

Group IV Metal Dimethylamido Complexes of the Chiral Cyclopentadienyl-type Ligand (Cp^C)⁻¹

Florian Nährig,^[a] Sergej Lauk,^[a,b] Yu Sun,^[a] Helmut Sitzmann,^[a] and Werner. R. Thiel^{*[a]}

Dedicated to Prof. Dr. Christoph Janiak on the Occasion of his 60th Birthday

Abstract. Trisdimethylamido complexes of the Group IV elements titanium, zirconium and hafnium bearing the chiral Cp-type ligand

(Cp^C)⁻¹ were synthesized and characterized by means of NMR spectroscopy, elemental analysis and single crystal X-ray diffraction.

Amidocyclopentadienyl complexes of the group IV transition metals in the oxidation state +IV are accessible by a treating the corresponding trichloridocyclopentadienyl complexes (Cp)MCl₃ (Cp = C₅H₅⁻, M = Ti, Zr, Hf) with appropriate lithium amides.^[1] Alternatively, these compounds can be prepared by the reacting tetrakis(dialkylamido) transition metal precursors with cyclopentadiene or its derivatives.^[2] The homoleptic dimethylamido compounds M(NMe₂)₄ of titanium and zirconium were obtained by *Bradley* et al. in 1960 by treatment of the corresponding metal chlorides with lithium dimethylamide,^[3] the hafnium compound followed in 1969.^[4] Nowadays these compounds are all commercially available, since they serve as precursors for the synthesis of other Group IV compounds.^[5]

In addition they are of particular importance for the chemical vapor deposition of Group IV metal nitrides and nitride carbides giving hard material layers.^[6] Due to their basicity, these amides are able to deprotonate acidic hydrocarbons such as cyclopentadiene (C₅H₆) in situ under the release of highly volatile dimethylamine. *Chandra* and *Lappert* used this strategy in 1968 to synthesize the monomeric cyclopentadienyl complexes (Cp)Ti(NMe₂)₃ and (η⁵-Cp₂)Zr(NMe₂)₂ which in the following served as precursors for the synthesis of according silylamide, alkoxide and thiolate derivatives.^[2b,2c] The stability of these compounds is due to the formation of very

strong bonds especially with hard donor atoms that are capable undergo efficient π-donation to the electron-deficient transition metal center.^[1a,1b] Since the discovery of this new class of (Cp)M(NR₂)₃ compounds, a broad variety of systems with modified cyclopentadienyl-type ligands was obtained: In 1994, (Cp*)Ti(NMe₂)₃ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) was reported followed by the corresponding zirconium derivative only one year later and the hafnium complex in 2007.^[11]

Single crystal X-ray analyses proved the monomeric structure of these compounds with their characteristic three-legged piano-stool structure. This was confirmed by *Haaland* et al. who determined the molecular structure of (Cp*)Ti(NMe₂)₃ in the gas-phase by electron diffraction.^[7] Additionally, indenyl derivatives of the type (η⁵-Ind)M(NMe₂)₃ (M = Ti, Zr, Ind = C₉H₇⁻) were reported in the literature.^[2a,8] The titanium compound was initially assumed to have an η³-coordinated indenyl ligand.^[2a] However, 25 years later, *Martins* et al. could prove by means of ¹H and ¹³C NMR spectroscopy and supported by DFT calculations, that the five-membered indenyl ring is nearly planar and prefers an η⁵-coordination to the central atom.^[9]

Many of these complexes have found use in catalysis, mainly in olefin polymerization or copolymerization.^[10] In this context *ansa*-bridged NMe₂ complexes are of particular importance.^[11] *Rhodes* et al. found that addition of trimethylaluminum to (Cp)Ti(NMe₂)₃, (Cp*)Ti(NMe₂)₃ or (η⁵-Ind)Ti(NMe₂)₃ results in a remarkable increase of activity in the polymerization of ethylene and styrene.^[10d] Furthermore, *Janiak* et al. have studied the influence of bulky Cp-type ligands on the performance of zirconocene dichloride complexes in olefin polymerization reactions.^[12]

In 2005 *Tikkanen* et al. synthesized (η⁵-C₅Ph₅)Zr(NMe₂)₃ possessing the very bulky pentaphenylcyclopentadienyl ligand.^[13] Treatment of this compound with (*R*)-(+)-1-phenylethanol was considered to lead to a monosubstituted alkoxide complex with potential application in stereospecific catalysis. In this case and in the case of many other cyclopentadienyl complexes, chirality does not result from the cyclopentadienyl ligand itself but from the addition of a chiral substituent or the

* Prof. Dr. W. R. Thiel
E-Mail: thiel@chemie.uni-kl.de

[a] Fachbereich Chemie
Technische Universität Kaiserslautern
Erwin-Schrödinger-Str. 54
67663 Kaiserslautern, Germany

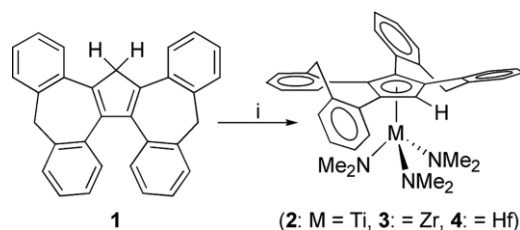
[b] Present address: Fachrichtung Chemie
Naturwissenschaftlich-Technische Fakultät
Universität des Saarlandes
Campus Saarbrücken
66123 Saarbrücken, Germany

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.202000271> or from the author.

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generation of an *ansa*-bridged system. However, there are some cyclopentadienyl ligands possessing intrinsic chirality. One example for such a compound is the 7*H*-dibenzo[*c,g*]fluorenide ligand (Dbf[−]).

The precursor DbfH was already synthesized in 1941 by Martin et al.^[14] but Dbf[−] was not noticed as an interesting ligand for transition metal chemistry until 2007, when we entered this field.^[15] However, DFT calculations showed that its barrier of racemization is only $\Delta G_{298}^{\ddagger} = 18.8 \text{ kJ}\cdot\text{mol}^{-1}$, which makes the isolation of enantiomerically pure DBF metal complexes impossible. To increase this barrier, we have designed the novel chiral and bulky cyclopentadiene derivative 5*H*-dibenzo[*e,h*]dibenzo[3,4:6,7]cyclohept-[1,2-*a*]azulene (**1**) (Scheme 1), which we abbreviate as Cp^CH due to the strong bending of its two double-benzannulated wings. Cp^CH (**1**) and its anion (Cp^C)[−] (**1**[−]) have significantly higher barriers of racemization (ca. 83 kJ·mol^{−1}).^[16] Starting from compound **1** we recently succeeded in the synthesis of a series of novel ferrocene analogues such as (Cp^C)₂Fe and (Cp^C)Fe(⁴Cp) (⁴Cp: 1,2,3,4-tetraisopropylcyclopentadienyl) as well as the first titanium(IV) half-sandwich complexes such as (Cp^C)Ti(OiPr)₃ and a series of platinum group metal complexes.



Scheme 1. Synthesis of compounds **2**, **3** and **4** by reaction of **1** with M(NMe₂)₄ (M = Ti, Zr, Hf): i) M(NMe₂)₄, benzene, 18 h, room temperature.

A common feature of all previous syntheses leading to (Cp^C)[−] complexes is an initial deprotonation of **1** using a strong base such as *n*BuLi, KN(SiMe₃)₂ or TIOEt followed by treatment of the lithium, potassium or thallium salts with suitable transition metal precursors.^[16] However, it is precisely this two-stage synthesis process that is circumvented by using the tetrakis(dialkylamido) complexes of titanium(IV), zirconium(IV), and hafnium(IV) (Scheme 1).

Treatment of M(NMe₂)₄ (M = Ti, Zr, Hf) with **1** in benzene at room temperature led, under release of dimethylamine, to the corresponding complexes of the type (Cp^C)M(NMe₂)₃ (**2**: M = Ti, **3**: = Zr, **4**: = Hf). After purification by crystallization, all three complexes could be obtained in good yields. The compounds are rather sensitive to moisture and have to be handled with great care to avoid hydrolysis. Since the complexes are only stable in nonpolar solvents such as benzene, *n*-pentane and toluene all NMR spectra were recorded in [D₆]benzene. The ¹H NMR spectra of **2**, **3** and **4** show the resonances of sixteen aromatic protons of the annulated benzene rings and one singlet of the remaining proton at the five-membered ring which is observed at a chemical shift of about 6.84 (**3,4**) and 6.62 ppm (**2**).

Due to the high barrier of inversion of the bent seven-membered rings all four methylene protons are magnetically inequivalent and their resonances appear as four doublets at approx. 3.48, 3.78, 3.96 and 4.23 ppm with typical geminal coupling constants of about 13 Hz. There is one resonance for the three NMe₂ groups in the ¹H NMR spectra of complexes **2**, **3** and **4** that appears as a singlet between 2.54 and 2.89 ppm depending on the central metal site. Accordingly, the rotations around the M–N bonds and around the axis defined by M and the center of the five-membered ring of the (Cp^C)[−] ligand are rapid at room temperature with respect to the NMR timescale. The titanium complex **2** shows the largest shift of this resonance to lower field, speaking for an efficient withdraw of electron density from the dimethylamido ligands. This is supported by the fact that the NMe₂ resonance of **2** is significantly broadened at room temperature compared to **3** and **4**. Increasing the recording temperature to 343 K, results in a sharpening of this resonance. A similar behavior was recently observed for the (Cp^C)TiI₂OiPr.^[16c]

Crystallization of the titanium complex **2** from toluene at room temperature yielded yellow prismatic single crystals of the triclinic space group *P* $\bar{1}$. In contrast to **2**, single crystals of the zirconium and hafnium complexes **3** and **4** were obtained by crystallizing saturated *n*-pentane solutions at 6 °C. The pink zirconium complex **3** also crystallizes in the triclinic space group *P* $\bar{1}$, with largely different cell parameters compared to compound **2**, whereas the colorless hafnium complex **4** crystallizes in the monoclinic space group *P*2₁/*c*. Figure 1 shows the molecular structure of **2–4** and summarizes typical bond parameters.

All three compounds have in common that they crystallize as racemic mixtures. As expected, they exhibit a distorted three-legged piano stool geometry with the five-membered ring of the (Cp^C)[−] ligand coordinating in a η^5 -mode to the central metal site. An analogue structure has been measured for (Cp^C)Ti(OiPr)₃.^[16c] In all complexes the individual M–C distances show some variations. Generally, the distance M–C1 is the shortest of the M–C distances, which is due to the least steric repulsion in this position. The other M–C distances are determined by the bending of the (Cp^C)[−] moiety and the positioning of the dimethylamido ligands and the steric consequences resulting from these.

The most important consequence results from the location of one of the dimethylamido methyl groups attached to the nitrogen atom N1 in the void opened-up from the upward orientation of the methylene unit at the right-hand wing of the (Cp^C)[−] ligand. This is a common feature of all three compounds and determines the orientation of the M–N vectors of the other two dimethylamido ligands. However, there are slight differences between the compounds: A top-view along the M–Cp axis (see the Supporting Information) shows the parallel orientation of the M–N1 bond to the C1–C_{Ph} bond in the titanium and the hafnium complexes **2** and **4** [torsion angles: 1.06(9)° and 0.3(1)°]. In the zirconium complex **3**, this torsion angle is larger [4.1(1)°], which can be explained by the longer bonds of zirconium compared to hafnium (lanthanide contraction) and titanium. This gives the N1-dimethylamido group in

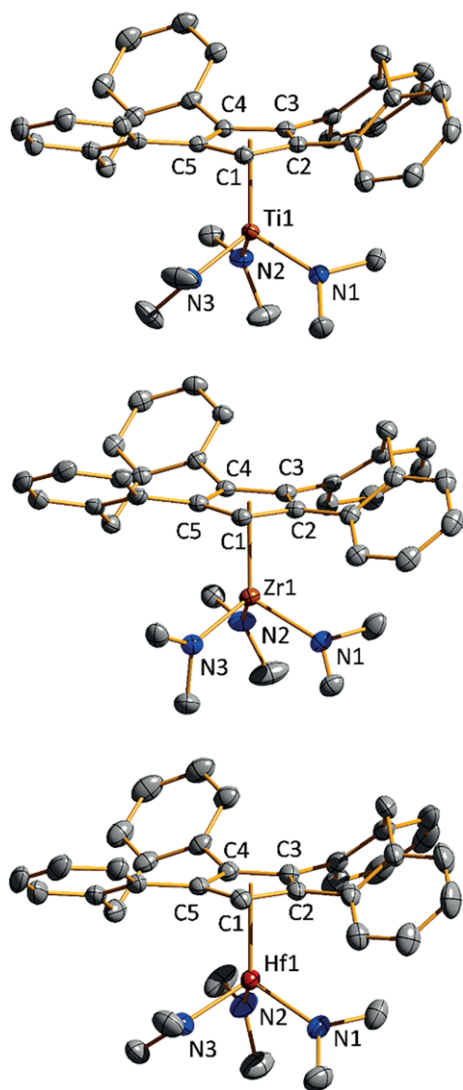


Figure 1. Molecular structure of compounds **2–4** in the solid state, hydrogen atoms are omitted for clarity. Characteristic bond lengths /Å and angles $^{\circ}$ of **2**: Ti1–N1 1.922(1), Ti1–N2 1.945(1), Ti1–N3 1.925(2), Ti1–C1 2.420(1), Ti1–C2 2.508(2), Ti1–C3 2.522(2), Ti1–C4 2.514(2), Ti1–C5 2.471(2), Ti1–Cp 2.173(2), N1–Ti1–N2 99.20(6), N1–Ti1–N3 100.39(6), N2–Ti1–N3 99.31(6), N1–Ti1–Cp 116.44(4), N2–Ti1–Cp 121.74(4), N3–Ti1–Cp 116.07(5). Characteristic bond lengths /Å and angles $^{\circ}$ of **3**: Zr1–N1 2.0381(18), Zr1–N2 2.096(2), Zr1–N3 2.067(2), Zr1–C1 2.568(2), Zr1–C2 2.596(2), Zr1–C3 2.603(2), Zr1–C4 2.648(2), Zr1–C5 2.641(2), Zr1–Cp 2.313(1), N1–Zr1–N2 98.28(8), N1–Zr1–N3 98.20(8), N2–Zr1–N3 107.13(8), N1–Zr1–Cp 116.09(5), N2–Zr1–Cp 121.24(5), N3–Zr1–Cp 112.72(5). Characteristic bond lengths /Å and angles $^{\circ}$ of **4**: Hf1–N1 2.037(2), Hf1–N2 2.046(2), Hf1–N3 2.037(2), Hf1–C1 2.523(2), Hf1–C2 2.595(2), Hf1–C3 2.619(2), Hf1–C4 2.625(2), Hf1–C5 2.584(2), Hf1–Cp 2.290(1), N1–Hf1–N2 101.19(9), N1–Hf1–N3 102.15(8), N2–Hf1–N3 98.85(9), N1–Hf1–Cp 116.81(6), N2–Hf1–Cp 120.76(6), N3–Hf1–Cp 114.02(6). Cp denotes the center of the five-membered ring of $(\text{Cp}^{\text{C}})^{-1}$.

3 a little bit more freedom and is the reason why the molecular structures in the solid state of **2** and **4** have more in common than those of **3** and **4**. Finally these little differences are responsible for the fact that the crystal space groups of **3** and **4** are different.

By comparing the Ti1–C distances [2.420(1)–2.522(1) Å, av.: 2.487(1) Å] measured for complex **2** with data from the literature, it becomes evident that these values are larger than those reported for structurally related compounds such as $(\text{Cp}^*)\text{Ti}(\text{NMe}_2)_3$ [2.385(15)–2.471(11) Å] or $(\eta^5\text{-Ind})\text{Ti}(\text{NMe}_2)\text{Cl}_2$ [2.32(1)–2.42(1) Å].^[1a,7,8] This can be explained by a steric repulsion between the bulky NMe_2 ligands and the two curved dibenzocycloheptatriene units of the $(\text{Cp}^{\text{C}})^{-1}$ ligand. The lengths of the Ti–N bonds [**2**, av.: 1.931(1) Å] are close to those of the complexes cited above. A comparison of the centroid metal bond [**2**: 2.173(2) Å] with the structurally analogue complex $(\text{Cp}^{\text{C}})\text{Ti}(\text{O}i\text{Pr})_3$ [2.112(1) Å], where the *i*Pr groups can bend away from the $(\text{Cp}^{\text{C}})^{-1}$ ligand,^[16c] again shows an increased value for compound **2**.

While the bond angles in the structurally similar zirconium complex **3** are almost identical to those of **2**, the bond lengths are as expected longer according to the larger atomic radius of zirconium. We found Zr1–C distances between 2.568(2) and 2.641(2) Å [average: 2.611(2) Å] and a Zr1–Cp (centroid) distance of 2.313(1) Å, which are larger than those found in the structurally related zirconium complex $(\eta^5\text{-Cp}^*)\text{Zr}(\text{NMe}_2)_3$ [av.: 2.558(15) Å] but comparable to values of $(\eta^5\text{-CpPh}_5)\text{Zr}(\text{NMe}_2)_3$ [av.: 2.634(3) Å].^[13] Although the differences in the Zr–N bond lengths [**2**, av.: 2.067(2) Å] are not as pronounced as for the Zr–C distances, a correlation between the Zr–N and Zr–Cp bond lengths with respect to the three different cyclopentadienyl-type ligands can be drawn. With an increase in the Zr–N bond lengths in the sequence $\text{CpPh}_5 < \text{Cp}^{\text{C}} < \text{Cp}^*$, a simultaneous decrease of the Zr–Cp distances in the sequence $\text{CpPh}_5 > \text{Cp}^{\text{C}} > \text{Cp}^*$ is observed. This gives an impression on the steric influence of those Cp-type ligands that in the end also influences the strength of the Zr–N bonds.

Compared to **3**, the structurally analogue hafnium complex **4** has slightly shorter M–C and M–N bond lengths [Hf1–C: 2.523(2)–2.625(2) Å, av.: 2.589(2) Å; Hf1–N: 2.036(2)–2.045(2) Å, av.: 2.039(2) Å], which is attributed to the lanthanide contraction as already mentioned above. The 5d orbitals can thus participate more strongly in the C–M and N–M bonds, which strengthens them.

In conclusion, although being a highly bulky CpH derivative, $\text{Cp}^{\text{C}}\text{H}$ undergoes coordination to Group IV metal sites when reacted with the homoleptic dimethylamido precursors $\text{M}(\text{NMe}_2)_4$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) and delivers complexes of the type $(\text{Cp}^{\text{C}})\text{M}(\text{NMe}_2)_3$ in good yields. Investigations in the solid-state structures of these compounds show the influence of the lanthanide contraction on bond parameters. The structural data also allow to evaluate the steric demand of the bent $(\text{Cp}^{\text{C}})^{-1}$ ligand in comparison to other bulky Cp derivatives. We are presently evaluating the application of the compounds in polymerization catalysis and material chemistry.

Experimental Section

General Remarks: All reactions were carried out in an inert atmosphere of dry nitrogen using standard Schlenk techniques. Chemicals were commercially achieved and used without further purifications.

Solvents used in reactions were dried by standard methods and degassed prior to use. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 (^1H , 400 MHz; ^{13}C , 101). The chemical shifts are referenced to internal solvent resonances. Elemental analyses were carried out with a Hanau Analyzer Vario MICRO cube. Copies of the NMR spectra are deposited in the Supporting Information to this manuscript. The X-ray structure analyses were recorded on an Oxford Diffraction Gemini S Ultra device. The ligand Cp^CH (**1**) was synthesized according to a published procedure.^[16a]

Synthesis of (Cp^C)Ti(NMe₂)₃ (2**):** A solution of 647 mg (1.64 mmol) of Cp^CH (**1**) in 10 mL of dry benzene was slowly added to 371 mg (1.64 mmol) Ti(NMe₂)₄ in 2 mL of dry benzene at 0 °C. The mixture was slowly warmed to room temperature and stirred for 16 h. During this time a color change from yellow to deep orange could be observed. All volatiles were removed under vacuum. The solid residue was washed three times with 10 mL *n*-pentane and dried under vacuum. Yellow crystals of **2** suitable for X-ray structure analysis were obtained by recrystallization of the crude product from toluene at room temperature. Yield 715 mg (76%). C₃₇H₃₉TiN₃ (573.59): calcd. C 77.48, H 6.85, N 7.33%; found: C 77.18, H 6.84, N 7.08%. **¹H NMR** (400 MHz, C₆D₆): δ = 7.74–7.66 (m, 1 H, H_{Ar}), 7.63–7.55 (m, 1 H, H_{Ar}), 7.45 (d, ³J_{HH} = 7.4 Hz, 1 H, H_{Ar}), 7.40 (d, ³J_{HH} = 7.8 Hz, 1 H, H_{Ar}), 7.20 (dd, ²J_{HH} = 14.7, ³J_{HH} = 6.1 Hz, 3 H, H_{Ar}), 7.15–6.93 (m, 8 H, H_{Ar}), 6.74 (t, ³J_{HH} = 7.3 Hz, 1 H, H_{Ar}), 6.62 (s, 1 H, H_{Cp}), 4.23 (d, ²J_{HH} = 13.0 Hz, 1 H, CH₂), 3.96 (d, ²J_{HH} = 13.1 Hz, 1 H, CH₂), 3.78 (d, ²J_{HH} = 13.0 Hz, 1 H, CH₂), 3.48 (d, ²J_{HH} = 13.2 Hz, 1 H, CH₂), 2.84 (s_{broad}, 18 H, N-CH₃). **¹³C{¹H} NMR** (101 MHz, C₆D₆): δ = 141.0, 140.8, 138.8, 138.8, 135.7, 134.8, 133.9, 133.6, 130.9, 130.7, 130.6, 129.5, 128.9, 128.7, 128.6, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.3, 126.4, 126.4, 126.2, 126.0, 121.7, 119.4, 108.3 (C_{CpH}), 49.0 (br., N-CH₃), 42.5 (CH₂), 42.0 (CH₂).

Synthesis of (Cp^C)Zr(NMe₂)₃ (3**):** Following the procedure given for complex **2**, 402 mg (1.02 mmol) of **1** were reacted with 273 mg

(1.02 mmol) of Zr(NMe₂)₄. Colorless crystals of **3** suitable for X-ray structure analysis were obtained by recrystallization of the crude product from *n*-pentane at 0 °C. Yield: 410 mg (65%). C₃₇H₃₉ZrN₃ (616.96): calcd. C 72.03, H 6.37, N 6.81%; found: C 71.56, H 6.12, N 6.67%. **¹H NMR** (400 MHz, C₆D₆): δ = 7.68–7.63 (m, 2 H, H_{Ar}), 7.47 (dd, ³J_{HH} = 7.6, ⁴J_{HH} = 1.0 Hz, 1 H, H_{Ar}), 7.37 (d, ³J_{HH} = 7.5 Hz, 1 H, H_{Ar}), 7.20 (td, ³J_{HH} = 7.7, ⁴J_{HH} = 4.2 Hz, 3 H, H_{Ar}), 7.16–6.92 (m, 8 H, H_{Ar}), 6.84 (s, 1 H, H_{Cp}), 6.77–6.70 (m, 1 H, H_{Ar}), 4.32 (d, ²J_{HH} = 13.3 Hz, 1 H, CH₂), 3.94 (d, ²J_{HH} = 13.1 Hz, 1 H, CH₂), 3.85 (d, ²J_{HH} = 13.4 Hz, 1 H, CH₂), 3.49 (d, ²J_{HH} = 13.1 Hz, 1 H, CH₂), 2.54 (s, 18 H, N-CH₃). **¹³C{¹H} NMR** (101 MHz, C₆D₆): δ = 140.9, 140.8, 138.6, 138.5, 135.0, 134.0, 133.5, 133.2, 131.0, 130.8, 129.6, 129.1, 128.8, 128.7, 128.7, 128.2, 128.0, 127.7, 127.6, 127.4, 126.7, 126.5, 126.2, 126.1, 122.4, 120.3, 108.0 (C_{CpH}), 44.3 (N-CH₃), 42.6 (CH₂), 42.0 (CH₂).

Synthesis of (Cp^C)Hf(NMe₂)₃ (4**):** Following the procedure given for complex **2**, 529 mg (1.34 mmol) of **1** were reacted with 475 mg (1.34 mmol) of Hf(NMe₂)₄. Colorless crystals of **4** suitable for X-ray structure analysis were obtained by recrystallization of the crude product from *n*-pentane at 0 °C. Yield: 577 mg (61%). C₃₇H₃₉HfN₃ (704.23): calcd. C 63.11, H 5.58, N 5.97%; found: C 63.09, H 5.62, N 5.94%. **¹H NMR** (400 MHz, C₆D₆): δ = 7.78–7.70 (m, 2 H, H_{Ar}), 7.49 (d, ³J_{HH} = 7.6 Hz, 1 H, H_{Ar}), 7.40 (d, ³J_{HH} = 7.9 Hz, 1 H, H_{Ar}), 7.30–7.18 (m, 6 H, H_{Ar}), 7.13 (td, ³J_{HH} = 7.4, ⁴J_{HH} = 1.2 Hz, 1 H, H_{Ar}), 7.09–6.98 (m, 4 H, H_{Ar}), 6.83 (s, 1 H, H_{Cp}), 6.80–6.74 (m, 1 H), 4.45 (d, ²J_{HH} = 13.4 Hz, 1 H, CH₂), 3.97 (d, ²J_{HH} = 13.1 Hz, 1 H, CH₂), 3.89 (d, ²J_{HH} = 13.4 Hz, 1 H, CH₂), 3.52 (d, ²J_{HH} = 13.2 Hz, 1 H, CH₂), 2.64 (s, 18 H, N-CH₃). **¹³C{¹H} NMR** (101 MHz): δ = 141.2, 141.1, 138.8, 138.6, 134.8, 133.7, 133.2, 133.0, 131.0, 130.7, 130.0, 129.3, 128.8, 128.8, 128.7, 128.6, 128.2, 127.9, 127.7, 127.5, 126.7, 126.6, 126.3, 126.2, 122.2, 120.0, 107.8 (C_{CpH}), 44.0 (N-CH₃), 42.5 (CH₂), 41.9 (CH₂).

Table 1. Crystallographic data, data collection and refinement.

	2	3	4
Emp. formula	C ₃₇ H ₃₉ N ₃ Ti	C ₃₇ H ₃₉ N ₃ Zr	C ₃₇ H ₃₉ HfN ₃
Form. weight	573.61	616.93	704.20
Crystal size /mm	0.418 × 0.174 × 0.072	0.248 × 0.077 × 0.053	0.369 × 0.118 × 0.063
<i>T</i> /K	150(2)	150(2)	150(2)
λ /Å	1.54184	1.54184	1.54184
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	10.6625(3)	9.9964(4)	10.1961(1)
<i>b</i> /Å	11.6363(5)	11.8114(5)	20.6039(3)
<i>c</i> /Å	14.0548(4)	13.7622(6)	14.6482(2)
α /°	104.752(3)	81.676(4)	90
β /°	95.364(3)	87.845(4)	92.953(1)
γ /°	113.858(3)	69.806(4)	90
<i>V</i> /Å ³	1503.69(10)	1508.84(12)	3073.20(7)
<i>Z</i>	2	2	4
$\rho_{\text{calcd.}}$ /g·cm ⁻³	1.267	1.358	1.522
μ /mm ⁻¹	2.630	3.204	6.491
θ -range /°	3.335–62.659	3.246–62.673	3.706–62.701
Refl. coll.	10024	9896	23270
Indep. refl.	4780 [R _{int} = 0.0251]	4812 [R _{int} = 0.0299]	4920 [R _{int} = 0.0336]
Data / restr. / param.	4780/0/376	4812/0/376	4920/0/376
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0331, 0.0840	0.0262, 0.0624	0.0189, 0.0421
<i>R</i> ind. (all data)	0.0346, 0.0854	0.0291, 0.0644	0.0217, 0.0437
GooF ^b	1.053	1.046	1.034
$\Delta\rho_{\text{max}}/\text{min}$ /e·Å ⁻³	0.323/–/–0.304	0.305/–/–0.371	0.368/–/–0.445

a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum \omega(F_o^2 - F_c^2)^2 / \sum \omega F_o^2]^{1/2}$. b) $GooF = [\sum \omega(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$.

X-ray Structure Analyses: Crystal data and refinement parameters are collected in Table 1. All structures were solved using direct method of SIR92,^[17] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.^[18] Analytical numeric absorption corrections were applied on all compounds.^[19] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined by using a riding model.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1998857, CCDC-1998858, and CCDC-1998859. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Supporting Information (see footnote on the first page of this article): NMR spectra, structural graphics.

Acknowledgements

The authors wish to thank the Carl Zeiss-Stiftung for donating a research grant to F.N. Open access funding enabled and organized by Projekt DEAL.

Keywords: Group IV elements / Cyclopentadienyl complexes / Bulky ligand / Chiral ligand / Half sandwich complexes

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Received: July 21, 2020

Published Online: November 23, 2020