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Synthesis and structural characterization of Group 4 metallocene complexes that contain remote carboxamide functionalities at their Cp-side chains †

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Treatment of the levulinic acid amides $CH_3COCH_2CH_2CONR_2$ **7** [$–NR_2$ = NMe_2 (**a**), NEt_2 (**b**), pyrrolidino (**c**)] with cyclopentadiene in the presence of excess pyrrolidine gave the corresponding pentafulvene derivatives **8(a–c)**. Their subsequent reaction with [Me_2CuLi] followed by hydrolysis furnished the corresponding C-methylated cyclopentadienes **9(a–c)**, each obtained as a mixture of isomers (**9-A** and **9-B**). Deprotonation of the cyclopentadiene units in these compounds was achieved by treatment with lithium diisopropylamide (LDA) to yield the substituted lithium cyclopentadienide reagents [$(C_5H_4)–CMe_2CH_2CH_2CONR_2$]Li (**10a–c**), that were resistant to intramolecular cyclization under the applied reaction conditions. The transmetalation reaction of **10a** with $FeCl_2$ furnished the ferrocene derivative [$(C_5H_4)–CMe_2CH_2CH_2CONMe_2$]$_2$Fe (**11a**). Treatment of **10a–c** with $CpTiCl_3$ gave the Group 4 bent metallocene complexes Cp[$(C_5H_4)–CMe_2CH_2CH_2CONR_2$]$TiCl_2$ (**12a–c**). Similarly, the reaction of **10b** with $CpZrCl_3$ led to formation of the complex Cp[$(C_5H_4)CMe_2CH_2CH_2CONEt_2$]$ZrCl_2$ (**13b**). Treatment of **12a** with Meerwein's reagent [$(Et_3O^+)(BF_4^-)$] resulted in chloride abstraction with formation of the metallocene cation complex **16** (with BF_4^- anion), in which, contrary to the 16-electron systems **12** and **13**, the carboxamido oxygen atom intramolecularly coordinates to the electron deficient Group 4 metal cation. The organic reagents **8a** and **9a** as well as the transition metal complexes **11a**, **13b**, and **16**[BF_4^-] were characterized by X-ray crystal structure analyses.

Introduction

Metal complexes that bear organic functional groups have become of interest in organometallic chemistry and catalysis.[1] Of special importance are a variety of systems that contain functional groups bonded to η^5-Cp or η^5-indenyl ligands.[2] In late transition metal chemistry this can often be achieved at a later stage in a synthetic sequence since such (η^5-Cp)M systems often undergo functionalization reactions at the organometallic framework rather easily and also allow for functional group interconversions. Ferrocene chemistry is a prominent but by no means a singular example.[3]

Introduction of functional groups and organic functional group interconversion at (η^5-Cp)M complexes of the oxophilic d-metals on the left side of the periodic table (and also the f-elements) is more tedious by far since such metal complex systems often are not compatible with many reagents and the typical reaction conditions that are used in organic functional group interconversions. Thus, Friedel–Crafts chemistry and aldol condensation-type chemistry, to mention typical examples, is often readily performed at *e.g.* ferrocene or ruthenocene systems[4] but similar reactions can only be carried out in very rare examples under special conditions at *e.g.* the Group 4 bent metallocene complexes.[5–7]

Therefore, in synthetic early d-metal chemistry functional groups are mostly attached at the Cp-ligand systems prior to the final transmetalation step. This has been carried out successfully in a great variety of systems that contain Cp–$(CR_2)_n$–X ligands featuring simple –OR, –SR or $–NR_2$ donor groups at the Cp-side chains[8] or similarly structured negatively charged donor ligand subunits.[9] It is more difficult to attach carbonyl or heterocarbonyl functional groups at the Cp-ligands, but a variety of synthetic protocols were established in the past to generate *e.g.* $[Cp–COR]^-$- or $[Cp–CONR_2]^-$-type Cp-anion equivalents and transmetalate them to *e.g.* titanium, zirconium or hafnium.[10–12] Attaching carbonyl functional groups at the end of Cp–hydrocarbyl side chains in this way is notoriously difficult, since the intermediate substituted Cp–lithium (or –sodium) reagent is a strong carbon nucleophile that will have a high tendency to attack the remote carbonyl functional group intramolecularly before transmetalation of such a $[Cp–(CH_2)_n–COR]^-$ anion reagent to an external electrophilic Group 4 metal reagent can be achieved. This is typically illustrated by the behaviour of the reagent **4** that instantaneously undergoes the intramolecular ring closure reaction to yield **5**, even when generated from **2** by treatment with a soft lithium dimethylcuprate nucleophile (see Scheme 1).[13,14]

We have now found that in the corresponding amide-functionalized $[CpCR_2CH_2CH_2CONR_2]^-$ anion systems reaction conditions can be achieved where transmetalation to titanium or zirconium can successfully compete, thus making the desired Group 4 bent metallocene complexes synthetically available that bear hydrocarbyl side chains with a terminal carbonyl functionality at their Cp-ligands.

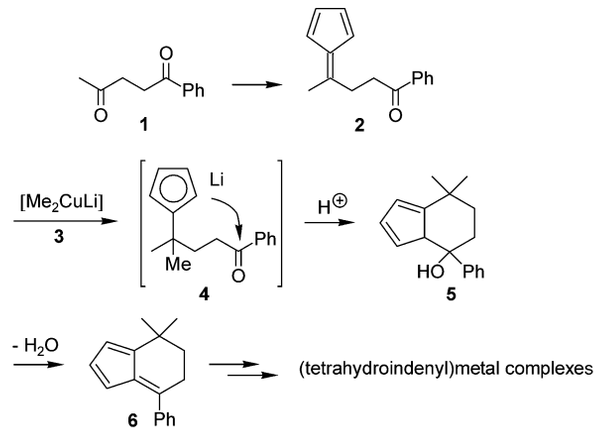
We here describe the synthesis of a series of selected examples, the structural characterization of such complexes and their synthetic precursors, and a typical organometallic reaction that such carbonyl-functionalized Group 4 bent metallocenes undergo upon electrophilic activation.

Results and discussion

Preparation of the ligand systems

For this study we selected the $[Cp–CMe_2CH_2CH_2CONR_2]^-$ ligand system as the target. The synthesis of the ligand system

† Electronic supplementary information (ESI) available: synthesis and characterisation details for **7b**,**c**, **8b**,**c**, **9b**,**c**, **10b**,**c**, and **12b**,**c**. See http://www.rsc.org/suppdata/dt/b1/b106026k/



Scheme 1

started from a series of three 4-oxo-pentanoic acid amides (**7a**–**c**) with the $-NR_2$ groups being dimethylamido, diethylamido and pyrrolidino. Treatment of **7a** with cyclopentadiene in the presence of excess pyrrolidine[15] gave the pentafulvene derivative **8a** (82% isolated). The ^{13}C NMR spectrum of **8a** shows four separate methine carbon resonances (δ 131.2, 131.1, 120.6, 120.2) and an *ipso*-C signal (δ 143.0) of the fulvene five-membered ring. The carboxamide functional group exhibits a characteristic ^{13}C NMR (C=O) carbon resonance at δ 171.6 and two separate methyl resonances of the *E*- and *Z*-amide N–CH_3 groups at δ 37.2 and 35.5. The amide carbonyl IR bond of **8a** is observed at 1652 cm^{-1}.

The pentafulvene derivative **8a** was characterized by X-ray diffraction. Suitable single crystals of this compound were obtained from a solution in diethyl ether at −30 °C. The molecular structure of **8a** shows a typical fulvene framework with alternating endocyclic C=C double bonds [C7–C8 1.347(3), C9–C10 1.345(2) Å (unsystematical atom numbering as used in Fig. 1)] and a marginally longer tetrasubstituted exo-

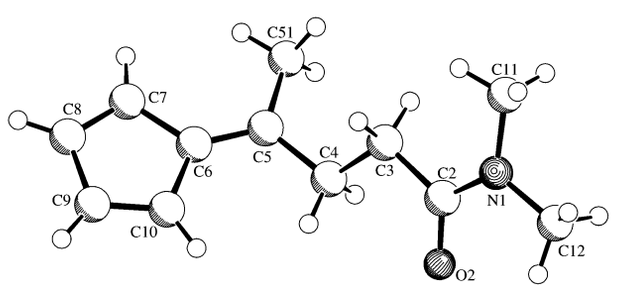
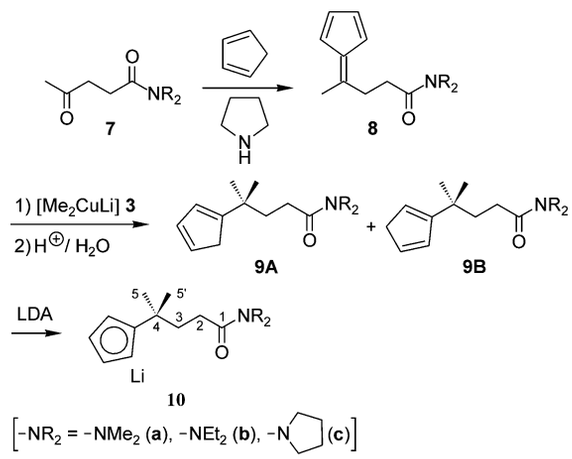


Fig. 1 Molecular structure of the substituted pentafulvene **8a**. Selected bond lengths (Å) and angles (°): N1–C2 1.355(2), C2–O2 1.229(2), C5–C6 1.356(2), C6–C7 1.464(2), C7–C8 1.347(3), C8–C9 1.446(3), C9–C10 1.345(2), C10–C6 1.468(2); N1–C2–O2 120.8(2), C4–C5–C6 121.9(2), C5–C6–C7 127.9(2), C5–C6–C10 127.3(2), C7–C6–C10 104.8(1).

cyclic olefin unit [C5–C6 1.356(2) Å].[16] The adjacent $-CH_2-CH_2-$ moiety has attained an anti-periplanar conformational arrangement [dihedral angle θ C5–C4–C3–C2 172.8(1)°]. The $-C(O)NMe_2$ unit is oriented almost perfectly in the hydrocarbon plane [θ C4–C3–C2–O2 −2.2(2), θ C4–C3–C2–N1 178.6(1)°], whereas the fulvenoid end of the structure is markedly rotated [θ C3–C4–C5–C6 −117.6(2)°]. The carboxamide unit is electronically delocalized in the typical way [C2–O2 1.229(2), C2–N1 1.355(2) Å]. These data will serve as a suitable reference for the characterization of the metal complexes derived from the related ligand systems (see below).

Similar treatment of the levulinic acid amides **7b** and **7c** (**7c** was generated *in situ*) with cyclopentadiene/pyrrolidine gave the corresponding pentafulvenes **8b** (82% isolated yield) and **8c** (isolated in 58% yield). Both products were obtained analytically pure as yellow oils.

Substituted cyclopentadienides can be prepared starting from suitably substituted pentafulvene systems by either nucleophilic addition at the exocyclic sp^2-carbon atom or by deprotonation at an sp^3-carbon center adjacent to it.[17] Cuprate reagents are of sufficiently low basicity to allow for a clean nucleophilic addition to the soft fulvene electrophile[18] as we had shown earlier. Therefore, we have reacted the fulvenes **8** employed in this study with [Me_2CuLi] (**3**). This led to a clean methyl addition to the pentafulvenes.[13] Subsequent hydrolysis by means of aqueous ammonium chloride solution gave in each case a mixture of the two substituted cyclopentadiene isomers **9A** and **9B** (see Scheme 2). The two **9a** isomers were obtained



Scheme 2

in a 1.8 : 1 ratio after chromatographic workup. The major isomer (**9a-A**) is characterized by ^1H NMR cyclopentadiene resonances at δ 6.48, 6.34, 5.91 (CH) and 2.87 (CH_2). The carboxamido ^{13}C NMR (C=O) resonance of **9a-A** was located at δ 173.3 and the corresponding ^{15}N NMR resonance at δ −286 (from a $^{15}N/^1H$ GHMBC experiment).[19]

Single crystals of the minor isomer (**9a-B**) were obtained from a solution of the **9a** mixture of isomers in diethyl ether at −30 °C. Compound **9a-B** was characterized by an X-ray crystal structure analysis (for its spectroscopic characterization see the Experimental section).

The C_4-chain of **9a-B** shows an extended conformation [θ C1–C2–C3–C4 168.1(3)°] with the carboxamide nitrogen being oriented anti-periplanar with the C2–C3 vector [θ C2–C3–C4–N5 174.9(3)°, C4–O4 1.223(4), C4–N5 1.357(4) Å]. One of the C1–methyl vectors is staged in an anti-conformation with C2–C3 [θ C3–C2–C1–C21 178.8(3)°], and the cyclopentadienyl substituent at the end of the chain is oriented in a *gauche* position [θ C3–C2–C1–C11 −62.9(4)°]. The conjugated diene inside the C_5H_5 substituent has the $-CMe_2CH_2CH_2CONMe_2$ chain attached at one of its central positions. The five-membered ring itself exhibits a planar C_5-framework (see Fig. 2).

The substituted $(C_5H_5)CMe_2CH_2CH_2CONR_2$ cyclopentadienes **9b** und **9c** were prepared analogously. Both systems were obtained as mixtures of regioisomers that bear the $-CMe_2-R'$ substituent chain either at the 1- or 2-position of the conjugated diene unit. The **9b-A** : **9b-B** ratio of the diethylamido system was again 1.8 : 1, whereas the pyrrolidine-substituted isomers **9c-A** and **9c-B** were obtained in a 1.6 : 1 ratio.

Deprotonation of the functionalized cyclopentadienes **9** was achieved cleanly by treatment with the amide-base LDA in ether in the temperature range between 0 °C and room temperature. The spectroscopic features of the isolated products **10** (obtained each in *ca.* 90% yield) showed that the carboxamido group was still intact. Contrary to the corresponding unstable

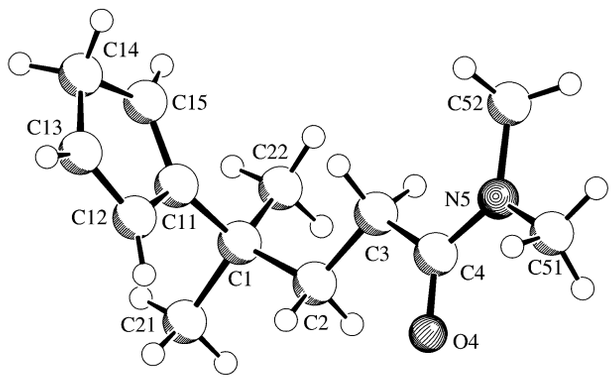


Fig. 2 A view of the molecular structure of the substituted cyclopentadiene isomer **9a-B** (minor isomer) with nonsystematic atom numbering scheme. Selected bond lengths (Å) and angles (°): N5–C4 1.357(4), C4–O4 1.223(4), C1–C11 1.505(4), C11–C12 1.464(4), C12–C13 1.337(5), C13–C14 1.448(6), C14–C15 1.491(5), C15–C11 1.337(4); C1–C11–C12 123.6(3), C1–C11–C15 129.1(3).

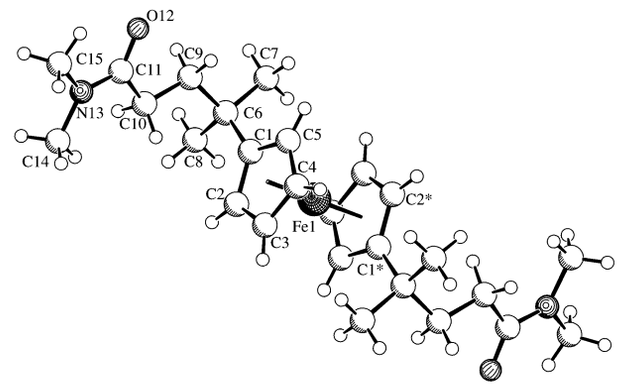
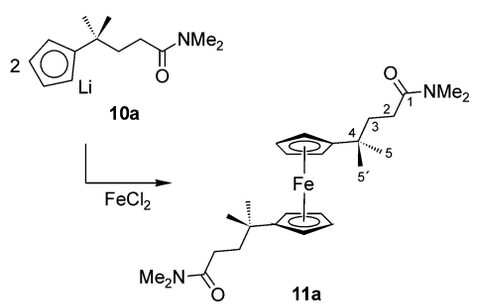


Fig. 3 Molecular structure of the disubstituted ferrocene derivative **11a** with nonsystematic atom numbering scheme. Selected bond lengths (Å) and angles (°): Fe–C1 2.082(1), Fe–C2 2.061(1), Fe–C3 2.048(1), Fe–C4 2.039(1), Fe–C5 2.052(1), N13–C11 1.346(2), C11–O12 1.225(2), C6–C1 1.516(2), C1–C2 1.424(2), C2–C3 1.419(2), C3–C4 1.407(2), C4–C5 1.421(2), C5–C1 1.428(2); C6–C1–C5 126.4(1), C2–C1–C5 106.4(1), C1–C2–C3 109.0(1), C2–C3–C4 107.9(1), C3–C4–C5 108.1(1), C4–C5–C1 108.7(1).

Cp-anion/keto-combination discussed above (see Scheme 1)[13] the Cp-anion/carboxamide is persistent in the intramolecular situation and does not lead to ring closure. In the functionalized lithium cyclopentadienide system **10a** (–NMe_2) the ^{13}C NMR carboxamido resonance is featured at δ 177.1 (**10b**: δ 176.3; **10c**: 175.1). Complex **10b** exhibits ^{13}C NMR Cp-methine resonances at δ 102.2 and 100.9 (Cp–*ipso*-C resonance at δ 126.3).

Synthesis and characterization of the transition metal complexes

In a scouting experiment we have first used the reagent **10a** for the preparation of a ferrocene derivative. Treatment of $FeCl_2$ with two molar equivalents of **10a** in an ether–THF (1 : 1) mixture gave the ferrocene derivative **11a** that was isolated as a yellow–orange solid in close to 70% yield (Scheme 3).



Scheme 3

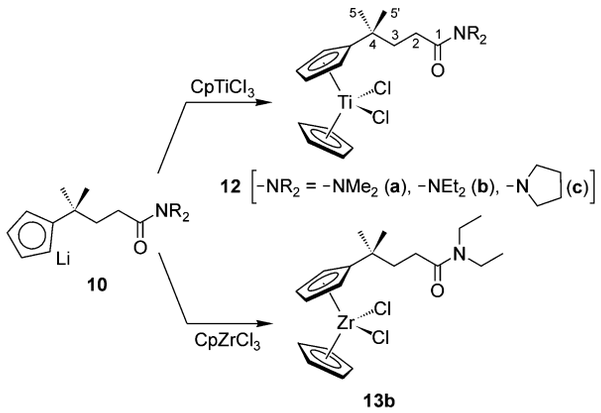
The X-ray crystal structure analysis of complex **11a** (single crystals were obtained from benzene) shows the presence of a symmetry-equivalent pair of η^5-C_5H_4–$CMe_2CH_2CH_2CONMe_2$ ligands at the transition metal center. The metallocene attains a conformation that features the two substituents in anti-positions. The substituent chains are in an extended conformational orientation that positions the –$CONH_2$ functional groups at their ends far away from the metal center and the metallocene core of the molecule. Actually, the substituent conformation in crystalline **11a** (Fig. 3) is almost identical with that found in its organic cyclopentadiene precursor **9a** (see above and Fig. 2). The anti-periplanar "zig-zag" chain in **11a** extends all the way from the carboxamido CH_3–N group to the C6-methyl substituent [with dihedral angles being: C15–N13–C11–C10: 176.3(2), C11–C10–C9–C6 163.3(1), C10–C9–C6–C7 175.8(1)°]. The attached η^5-Cp ring itself is found close to *gauche*-positioned at the C9–C6 bond [θ C10–C9–C6–C1 −64.4(2)°]. The bonding features of the –$CONMe_2$ functional group are in the typical range [C11–O12 1.225(2), C11–N13 1.346(2) Å; N13–C11–O12 121.7(1)°].

As expected, there is also no indication of any interaction in **11a** between the metal center and the –$CONMe_2$ group (^{13}C NMR carboxamide resonance at δ 172.1, Cp-methine signals at δ 68.0 and 66.2, *ipso*-C signal of the η^5-C_5H_4 subunit at δ 99.9).

The reagents **10** undergo clean transmetalation to the oxophilic Group 4 metals. This was shown by the preparation of a series of respective titanium and zirconium complexes. The functionalized lithium cyclopentadienide was reacted with $CpTiCl_3$[20] in toluene (−78 °C to room temperature). From the concentrated reaction solution the titanocene complex **12a** was precipitated at −30 °C and isolated as a bright red amorphous solid in 65% yield. The ^1H NMR spectrum of **12a** (in CD_2Cl_2) shows the typical signals for an η^5-C_5H_5 ligand (sharp singlet at δ 6.55) and a monosubstituted η^5-C_5H_4–R′ system (two multiplets at δ 6.60 and 6.50). The corresponding ^{13}C NMR signals are observed at δ 120.7 (η^5-C_5H_5), 119.7, 119.1/148.4 (CH/*ipso*-C of η^5-C_5H_4–R′). The functionalized side chain gives rise to a set of ^{13}C NMR signals at δ 37.2/26.8 (CMe_2), 41.9 (C3), 28.8 (C4), 37.4/35.5 (of the two N-CH_3 groups), and 172.7 (carboxamide C=O). The latter resonance is in the same range as was observed for the ferrocene derivative **10a** and the organic ligand precursors **7a** and **8a** (see above), which indicates the absence of any significant electronic or coordinative interaction of the remote –$CONMe_2$ functional group with the electrophilic (16-electron)[21] titanium metal center in complex **12a**. The observation of a 1641 cm^{-1} carbonyl band in the IR spectrum of complex **12a** supports this assessment.

Treatment of the $CpTiCl_3$ with the lithium cyclopentadienides **10b** or **10c** gave the corresponding (η^5-C_5H_5)/[(η^5-C_5H_4)–$CMe_2CH_2CH_2CONR_2$]$TiCl_2$ complexes **12b** and **12c**, respectively (see Scheme 4).

We also prepared a zirconium complex. The functionalized zirconocene complex **13b** was obtained by treatment of the reagent **10b** (–NR_2 = –NEt_2) with (η^5-cyclopentadienyl)-zirconiumtrichloride.[22] The bent metallocene complex **13b** was isolated as a violet solid in *ca.* 60% yield. The remote carboxamide functional group is characterized by a ^{13}C NMR (C=O) resonance in the typical range at δ 170.3 and a ^{15}N NMR signal at δ −258. Single crystals of the complex **13b** were grown from a toluene solution, that allowed for a X-ray crystal structure analysis of the Group 4 metallocene complex (see Fig. 4). The structure of **13b** shows a pseudotetrahedral coordination geometry around the central zirconium atom with Zr–Cl1 and Zr–Cl2 bond lengths of 2.431(1) and 2.442(1) Å, respectively [angle Cl1–Zr–Cl2 95.82(1)°]. The Cp(centroid)–Zr–Cp(centroid) angle in **13b** amounts to 129.4°. The C_5H_5-ligand is uniformly η^5-coordinated to zirconium with Zr–C(Cp) bond



Scheme 4

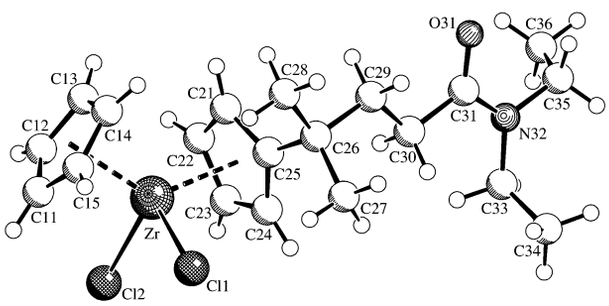
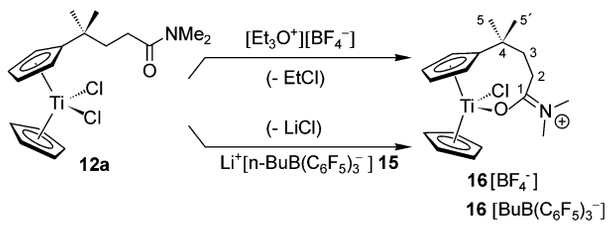


Fig. 4 A projection of the molecular structure of complex **13b** (with nonsystematic atom numbering scheme). Selected bond lengths (Å) and angles (°): Zr–Cl1 2.431(1), Zr–Cl2 2.442(1), Zr–C11 2.529(1), Zr–C12 2.523(1), Zr–C13 2.508(1), Zr–C14 2.482(1), Zr–C15 2.518(1), Zr–C21 2.503(1), Zr–C22 2.437(1), Zr–C23 2.493(1), Zr–C24 2.552(1), Zr–C25 2.591(1), N32–C31 1.350(2), C31–O31 1.228(2), C26–C25 1.517(2); Cl1–Zr–Cl2 95.82(1), C26–C25–C21 125.6(1), C26–C25–C24 126.9(1), C21–C25–C24 106.5(1).

lengths found to be in a narrow range between 2.482(1) and 2.529(1) Å. The monosubstituted C_5H_4–R′ ring is also η^5-coordinated, but here the Zr–C(Cp) bond lengths span a much wider range. There is a systematic distortion from an ideal η^5-coordination towards a markedly increased separation between the metal center and the *ipso*-carbon atom of that ring system. While the "distal" Zr–C(Cp) bonds are rather short at 2.437(1) (Zr–C22) and 2.493(1) Å (Zr–C23), the "proximal" Zr–C(Cp) linkages are elongated at 2.503(1) (Zr–C21) and 2.552(1) Å (Zr–C24), whereas the Zr–C_{ipso}(Cp) bond to the monosubstituted Cp-ring is markedly longer at 2.591(1) Å (Zr–C25).

The long side-chain, that is attached at the C21–C25 ring system, attains an elongated conformation, which is practically identical to the structural situation of the analogous moieties found in the structurally characterized compounds **8a**, **9a**, and **11a** (see above), featuring an anti-periplanar arrangement from the methyl group (C28) through the framework atoms C26, C29, C30, C30, N32 to the substituent center C35 [see Fig. 4, the corresponding dihedral angles are: θ C28–C26–C29–C30 178.6(1), C26–C29–C30–C31 −177.7(1), C29–C30–C31–N32 173.7(1), and C30–C31–N32–C35 179.6(1)°]. The carbon atom C33 is oriented syn-periplanar to the C30–C31 vector at their connecting C31–N32 [1.350(2) Å] bond [θ C30–C31–N32–C33 0.7(2)°]. The C31–O31 bond length is in the typical range at 1.228(2) Å. Again the Cp-ligand at the "C-terminus" of the substituent chain is found in a *gauche* conformational orientation as seen from the substituent main chain [θ C30–C29–C26–C25 −61.9(2)°]. Overall, the –$CMe_2CH_2CH_2CONEt_2$ substituent is oriented toward a lateral position at the Group 4 bent metallocene wedge[23] and it is pointing with its functional group as far away from the central transition metal center as possible (see Fig. 4).

The 16-electron Group 4 metallocene complexes **12** and **13** are all characterized by a complete lack of any significant interaction between the remote –$CONR_2$ carbonyl functional group and the mildly electrophilic transition metal center. That changes drastically when the Cp(CpR′)MCl_2 complexes are converted to their respective metallocene cations.[24] We have used two different synthetic protocols for the conversion of the titanocene dichloride complex **12a** to a corresponding bent metallocene cation complex (see Scheme 5).[25] In the first case the



Scheme 5

neutral titanocene complex **12a** was treated with "Meerwein's reagent" [triethyloxonium tetrafluoroborate (**14**)] in dichloromethane (−78 °C to room temperature). This led to a clean abstraction of a chloride ion from the titanium center (with formation of ethylchloride as shown by $^1H/^{13}C$ NMR spectroscopy) and formation of the product **16**[BF_4^-]. The metallocene cation complex **16**[BF_4^-] was isolated as a red–brown solid in *ca.* 70% yield. From a dichloromethane solution single crystals of **16**[BF_4^-] were obtained at −30 °C that were suited for an X-ray crystal structure analysis (see below).

As an alternative method we have used a salt metathesis route[26] for carrying out chloride removal starting from **12a**. As a suitable Cl^- abstracting agent we have employed the lithium tetraorganylborate salt Li^+[n-butyl-$B(C_6F_5)_3$]$^-$ (**15**) that we had used previously for halide abstraction in Group 4 metallocene cation formation.[27] The product **16**[$BuB(C_6F_5)_3^-$] was generated in this way in CD_2Cl_2 solution and characterized spectroscopically (for details see the Experimental section).

The X-ray crystal structure analysis of the product **16**[BF_4^-] shows that a chloride has been removed from the Group 4 metal center. A salt was formed that shows separate complex cations and anions in the crystal. The strongly electrophilic [Cp(CpR)-$TiCl^+$] cation interacts strongly with the carboxamide functionality that is attached at the end of the substituent side chain. That has resulted in a very characteristic distorted pseudo-tetrahedral coordination geometry of the central Group 4 transition metal center. It is bonded to a η^5-C_5H_5 ligand [with the Ti–C(Cp) bond lengths being in a very narrow range between 2.341(5) and 2.370(6) Å; averaged value: 2.358(6) Å], a monosubstituted η^5-C_5H_4–R′ ligand [Ti–C(Cp′) bond lengths ranging from 2.344(4) to 2.419(5) Å, the latter value is found for the Ti–C_{ipso}(Cp′) linkage], a chloride ligand [Ti–Cl1 2.376(1) Å] and the carboxamide carbonyl oxygen atom. The Cl1–Ti–O29 angle amounts to 92.6(1)°. The Ti–O29 bond is short at 1.948(3) Å, and the Ti–O29–C25 angle is very large at 165.5(3)°. Both these features indicate a considerable ligand-to-metal π-bonding component of the titanium–oxygen coordination in complex **16**[BF_4^-].[28,29] This probably leads to a marked stabilization of the strongly electrophilic metal center in this complex. Coordination of the carboxamide group to Ti^+ has altered the structural features of the –$CONMe_2$ functionality considerably. The C=O bond has become elongated [C25–O29 1.268(5) *vs.* 1.228(2) Å in the non-coordinated neutral Zr-complex **13b**, see above] and the C–NR_2 bond length in **16**[BF_4^-] is decreased [C25–N26 1.306(5) Å] relative to this reference [**13b**: 1.350(2) Å].

The methyl groups at the carboxamide nitrogen atom in complex **16**[BF_4^-] are oriented in the central plane, *i.e.* coplanar with the metallocene σ-ligands. The formation of the metalla-

cycle by intramolecular coordination of the functional group to titanium does not impose any considerable strain to the framework as judged from the endocyclic bonding angles and the resulting conformational properties, which are all within the normal range (see Fig. 5).

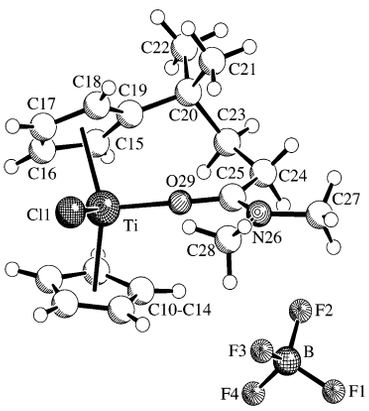


Fig. 5 Molecular structure of complex **16**[BF_4^-] (with nonsystematic atom numbering scheme). Selected bond lengths (Å) and angles (°): Ti–Cl1 2.376(1), Ti–O29 1.948(3), Ti–C10 2.370(6), Ti–C11 2.367(6), Ti–C12 2.369(5), Ti–C13 2.341(5), Ti–C14 2.344(6), Ti–C15 2.344(4), Ti–C16 2.349(4), Ti–C17 2.357(5), Ti–C18 2.386(5), Ti–C19 2.419(5), N26–C25 1.306(5), C25–O29 1.268(5); Cl1–Ti–O29 92.6(1), Ti–O29–C25 165.5(3), C25–N26–C27 122.3(4), C25–N26–C28 119.8(4), C27–N26–C28 117.4(3), N26–C25–O29 119.4(4), N26–C25–C24 120.7(4), O29–C25–C24 119.9(4).

The spectroscopic features of **16**[BF_4^-] are also consistent with the presence of a complex with persistent chirality in solution. This is evident by the observation of four separate ^{1}H NMR resonances of the C_5H_4R' ring system at δ 7.00, 6.72, 6.47, and 6.23. The methyl substituent at carbon atom C2 of the newly formed metallacyclic ring system are diastereotopic (^{1}H NMR: δ 1.32, 1.19) as are the protons of the adjacent $–CH_2–CH_2$ linker (four multiplets at δ 2.85, 2.72, 1.82, 1.67). The two *N*-methyl groups are different, as expected (^{1}H NMR signals at δ 3.24 and 3.07). The ^{13}C NMR resonance of the carboxamido carbonyl group appears at δ 180.2. It is thus shifted by $\Delta\delta$ = 7.5 ppm to low field, which is clear indication that the C=O group is oxygen-coordinated intramolecularly to the Lewis-acidic cationic titanium center.[30] The ^{15}N NMR chemical shift is actually only slightly affected by this coordination (measured at **16**[$BuB(C_6F_5)_3^-$]: δ −254 *vs.* −258 observed in **13b**, see above).

In conclusion, this study has shown that a remote carboxamide functional group attached at a Cp-side chain can be introduced into Group 4 metallocene chemistry rather easily by means of the corresponding [$Cp–CR_2CH_2CH_2–CONR_2$]$^-$ reagents. In contrast to the keto-group (see Scheme 1)[13] the carboxamido group has turned out to be sufficiently inert toward nucleophilic attack to allow for the presence of a hard Cp-anion equivalent inside the same molecule. The resistance of the systems **10** to undergo intramolecular ring closure under the typical conditions necessarily used in organometallic synthesis has allowed us to prepare the Group 4 metal complexes **12** and **13**, that each contain a $–CONR_2$ group at the Cp-substituent, by a simple transmetalation route. In the respective 16-electron Group 4 metallocene systems, the $–CONR_2$ functionality does not directly interact with the transition metal center. This is changed to a strong metal–O=C(NR_2)– interaction upon activation of the metal center by metallocene cation formation. We are hopeful that this synthetic development might become useful for the development of a selective functional group chemistry in the organometallic chemistry of the Group 4 metallocenes and their catalytically important strongly electrophilic Group 4 metallocene cation derivatives.

Experimental

Reactions with organometallic compounds were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glove-box. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds: Bruker AC 200 P (200 MHz), Bruker ARX (300 MHz) and Varian Unity plus (^{1}H 600 MHz) NMR spectrometers; Nicolet 5 DXC FT-IR spectrometer; Finnigan MAT 312 and Micromass Quattro LC-Z mass spectrometers were used for HRMS determination; elemental analyses were carried out with a Foss-Heraeus CHN-rapid elemental analyzer or a Vario El III micro elemental analyzer; melting points were determined by differential scanning calorimetry (2910 DSC, Du Pont/STA Instruments). The 4-oxo-pentanoic acid amides **7a** and **7b** were prepared by modified literature procedures.[31,32] Mono(η^5-cyclopentadienyl)titanium trichloride and mono(η^5-cyclopentadienyl)zirconium trichloride were prepared in analogy to published procedures.[20,22,33] Details of the preparation and characterization of the compounds **7b**,**c**, **8b**,**c**, **9b**,**c**, **10b**,**c**, and **12b**,**c** are available as ESI.

Syntheses

4-Oxo-pentanoic acid dimethylamide 7a. A mixture of 20.0 g (204 mmol) α-angelica lactone and 40.0 mL (37.5 g, 832 mmol) of an aqueous dimethylamine solution in 100 mL toluene was refluxed with separation of water. The mixture was refluxed until all water had been removed. The reaction mixture was fractionated by vacuum distillation to yield 26.6 g (91%) of compound **7a** as a yellow liquid (Found: C, 58.93; H, 9.25; N, 9.61%. $C_7H_{13}NO_2$ requires C, 58.72; H, 9.15; N, 9.78%). $\tilde{\nu}$/cm^{-1} (NaCl) 3007, 2932, 1723, 1659, 1510, 1412, 1371, 1274, 1147, 1066, 1026 and 1003. δ_H (Chloroform-*d*, 298 K, 300 MHz) 2.68, 2.55 (each s, each 3H, NCH_3), 2.38 (m, 2H, 3-H), 2.22 (m, 2H, 2-H), 1.83 (s, 3H, 5-H). δ_C (Chloroform-*d*, 298 K, 75.5 MHz) 206.6 (C, C-4), 170.6 (C, C-1), 37.2 (CH_2, C-3), 36.1, 34.5 (each CH_3, NCH_3), 29.1 (CH_3, C-5), 26.4 (CH_2, C-2).

Preparation of the pentafulvenes 8(a–c), general procedure. Levulinic acid amides **7a** or **7b** or 4-oxo-pentanoic acid methylester (*ca.* 182 mmol) were dissolved in 200 mL of methanol in an inert atmosphere (argon) and cooled to 0 °C. Freshly distilled cyclopentadiene (2.5 molar equivalents) was added, and then the condensation reaction was started by adding 5 molar equivalents of pyrrolidine. The mixture was allowed to warm to room temperature with stirring during 14 h and then the yellow suspension was poured into 400 mL of ice water. The phases were separated and the aqueous layer was extracted with diethyl ether (3 × 150 mL). The combined organic phases were dried over magnesium sulfate and the solvent was removed *in vacuo*. Column chromatography of the reaction mixture on silica gel 60 gave crude products.

4-(Cyclopenta-2′,4′-dienylidene)pentanoic acid dimethylamide 8a. Reaction of 26.6 g (192 mmol) of compound **7a** with 34.2 mL (28.7 g, 433 mmol) freshly distilled cyclopentadiene and 70.2 mL (63.5 g, 892 mmol) pyrrolidine, carried out as described above, gave after column chromatography on silica gel 60 (diethyl ether–ethanol = 95 : 5, R_f = 0.26) 28.1 g (82%) of the pentafulvene **8a** as a yellow oil (Found: C, 75.53; H, 8.73; N, 7.39%. $C_{12}H_{17}NO$ requires C, 75.35; H, 8.96; N, 7.32%). $\tilde{\nu}$/cm^{-1} (NaCl) 3106, 3066, 2935, 1652, 1505, 1473, 1408, 1383, 1286 and 782. δ_H (Chloroform-*d*, 298 K, 600 MHz) 6.45 (m, 4H, Fulv.-H), 2.94, 2.92 (each s, each 3H, NCH_3), 2.83 (m, 2H, 3-H), 2.50 (m, 2H, 2-H), 2.19 (s, 3H, 5-H). δ_C (Chloroform-*d*, 298 K, 150.8 MHz) 171.6 (C, C-1), 152.1 (C, C-4), 143.0 (C, C-1′), 131.2, 120.2 (each CH, C-3′, C-4′), 131.1, 120.6 (each CH, C-2′, C-5′), 37.2, 35.5 (each CH_3, NCH_3), 33.1 (CH_2, C-2),

Table 1 X-Ray crystal structure analyses: compilation of the crystallographic data [a]

	8a	**9a**	**11a**	**13b**	**16**
Empirical formula	$C_{12}H_{17}NO$	$C_{13}H_{19}NO$	$C_{26}H_{40}N_2O_2Fe$	$C_{20}H_{29}NOCl_2Zr$	$C_{18}H_{25}NOClTi^+BF_4^-\cdot 0.5CH_2Cl_2$
Formula weight	191.27	205.29	468.45	461.56	484.01
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*Pbca*	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	7.715(1)	10.916(3)	6.001(1)	6.975(1)	12.967(1)
b/Å	11.021(1)	10.601(3)	8.113(1)	12.127(1)	13.167(1)
c/Å	26.172(3)	11.246(8)	12.399(1)	12.384(1)	12.702(1)
α/°			99.19(1)	95.65(1)	
β/°		109.37(3)	94.36(1)	91.35(1)	95.07(1)
γ/°			93.36(1)	90.44(1)	
V/Å^3	2225.3(4)	1227.7(10)	592.7(1)	1042.1(2)	2160.2(3)
Z	8	4	1	2	4
Crystal size/mm	0.35 × 0.30 × 0.15	0.50 × 0.40 × 0.30	0.20 × 0.20 × 0.05	0.30 × 0.15 × 0.10	0.20 × 0.15 × 0.05
D_c/g cm^{-3}	1.142	1.111	1.313	1.471	1.488
F(000)	832	448	252	476	996
μ/mm^{-1}; correction	0.563; empirical	0.070; none	0.661; empirical	0.792; none	0.687; empirical
Temperature/K	223	223	198	198	198
θ limits/°; λ/Å	3.38/74.29; 1.54178	2.72/24.62; 0.71073	2.55/27.54; 0.71073	3.36/30.52; 0.71073	1.58/24.99; 0.71073
Reflections collected	2268	2188	4789	14680	17676
Reflections unique; R_{int}	2268	2072; 0.049	2720; 0.017	6265; 0.024	3801; 0.125
Reflections ($I > 2\sigma(I)$)	1898	1095	2611	5834	2084
No. of variables	131	140	146	230	275
R	0.058	0.060	0.029	0.022	0.058
*wR*2	0.170	0.165	0.075	0.053	0.102
Remaining density/e Å^{-3}	0.28/−0.23	0.25/−0.23	0.32/−0.28	0.34/−0.29	0.39/−0.34

[a] Data sets were collected on Enraf-Nonius CAD4 and Nonius KappaCCD diffractometers, the latter equipped with a Nonius FR591 rotating anode generator. Programs used: data collection EXPRESS and COLLECT,[34a] data reduction MolEN[34b] and Denzo-SMN,[34c] absorption correction for CCD data SORTAV,[34d] structure solution SHELXS-97,[34e] structure refinement SHELXL-97,[34f] graphics SCHAKAL.[34g] CCDC reference numbers 179005–179009. See http://www.rsc.org/suppdata/dt/b1/b106026k/ for crystallographic data in CIF or other electronic format.

32.2 (CH_2, C-3), 21.0 (CH_3, C-5). Single crystals for the X-ray crystal structure analysis (see Table 1) were obtained from diethyl ether at −30 °C.

Preparation of the substituted cyclopentadienides 9(a–c), general procedure. A lithium dimethylcuprate solution was prepared as follows. Copper(I) iodide (11.0 g, 57.8 mmol) was suspended in 150 mL of absolute diethyl ether. The suspension was cooled to *ca.* at −60 °C. During a period of 30 min two equivalents of a 1.83 M ethereal methyllithium solution was added dropwise with stirring. Initially a yellow precipitate of methylcopper was formed that redissolved toward the end of the reaction when the total volume of the methyllithium solution was added. An almost colorless dimethylcuprate solution was thus obtained. This was stirred for *ca.* 15 min at −50 °C and then used for the reaction with the pentafulvenes **8(a–c)**.

Pentafulvenes **8(a–c)** (27 mmol) were dissolved in 100 mL of diethyl ether at 0 °C. Into the vigorously stirred solution the cold (−78 °C) cuprate solution was added dropwise during a period of 30 min. The mixture was then allowed to warm to room temperature and stirred for 48 h. A saturated aqueous ammonium chloride solution (300 mL) was then added (under argon). The reaction mixture was extracted with diethyl ether (3 × 200 mL). The combined organic phases were dried over magnesium sulfate and the solvent was removed *in vacuo*.

4-[1-(Cyclopenta-1,3-dienyl)]-4-methylpentanoic acid dimethylamide 9a-A/4-[2-(cyclopenta-1,3-dienyl)]-4-methylpentanoic acid dimethylamide 9a-B. Reaction of 5.00 g (26.1 mmol) of compound **8a** with a dimethylcuprate solution [prepared from 10.7 g, 56.0 mmol copper(I) iodide and 61.2 mL, 112 mmol, of a 1.83 M ethereal methyllithium solution] carried out as described above gave 3.40 g (63%) of the **9a-A/9a-B** (1.8 : 1) mixture of isomers, mp 45 °C (Found: C, 75.29; H, 10.21; N, 6.89%. $C_{13}H_{21}NO$ requires C, 75.32; H, 10.21; N, 6.76%). $\tilde{\nu}$/cm^{-1} (KBr) 3077, 2942, 1657, 1465, 1401, 1266, 1146, 869 and 783. δ_H (Chloroform-*d*, 298 K, 600 MHz, **9a-A**) 6.48, 6.34, 5.91 (each m, each 1H, Cp–H), 2.87 (m, 2H, Cp–H), 2.82 (br, 6H, NCH_3), 2.03 (m, 2H, 2-H), 1.73 (m, 2H, 3-H), 1.10 (s, 6H, 5-/5′-H). δ_C (Chloroform-*d*, 298 K, 150.8 MHz, **9a-A**) 173.3 (C, C-1), 154.2 (C, Cp), 133.8, 132.2, 124.3 (each CH, Cp), 40.8 (CH_2, Cp), 37.0 (CH_3, NCH_3), 36.7 (CH_2, C-3), 34.7 (C, C-4), 29.0 (CH_2, C-2), 27.3 (CH_3, C-5/-5′).

δ_H (Chloroform-*d*, 298 K, 600 MHz, **9a-B**) 6.31, 6.19, 6.09 (each m, each 1H, Cp–H), 2.82 (m, 2H, Cp–H), 2.81 (br, 6H, NCH_3), 2.03 (m, 2H, 2-H), 1.73 (m, 2H, 3-H), 1.11 (s, 6H, 5-/5′-H). δ_C (Chloroform-*d*, 298 K, 150.8 MHz, **9a-B**) 173.1 (C, C-1), 156.7 (C, Cp), 131.6, 130.8, 125.4 (each CH, Cp), 40.0 (CH_2, Cp), 38.2 (CH_2, C-3), 35.8 (C, C-4), 35.2 (CH_3, NCH_3), 28.8 (CH_2, C-2), 28.3 (CH_3, C-5/-5′). Single crystals of the minor isomer **9a-B**, that were suited for the X-ray crystal structure analysis (see Table 1) were obtained from diethyl ether at −30 °C.

Preparation of the substituted lithium cyclopentadienides 10(a–c), general procedure. The cyclopentadienides **9(a–c)** (29.0 mmol) were dissolved in 200 mL of diethyl ether and cooled to 0 °C. A solution of lithium diisopropylamide (1 molar equivalent) in 100 mL diethyl ether was added dropwise with stirring. Stirring was continued overnight and then the solvent removed *in vacuo*. The residue was dissolved in 50 mL of pentane and the resulting precipitate was recovered by filtration and washed with 20 mL of diethyl ether and 20 mL pentane to give the lithium compounds.

Lithium(4-cyclopentadienyl-4-methylpentanoic acid dimethylamide) 10a. Reaction of 6.30 g (30.3 mmol) of compound **9a** with 3.30 g (30.3 mmol) of lithium diisopropylamide carried out as described above gave 5.90 g (92%) of the compound **10a** as a brown powder (Found C, 72.41; H, 9.16; N, 5.87%. $C_{13}H_{20}NO$ requires C, 73.21; H, 9.45; N, 6.57%). δ_H [Benzene-d_6–tetrahydrofuran-d_8 (1 : 2), 298 K, 300.14 MHz] 5.67, 5.60 (each m, each 2H, Cp–H), 2.67, 2.53 (each s, each 3H, NCH_3), 2.23, 1.65 (each m, each 2H, 3-H, 2-H), 1.20 (s, 6H, 5-/5′-H). δ_C [Benzene-d_6–tetrahydrofuran-d_8 (1 : 2), 298 K, 75.7 MHz]

177.1 (C, C-1), 126.6 (C, Cp), 102.0, 100.8 (each CH, Cp), 40.8, 29.7 (each CH_2, C-3, C-2), 37.0, 35.0 (each CH_3, NCH_3), 35.4 (C, C-4), 31.0 (CH_3, C-5/-5′).

Reaction of 10a with $FeCl_2$, preparation of the ferrocene derivative 11a. To a solid mixture of 704 mg (3.30 mmol) of the starting material **10a** with 209 mg (1.65 mmol) of iron(II) chloride was added slowly a 1 : 1 mixture of diethyl ether and tetrahydrofuran (*ca.* 100 mL) at −78 °C. The mixture was allowed to warm to room temperature with stirring. Solvent was then removed *in vacuo*, and the resulting solid was taken up in 30 mL dichloromethane and the precipitated lithium chloride filtered off. The solvent was removed *in vacuo* and the compound was again dissolved in 30 mL of pentane. The resulting precipitate was collected by filtration and washed with 20 mL of pentane to yield a yellow–orange powder, mp 103 °C (Found: C, 67.13; H, 9.06; N, 5.73%. $C_{26}H_{40}FeN_2O_2$ requires C, 66.66; H, 8.61; N, 5.98%). $\tilde{\nu}/cm^{-1}$ (KBr) 3110, 2955, 2921, 1647, 1498, 1475, 1418, 1395, 1349, 1263, 1131, 1034, 907, 827 and 804. δ_H (Benzene-d_6, 298 K, 600 MHz) 4.00, 3.87 (each m, each 4H, Cp–H), 2.63, 2.14 (each s, each 6H, NCH_3), 1.95 (m, 4H, 2-H), 1.88 (m, 4H, 3-H), 1.20 (s, 12H, 5-/5′-H). δ_C (Benzene-d_6, 298 K, 150.8 MHz) 172.1 (C, C-1), 99.9 (C, Cp), 68.0, 66.2 (each CH, Cp), 40.9 (CH_2, C-3), 36.2, 34.9 (each CH_3, NCH_3), 33.3 (C, C-4), 29.2 (CH_2, C-2), 28.3 (CH_3, C-5/-5′). Single crystals for the X-ray crystal structure analysis (see Table 1) were obtained from (benzene-d_6).

Preparation of the substituted Group 4 metal complexes 12(a–c), general procedure. To a solid mixture of *ca.* 1.9 mmol of the starting material with 1 equivalent of the mono(η^5-cyclopentadienyl) Group 4 metal trichloride was added slowly *ca.* 60 mL of toluene at −78 °C. The mixture was allowed to warm to room temperature with stirring for 6 h and then stirred for 6 h at ambient temperature. The precipitated lithium chloride was removed by filtration and washed twice with toluene (20 mL). The combined organic solutions were concentrated *in vacuo* to a volume of 20 mL and then the product precipitated at −30 °C. It was collected by filtration, washed with pentane (20 mL) and dried *in vacuo*.

4-[1-(Dichlorotitanocenyl)]-4-methylpentanoic acid dimethylamide 12a. Reaction of 405 mg (1.90 mmol) of compound **10a** with 416 mg (1.90 mmol) of mono(η^5-cyclopentadienyl)-titanium trichloride carried out as described above gave 480 mg (65%) of the compound **12a** as a red powder, mp 55 °C (Found: C, 56.80; H, 6.59; N, 3.01%. $C_{18}H_{25}Cl_2NOTi$ requires C, 55.41; H, 6.41; N, 3.59%); HRMS: calculated for [$C_{18}H_{25}Cl_2NO$-Ti(−H)$^+$], *m*/*z* 389.082; found 389.082). $\tilde{\nu}/cm^{-1}$ (KBr) 3103, 2967, 2922, 1698, 1641, 1596, 1437, 1267, 1103, 1023, 808 and 610. δ_H (Dichloromethane-d_2, 298 K, 600 MHz) 6.60, 6.50 (each m, each 2H, Cp–H), 6.55 (s, 5H, Cp′–H), 2.85 (br, 6H, NCH_3), 1.99 (m, 2H, 2-H), 1.76 (m, 2H, 3-H), 1.34 (s, 6H, 5-/5′-H). δ_C (Dichloromethane-d_2, 298 K, 150.8 MHz) 172.7 (C, C-1), 148.4 (C, Cp), 120.7 (CH, Cp′), 119.7, 119.1 (each CH, Cp), 41.9 (CH_2, C-3), 37.4, 35.5 (each CH_3, NCH_3), 37.2 (C, C-4), 28.8 (CH_2, C-2), 26.8 (CH_3, C-5/-5′).

4-[1-(Dichlorozirconocenyl)]-4-methylpentanoic acid diethylamide 13b. To a solid mixture of 964 mg (4.00 mmol) of the starting material **10b** with 1.05 g (4.00 mmol) of mono-(η^5-cyclopentadienyl)zirconium trichloride was added slowly *ca.* 60 mL of toluene at −78 °C. The mixture was allowed to warm to room temperature with stirring for 6 h and then stirred for 6 h at ambient temperature. The precipitated lithium chloride was removed by filtration and washed twice with toluene (20 mL). The combined organic solutions were concentrated *in vacuo* to 20 mL of toluene and then crystallized at −30 °C. The product was collected by filtration, washed with pentane (20 mL) and dried *in vacuo* to yield 1.16 g (63%) of compound **13b** as a violet powder, mp 83 °C. HRMS: calculated for [$C_{20}H_{29}Cl_2NOZr$(−HCl)$^+$], *m*/*z* 424.099; found 424.099. $\tilde{\nu}/cm^{-1}$ (KBr) 3084, 2965, 2931, 2875, 1659, 1586, 1490, 1457, 1394, 1366, 1315, 1270, 1214, 1101, 1022, 909, 818, 762 and 643. δ_H (Toluene-d_8, 298 K, 600 MHz) 5.93 (s, 5H, Cp′–H), 5.88, 5.74 (each m, each 2H, Cp–H), 3.11, 2.64 (each q, each ^3J = 7.1 Hz, each 2H, NCH_2CH$_3$), 1.77 (m, 2H, 3-H), 1.72 (m, 2H, 2-H), 1.20 (s, 6H, 5-/5′-H), 0.91, 0.66 (each t, each ^3J = 7.1 Hz, each 3H, NCH$_2$CH_3). δ_C (Toluene-d_8, 298 K, 150.8 MHz) 170.3 (C, C-1), 142.4 (C, Cp), 115.4 (CH, Cp′), 114.5, 113.3 (each CH, Cp), 41.7 (CH_2, C-3), 41.2, 39.8 (each CH_2, NCH_2CH$_3$), 35.6 (C, C-4), 28.0 (CH_2, C-2), 26.5 (CH_3, C-5/-5′), 14.0, 13.0 (each CH_3, NCH$_2$CH_3). δ_{15N}/δ_{1H} (Toluene-d_8, 60.7/599.9 MHz, 298 K) −258/0.91 (N/NCH$_2$CH_3), −258/0.66 (N/NCH$_2$CH_3). Single crystals for the X-ray crystal structure analysis (see Table 1) were obtained from toluene at room temperature.

Treatment of compound 12a with Meerwein's reagent, preparation of the metallocene cation complex 16. To a solid mixture of 418 mg (1.07 mmol) of the starting material **12a** with 204 mg (1.07 mmol) of the Meerwein's reagent ([Et_3O]$^+$[BF_4]$^-$) was added slowly *ca.* 80 mL of dichloromethane at −78 °C. The mixture was allowed to warm to room temperature with stirring for 6 h and then stirred for 6 h at ambient temperature. The solvent was removed *in vacuo* and the resulting precipitate was washed with a 1 : 1 mixture of dichloromethane and pentane (10 mL) to yield 335 mg (71%) of complex **16** as a brown powder, mp 151 °C. HRMS: calculated for [$C_{18}H_{25}Cl_2NO$-Ti(−Cl)$^+$], *m*/*z* 424.099; found 424.099. $\tilde{\nu}/cm^{-1}$ (KBr) 3112, 2975, 1618, 1515, 1492, 1418, 1350, 1259, 1053, 831, 802. δ_H (Dichloromethane-d_2, 298 K, 600 MHz) 7.00, 6.72, 6.47, 6.23 (each m, each 1H, Cp–H), 6.68 (s, 5H, Cp′–H), 3.24, 3.07 (each s, each 3H, NCH_3), 2.85 (m, 1H, 2-H), 2.72 (m, 1H, 2-H′), 1.82 (m, 1H, 3-H), 1.67 (m, 1H, 3-H′), 1.32 (s, 3H, 5-H), 1.19 (s, 3H, 5′-H). δ_C (Dichloromethane-d_2, 298 K, 150.8 MHz). 180.2 (C, C-1), 151.4 (C, Cp), 132.0, 119.7, 112.6, 111.9 (each CH, Cp), 121.7 (CH, Cp′), 39.9, 38.9 (each CH_3, NCH_3), 35.6 (C, C-4), 35.1 (CH_2, C-3), 32.7 (CH_3, C-5), 27.6 (CH_3, C-5′), 28.4 (CH_2, C-2). Single crystals for X-ray crystal structure analysis (see Table 1) were obtained from dichloromethane at −30 °C.

Treatment of compound 12a with lithium[n-butyltris(pentafluorphenyl)borate], generation of the metallocene cation complex 16. To a solid mixture of 20.0 mg (0.04 mmol) of the starting material **12a** with 21.2 mg (0.04 mmol) of lithium-[n-butyltris(pentafluorphenyl)borate] 1.5 mL of dichloromethane-d_2 was added. After filtration, the complex **16** was directly characterized by NMR spectroscopy. δ_H (Dichloromethane-d_2, 298 K, 600 MHz) 6.92, 6.84, 6.36, 6.15 (each m, each 1H, Cp–H), 6.62 (s, 5H, Cp′–H), 3.22, 3.08 (each s, each 3H, NCH_3), 2.86 (m, 1H, 2-H), 2.50 (m, 1H, 2-H′), 1.82 (m, 1H, 3-H), 1.56 (m, 1H, 3-H′), 1.34 (s, 3H, 5-H), 1.18 (s, 3H, 5′-H); Bu–B(C_6F_5)$_3$: 1.24 (m, 2H, 3-H), 1.16 (br, 2H, 1-H), 0.82 (br, 2H, 2-H), 0.78 (t, ^3J = 7.3 Hz, 3H, 4-H). δ_C (Dichloromethane-d_2, 298 K, 150.8 MHz) 180.4 (C, C-1), 150.2 (C, Cp), 134.0, 119.4, 112.6, 111.5 (each CH, Cp), 121.5 (CH, Cp′), 39.9, 39.3 (each CH_3, NCH_3), 35.6 (C, C-4), 35.1 (CH_2, C-3), 31.7 (CH_3, C-5), 28.3 (CH_3 and CH_2, C-2 and C-5′); Bu–B(C_6F_5)$_3$: 31.2 (C-2), 28.4 (C-1), 27.4 (C-3), 14.5 (C-4). δ_{15N}/δ_{1H} (Dichloromethane-d_2, 60.7/599.9 MHz, 298 K) −254/3.22 (N/NCH_3), −254/3.08 (N/NCH_3).

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