2.436(2); Ti–C15, 2.446(2); Ti–Cp(centroid)1, 2.095; Ti–Cp(centroid)2, 2.092; C1–C6, 1.529(3); C11–C16, 1.528(3); C6–N1, 1.498(3); C16–N2, 1.496(3); N1–C9, 1.457(3); N2–C19, 1.458(3); N1–C10, 1.463(3); N2–C20, 1.461(3). Selected bond angles (°): Cl1–Ti–Cl2, 94.87(2); Cp(centroid)1–Ti–Cp(centroid)2, 131.3; C1–C6–N1, 109.2(2); C11–C16–N2, 109.0(2); C6–N1–C9, 115.1(2); C16–N2–C19, 115.4(2); C6–N1–C10, 116.0(2); C16–N2–C20, 114.5(2); C9–N1–C10, 108.4(2); C19–N2–C20, 108.8(2).

Ti–C(Cp) distances which are in a range between 2.326(2) and 2.446(2) Å. Both the C–NMe_2 vectors in **4** are pointing away from the central Group 4 metal center (dihedral angles θ C2–C1–C6–N1: 70.4(2)° and θ C12–C11–C16–N2: −73.3(2)°). However, the metallocene conformation in **4** is different from **3**, and different from its related $[C_5H_4–CR^1R^2–NMe_2]_2ZrX_2$ relatives, that were described in the literature [4]. The latter exhibit antiperiplanar metallocene conformations with the Cp–CR_2 vectors being grossly oriented towards the lateral sectors of the bent metallocene wedge. This is different in the titanocene derivative **4**: one of the substituents (C16) is oriented towards a lateral sector whereas the other one (C6) is positioned towards the front side of the bent metallocene wedge (see Fig. 3) [13]. The Cl1–Ti–Cl2 angle in **4** amounts to 94.87(2)°, the Ti–Cl bond lengths are in the usual range at 2.372(1) Å (Ti–Cl1) and 2.357(1) Å (Ti–Cl2). Both nitrogen atoms exhibit a pyramidal structure with sums of C–N bonding angles of 339.5° (N1) and 338.7° (N2), respectively. The adjacent N1–C6–C1 (109.2(2)°) and N2–C16–C11 (109.0(2)°) angles are almost ideally tetrahedral.

The structural features of the titanium(III) complex **5** (Fig. 4) are markedly different. Again, there are two $[C_5H_4–CMe_2–NMe_2]$ ligands bonded to titanium; one of the ligands (C6–C10) is similarly η^5-coordinated to the central Group 4 metal center as it was found in **4**. The Ti–C(ipso) distance (Ti–C6: 2.443(2) Å) is slightly elongated with the remaining Ti–C(Cp) bond lengths

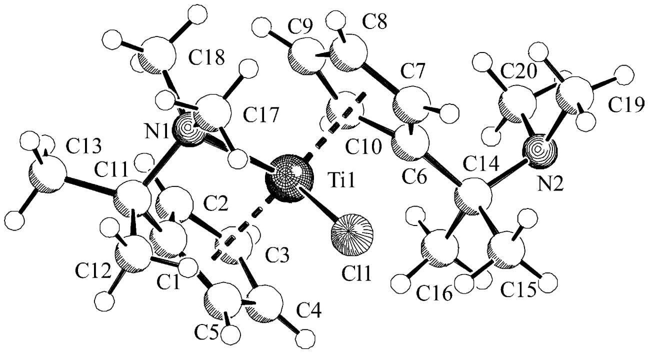


Fig. 4. A view of the molecular structure of the Ti(III) complex **5**. Selected bond lengths (Å): Ti–Cl1, 2.456(1); Ti–N1, 2.420(2); Ti–C1, 2.322(2); Ti–C6, 2.443(2); Ti–C2, 2.326(2); Ti–C7, 2.439(2); Ti–C3, 2.378(2); Ti–C8, 2.383(3); Ti–C4, 2.411(2); Ti–C9, 2.350(3); Ti–C5, 2.394(2); Ti–C10, 2.380(2); Ti–Cp(centroid)1, 2.041; Ti–Cp(centroid)2, 2.079; C1–C11, 1.511(3); C6–C14, 1.530(3); C11–N1, 1.549(3); C14–N2, 1.495(3); N1–C17, 1.488(3); N2–C19, 1.434(4); N1–C18, 1.483(3); N2–C20, 1.451(4). Selected bond angles (°): Cl1–Ti–N1, 86.49(5); Cp(centroid)1–Ti–Cp(centroid)2, 137.6; C1–C11–N1, 100.8(2); C6–C14–N2, 111.8(2); C11–N1–C17, 114.6(2); C14–N2–C19, 114.9(2); C11–N1–C18, 112.2(2); C14–N2–C20, 113.4(2); C17–N1–C18, 105.4(2); C19–N2–C20, 108.5(3).

being in the range between 2.350(3) and 2.439(2) Å. In this ligand the C–NMe$_2$ vector (C14–N2) is again pointing away from the metal center of the molecule (angle C6–C14–N2, 111.8(2)°). The second [C$_5$H$_4$–CMe$_2$–NMe$_2$] ligand in **5** is η^5-Cp,κN-coordinated through the cyclopentadienide carbon centers C1 to C5 and the nitrogen center N1. Consequently, the overall structural features of this ligand are quite different. The C11–N1 vector is oriented towards the metal-containing center of the molecule to allow for a strong N1–Ti (2.420(2) Å) interaction. The C1–C11–N1 angle amounts to 100.8(2)°. The internal C11–N1–Ti angle inside the resulting metallacycle is very small at 96.2(1)°. The remaining C18–N1–Ti (110.0(1)°) and C17–N1–Ti (118.5(2)°) are substantially different to allow for a minimal staggering of the substituents inside the metallacycle (dihedral angles θ C12–C11–N1–C17, −20.6(3)° and θ C12–C11–N1–C18, −140.8(2)°). Contrary to the other [C$_5$H$_4$–CMe$_2$–NMe$_2$]Ti unit, the Ti–C(ipso) (Ti–C1: 2.322(2) Å) of the metallacyclic subunit is slightly shorter than the remaining Ti–C(Cp) bonds (range: 2.326(2)–2.411(2) Å). The Ti–Cl1 bond in **5** (2.456(1) Å) is by ca. 0.1 Å longer than in **4** (see above) and the N1–Ti–Cl angle in **5** (86.49(5)°) is by $>8°$ smaller than the Cl–Ti–Cl angle in **4**.

3. Conclusions

The Ti(IV) complex **4** formally contains a coordinatively unsaturated 16-electron metal center. In principle it could, therefore, accommodate one of the pendant –NR$_2$ donor ligands using its laterally extending metal acceptor orbital [14]. Similarly as found in the corresponding neutral zirconium(IV) complexes, the titanium(IV) center in **4** is apparently not Lewis acidic enough to serve as a suitable binding site. This seems to be different in the titanium(III) complex **5**. Although one metal centered orbital is occupied by one electron, the electrophilicity of the system is just sufficient to bind the available amino donor ligand. As judged from the comparison of the Ti–Cl bond lengths, the overall bonding of the σ-ligands in **5** using the NMe$_2$ donor is slightly weaker as compared with **4**. The N–Ti–Cl angle in **5** is smaller by ca. 8° than the Cl–Ti–Cl angle in **4**, which possibly indicates an electron repulsion between the bonding electrons of the σ-ligands and the single electron in the laterally extending metal centered (SOMO) molecular orbital in the titanium(III) complex **5** [15,16]. The observed internal –NMe$_2$ coordination in **5**, but not in **4**, indicates the increased electrophilicity of the Ti(III) center and thus places such paramagnetic Group 4 metallocenes in an intermediate position between the weakly Lewis acidic neutral (^{R}Cp)$_2$TiX$_2$ metallocenes and their strongly electrophilic charged Group 4 bent metallocene cation relatives.

4. Experimental

General remarks: Reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents (including the deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. The following instruments were used for the characterization of synthesized compounds: Bruker ARX 300 NMR spectrometer (^{1}H 300 MHz, ^{13}C 75 MHz) at 298 K or a Varian Unity Plus NMR spectrometer (^{1}H 600 MHz, ^{13}C 150 MHz) at variable temperature (most NMR assignments were secured by 2D NMR experiments [17]); a Nicolet 5 DXC FT-IR spectrometer; a Micromass Quattro LC-Z mass spectrometer; elemental analyses were carried out with a Foss-Heraeus CHN-rapid elemental analyzer or a Vario El III micro elemental analyzer. 6-Dimethylamino-6-methylfulvene C$_5$H$_4$CMe(NMe$_2$) (**1**) [5] and the corresponding lithium salt [C$_5$H$_4$–CMe$_2$–NMe$_2$]Li (**2**) [4] were prepared according to the literature methods. X-ray crystal structure analyses: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307–326), absorption correction SORTAV (R.H. Blessing, Acta Crystallogr. A 51 (1995) 33; R.H. Blessing, J. Appl. Crystallogr. 30 (1997) 421), structure solution SHELXS-97 (G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467), structure refinement SHELXL-97 (G.M. Sheldrick, Universität

Göttingen, 1997), and graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

4.1. X-ray crystal structure analysis of [C_5H_4–CMe_2–NMe_2]Li (**2**)

Formula $C_{10}H_{16}LiN$, $M = 157.18$, colorless crystal $0.25 \times 0.20 \times 0.10$ mm, $a = 8.7582(2)$ Å, $b = 8.8582(2)$ Å, $c = 12.8809(4)$ Å, $V = 999.32(4)$ Å^3, $\rho_{calc} = 1.045$ g cm^{-3}, $\mu = 0.59$ cm^{-1}, empirical absorption correction via SORTAV ($0.986 \leq T \leq 0.994$), $Z = 4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 6265 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.66$ Å^{-1}, 2355 independent ($R_{int} = 0.040$) and 1719 observed reflections [$I \geq 2\sigma(I)$], 113 refined parameters, $R = 0.049$, $wR^2 = 0.112$, max residual electron density 0.12 (−0.15) e Å^{-3}, hydrogens calculated and refined as riding atoms.

4.2. Preparation of [C_5H_4–CMe_2–NMe_2]$_2$Fe (**3**)

To a suspension of $FeCl_2$ (1.0 g, 7.8 mmol) in 80 ml THF at 0 °C was slowly added a solution of lithium salt (**2**) (2.48 g, 15.6 mmol) in 30 ml THF. The reaction mixture was allowed to warm to room temperature and stirred for additional 10 h. The reaction mixture was concentrated in vacuo. The product was extracted with toluene. After removing the solvent, the resulting deep red solid was washed twice with pentane and dried in vacuo, yield of **3**: 1.4 g (50%). — m.p. 93 °C (192 °C dec.). — IR (KBr): $\tilde{\nu} = 3105$, 2944, 2870, 2812, 2768, 1727, 1690, 1646, 1463, 1382, 1257, 1162, 1045, 986, 927, 883, 817, 744, 693, 524, 488 cm^{-1}. — ^{1}H-NMR (600 MHz, CD_2Cl_2, 298 K): δ 3.61 (s, 6H, Me), 4.1 (s, 6H, NMe_2), 6.15 (m, 4H, Cp). — $^{13}C\{^1H\}$-NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 27.5 (Me), 40.5 (NMe_2), 57.9 (CMe_2), 69.5, 70.0 and 93.6 (Cp). — EIMS: m/z (%) 356 (38) [M$^+$]. — $C_{20}H_{32}N_2Fe$ (356.3): Calc.: C, 67.41; H, 9.05; N, 7.86; Found: C, 66.92; H, 9.05; N, 7.63%.

4.2.1. X-ray crystal structure analysis of **3**

Formula $C_{20}H_{32}N_2Fe$, $M = 356.33$, orange crystal 0.20 mm × 0.10 mm × 0.05 mm, $a = 11.9997(1)$ Å, $b = 12.5713(2)$ Å, $c = 12.7620(2)$ Å, $\alpha = 90.282(1)°$, $\beta = 92.867(1)°$, $\gamma = 108.464(1)°$, $V = 1823.34(4)$ Å^3, $\rho_{calc} = 1.298$ g cm^{-3}, $\mu = 8.29$ cm^{-1}, empirical absorption correction via SORTAV ($0.852 \leq T \leq 0.960$), $Z = 4$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 14 075 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.68$ Å^{-1}, 8930 independent ($R_{int} = 0.022$) and 6544 observed reflections [$I \geq 2\sigma(I)$], 431 refined parameters, $R = 0.045$, $wR^2 = 0.106$, max residual electron density 0.80 (−0.36) e Å^{-3}, two independent almost identical molecules in the asymmetric unit, hydrogens calculated and refined as riding atoms.

4.3. Preparation of [C_5H_4–CMe_2–NMe_2]$_2$$TiCl_2$ (**4**)

A suspension of $TiCl_4(THF)_2$ (1.99 g, 5.98 mmol) adduct in 25 ml ether was added to a suspension of the lithium compound (**2**) (1.88 g, 11.90 mmol) in 50 ml ether at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for additional 30 min. During this time the brown color of the reaction mixture turned to deep red. The precipitate of complex **4** and LiCl was filtered off, and the mother liquor was evaporated to two-thirds of the starting volume in vacuo and cooled to −30 °C. The precipitated titanocene was collected by filtration and washed with small amounts of cold ether. The mixture of complex and LiCl was extracted three times with 10 ml of CH_2Cl_2. The solvent was removed from the filtrate in vacuo giving a red-brown powder, yield of **4**: 0.99 g (20%). — m.p. 131 °C (161 °C dec.). — IR (KBr): $\tilde{\nu} = 3101$, 2990, 2949, 2927, 2855, 2814, 2775, 2346, 1640, 1468, 1418, 1379, 1261, 1147, 1133, 1092, 1047, 1020, 980, 857, 848, 837, 803 cm^{-1}. — H-NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.53 (s, 12H, Me), 2.05 (s, 12H, NMe_2), 6.50 and 6.62 (each m, each 4H, Cp). — $^{13}C\{^1H\}$-NMR (75.5 MHz, CD_2Cl_2, 298 K): δ 23.8 (Me), 39.1 (NMe_2), 63.2 (CMe_2), 116.9, 122.7 and 130.7 (Cp). — $C_{20}H_{32}Cl_2N_2Ti$ (419.3): Calc. C, 57.29; H, 7.69; N, 6.68; Found: C, 56.16; H, 7.31; N, 5.65%.

4.3.1. X-ray crystal structure analysis of **4**

Formula $C_{20}H_{32}Cl_2N_2Ti$, $M = 419.28$, red-orange crystal 0.35 mm × 0.30 mm × 0.05 mm, $a = 7.063(1)$ Å, $b = 24.283(1)$ Å, $c = 12.265(1)$ Å, $\beta = 98.55(1)°$, $V = 2080.2(4)$ Å^3, $\rho_{calc} = 1.339$ g cm^{-3}, $\mu = 6.74$ cm^{-1}, empirical absorption correction via SORTAV ($0.798 \leq T \leq 0.967$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 13 702 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.66$ Å^{-1}, 4953 independent ($R_{int} = 0.048$) and 3488 observed reflections [$I \geq 2\sigma(I)$], 234 refined parameters, $R = 0.040$, $wR^2 = 0.081$, max residual electron density 0.30 (−0.43) e Å^{-3}, hydrogens calculated and refined as riding atoms.

4.4. Preparation of [C_5H_4–CMe_2–NMe_2]$_2$TiCl (**5**)

To a suspension of $TiCl_3(THF)_3$ (1.0 g, 2.7 mmol) in 80 ml THF at −50 °C was slowly added a solution of lithium salt (**2**) (0.83 g, 5.4 mmol) in 30 ml of THF. The reaction mixture was allowed to warm to room temperature and then stirred for additional 10 h. The reaction mixture was concentrated in vacuo. The product was extracted with toluene. After removing the solvent, the obtained green solid was washed twice with pentane and dried in vacuo. Isolated yield of **5**: 0.77 g (75%). — m.p. 145 °C (202 °C dec.). — IR (KBr): $\tilde{\nu} = 3068$, 2966, 2782, 2445, 1653, 1477, 1382, 1272, 1096, 1067, 810, 568, 451 cm^{-1}. — ESI-MS: m/z (%) 354 (65) [$M^+ - 2Me + H$], 135 (60) [$C_9H_{13}N^+$], 46 (100) [$Me_2NH_2^+$]. — $C_{20}H_{32}ClN_2Ti$ (383.8): Calc.: C, 62.58; H, 8.40; N, 7.30; Found: C, 61.21; H, 8.71; N, 6.93%.

4.4.1. *X-ray crystal structure analysis of* **5**

Formula $C_{20}H_{32}ClN_2Ti$, $M = 383.83$, green crystal 0.25 mm × 0.20 mm × 0.10 mm, $a = 11.659(1)$ Å, $b = 12.977(1)$ Å, $c = 14.209(1)$ Å, $\beta = 111.16(1)^\circ$, $V = 2004.9(3)$ Å^3, $\rho_{calc} = 1.272$ g cm^{-3}, $\mu = 5.64$ cm^{-1}, empirical absorption correction via SORTAV ($0.872 \leq T \leq 0.946$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 14 583 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.66$ Å^{-1}, 4773 independent ($R_{int} = 0.063$) and 3014 observed reflections [$I \geq 2\sigma(I)$], 225 refined parameters, $R = 0.049$, $wR^2 = 0.100$, max residual electron density 0.28 (−0.47) e Å^{-3}, hydrogens calculated and refined as riding atoms.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC Nos. 196113–196116. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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