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Synthesis and characterization of *rac*-[ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium bisamides (EBTHI)Zr(NHR)$_2$

Rudolf Wartchow [a], Sven Doye [b,*]

[a] *Institut für Anorganische Chemie der Universität Hannover, Callinstr. 9, D-30167 Hannover, Germany*
[b] *Institut für Organische Chemie der Universität Hannover, Schneiderberg 1B, D-30167 Hannover, Germany*

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Abstract

C_2-symmetric *rac*-ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)-zirconium dichloride (EBTHI)ZrCl$_2$ (*rac*-**1**) reacts with the lithium amides of 2,6-dimethylaniline, aniline and 2,3,4,5,6-pentafluoroaniline to yield the corresponding *rac*-ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)-zirconium bis(monoarylamido) complexes (EBTHI)Zr(NHR)$_2$ (*rac*-**3a-c**). These new bisamides represent potential chiral versions of the known Cp$_2$Zr(NHR)$_2$ derivatives which are active hydroamination catalysts. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Zirconocene; *ansa*-Metallocene; bis(Tetrahydroindenyl); Crystal structure; Metal amide

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1. Introduction

In 1988, Bergman et al. reported the synthesis of several zirconocene bisamides Cp$_2$Zr(NHR)$_2$ (Cp = η^5-C$_5$H$_5$, R = *t*-Bu, C$_6$H$_4$-*t*-Bu, 2,6-Me$_2$C$_6$H$_3$, CH(SiMe$_3$)$_2$) [1–7]. Upon heating to temperatures of ≥ 85°C these complexes lose 1 equiv of amine RNH$_2$ resulting in the formation of very reactive zirconocene imidoderivatives Cp$_2$Zr=NR. These compounds show an extensive reaction chemistry including [2 + 2]-cycloadditions with alkynes leading to azametallacyclobutenes which can be protonated by additional amine leading to enamines and regenerating the bisamides. Combining these facts mentioned above, Bergman et al. developed an intermolecular hydroamination procedure for alkynes based on zirconocene bisamides Cp$_2$Zr(NHR)$_2$ as catalysts [2,3]. A related CpTiCl$_3$-catalyzed intramolecular hydroamination procedure for amino alkynes was developed in the Livinghouse group in 1992. The reactive intermediate is a titanium imidoderivative [8]. In addition, Bergman et al. showed that [2 + 2]-cycloadditions between zirconocene imidoderivatives and alkenes (norbornene, ethylene), giving access to azametallacyclobutanes, are also possible [4,9]. A similar cycloaddition between the titanium imidocomplex (*t*-Bu$_3$SiO)$_2$Ti=NSi*t*-Bu$_3$ and ethylene was reported by Wolczanski et al. [9]. Unfortunately, the Bergman group did not succeed in developing an analogous and much more interesting hydroamination protocol for olefins (except in the case of the more reactive allene) using Cp$_2$Zr(NHR)$_2$ as catalysts [2,10]. However, to the best of our knowledge no zirconium complexes with other ligands than Cp has been used for these investigations. Furthermore, no effort has been made to increase the scope of the alkyne hydroamination (e.g. regarding turnover numbers and frequencies) or to extend it to alkene substrates by varying the ligands in compounds like L$_2$M(NHR)$_2$ (M = Ti, Zr, Hf).

Regarding these facts, it seems to be a challenging and promising goal to develop a hydroamination pro-

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* Corresponding author. Fax: +49 511 7623011; e-mail: sven.doye@oci.uni-hannover.de

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cess for olefins based on related in situ prepared group IV transition metal imidocomplexes. Therefore the synthesis of a wide variety of group IV metallocene bisamides as potential catalyst precursors is of great interest to us. Being aware of the big differences between group IV *ansa*-metallocenes and simple metallocenes in their performance as catalysts for Ziegler-Natta-olefin-polymerisations [11], we were first interested in the synthesis of *ansa*-zirconocene bisamides which may possess some advantages in their catalytic behavior for hydroamination processes compared with $Cp_2Zr(NHR)_2$. Keeping in mind that the hydroamination of olefins can be an enantioselective process, we focused on chiral *ansa*-zirconocene complexes, in particular on compounds bearing the extensively and successfully used C_2-symmetric ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl) ligand (EBTHI), introduced by Brintzinger et al. [12]. Whereas *ansa*-bis(indenyl) dialkylamido complexes are well known [13], to the best of our knowledge, related monoalkyl or monoarylamido complexes have never been reported.

Herein we want to report the synthesis and characterization of C_2-symmetric and potential chiral *ansa*-zirconocene bisamides *rac*-(EBTHI)Zr$(NHR)_2$ (R = 2,6-$Me_2C_6H_3$, Ph, C_6F_5) [14].

2. Results and discussion

2.1. Synthesis of rac-(EBTHI)Zr(NHR)$_2$

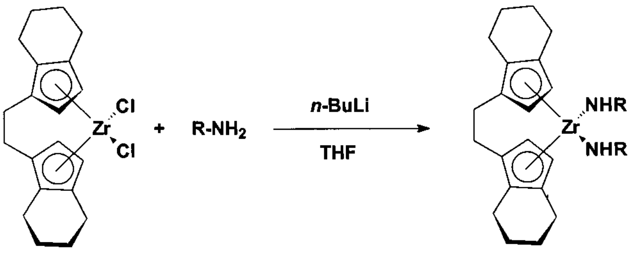
According to the work of Bergman et al. [1–7], there are two promising approaches to the synthesis of complexes (EBTHI)Zr$(NHR)_2$: (a) the reaction of lithium amides LiNHR with (EBTHI)$ZrCl_2$ resulting in the elimination of 2 equiv of LiCl, and (b) the reaction of amines RNH_2 with (EBTHI)$ZrMe_2$ at elevated temperatures which proceeds under loss of methane. For our initial studies we have chosen path (a) because (EBTHI)$ZrCl_2$ is commercially available and less sensitive than (EBTHI)$ZrMe_2$, which must be prepared first from the mentioned dichloride. Reactions using this approach can also be run in usual Schlenk-glassware and do not require the use of glass bombs, which have to be used for the high temperature reaction of amines with (EBTHI)$ZrMe_2$.

Due to the steric, more demanding (EBTHI)-ligand, compared with Cp used by Bergman et al., we were prepared to apply longer reaction times or elevated temperatures for the substitution reactions, in particular for bulky amides such as LiNH-2,6-$Me_2C_6H_3$. Surprisingly, the reaction of in situ prepared lithium amides LiNHR (R = 2,6-$Me_2C_6H_3$, Ph, C_6F_6) with (EBTHI)$ZrCl_2$ proceeds smoothly at room temperature in THF. All reactions went to completion in less than 6 h and resulted in the formation of the desired products *rac*-**3a**–**c** in good to modest yields (Scheme 1). However, due to their greater solubility in most solvents, the benzylamido-, *n*-butylamido- and cylohexylamido compounds could not be isolated yet.

The sensitivity of the title compounds *rac*-**3a**–**c** to moisture increases with less steric demanding amido ligands. Therefore compound *rac*-**3a** with the bulky 2,6-dimethylphenylamido-ligand shows only modest sensitivity to moisture and can be exposed briefly to air, in particular in a crystalline form. *rac*-**3b** and *rac*-**3c** are much more sensitive against moisture and should be handled only under an inert atmosphere [15].

2.2. Characterization of rac-(EBTHI)Zr(NHR)$_2$

The new compounds were characterized by ^{1}H- and ^{13}C-NMR and MS spectra as well as elemental analysis in the case of *rac*-**3a** [15]. All ^{1}H- and ^{13}C-NMR spectra of *rac*-**3a**–**c** showed the presence of small amounts of the corresponding free anilines. These were presumably produced by hydrolysis of *rac*-**3a**–**c** due to traces of water on the glassware. An analogous decomposition has also been reported for $Cp_2Zr(NHR)_2$ derivatives [2] and could not be prevented. Nevertheless, the NMR spectra show that in solution all (EBTHI)Zr$(NHR)_2$ derivatives possess the desired C_2 symmetry and therefore represent potential chiral hydroamination catalyst precursors. Furthermore, it can be seen from the NMR spectra that the two *ortho* hydrogen atoms (*rac*-**3b**) or methyl carbon atoms (*rac*-**3a**) and the two *meta* hydrogen atoms (*rac*-**3a**, *rac*-**3b**) in the arylamido ligands are equivalent. Only one signal for each pair of atoms is observed. This indicates that the rotation around the aryl-nitrogen-bond is not hindered by steric interactions and therefore fast at the NMR time scale, even for the bulky 2,6-dimethylphenylamido ligand in *rac*-**3a**. However, a very interesting and surprising fact is that at room temperature the ^{1}H-NMR of *rac*-**3a** shows no typical CH_3 singlet signal for the aromatic methyl



rac-1 2a-c *rac*-3a-c

a: R = 2,6-$Me_2C_6H_3$, Yield: 77 %
b: R = C_6H_5, Yield: 69 %
c: R = C_6F_5, Yield: 68 %

Scheme 1.

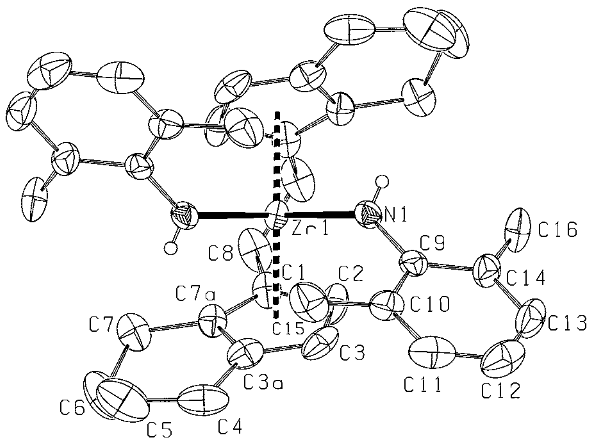


Fig. 1. PLATON-drawing of *rac*-**3a**. Hydrogen atoms (except NH) are omitted for clarity. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (pm) and angles (°): Zr(1)–C(1) 253.2(4), Zr(1)–C(2) 246.0(5), Zr(1)–C(3) 252.4(3), Zr(1)–C(3a) 264.0(4), Zr(1)–C(7a) 262.8(4), Zr(1)–N(1) 213.7(3), C(1)–C(8) 150.7(5), C(8)–C(8‘) 153.0(6), N(1)–C(9) 141.9(5), C(9)–C(10) 140.2(6), C(9)–C(14) 141.2(5), C(10)–C(15) 151.3(6), C(14)–C(16) 150.4(6), N(1)–Zr(1)–N(1) 105.9(1), Zr(1)–N(1)–C(9) 138.9(2), N(1)–C(9)–C(10) 121.1(3), N(1)–C(9)–C(14) 121.5(4), C(9)–C(10)–C(15) 122.7(4), C(9)–C(14)–C(16) 119.9(4), C_g–Zr(1)–C'_g 123.7, (C_g defines the centers of gravity of the five-membered rings of the corresponding tetrahydroindenyl systems).

groups. This can only be explained by a strong hindrance of the rotation of the methyl groups around the corresponding C–C bonds which results in the presence of three non-equivalent hydrogen atoms in each methyl group. The reason for this rotational barrier must be a steric or electronic interaction between the methyl groups and the (EBTHI) ligand, because an analogous behavior has not been observed for the $Cp_2Zr(NH\text{-}2,6\text{-}Me_2C_6H_3)_2$ derivative [4]. In order to investigate this different behavior, and to prove the proposed structure for the (EBTHI)$Zr(NHR)_2$ derivatives, the molecular structure of *rac*-**3a** has been determined by X-ray crystal structure analysis. A PLATON-drawing of *rac*-**3a** is shown in Fig. 1. Table 1 gives the atomic coordinates and equivalent isotropic thermal parameters of *rac*-**3a**. Crystallographic data (excluding structure factors) for the structure of *rac*-**3a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101562.

Fig. 1 shows that the structure of *rac*-**3a** obtained by X-ray analysis is in agreement with the spectroscopic data. However, an obvious reason for the lack of methyl signals in the ^{1}H-NMR of *rac*-**3a** could not be found. In the solid state all distances between other atoms and the methyl carbon atoms are longer than 2.7 Å. Therefore a restricted rotation of the methyl groups caused by steric interactions between the methyl groups and parts of the (EBTHI) ligand is unlikely. Further investigations to clarify this behavior of *rac*-**3a** in the ^{1}H-NMR are underway in our laboratories.

The X-ray crystal structure analysis further shows that the exchange of the chloro ligands in (EBTHI)$ZrCl_2$ by the much bulkier NH-2,6-$Me_2C_6H_3$ ligands leads to significant changes in the geometry of the complex [16]. In (EBTHI)$ZrCl_2$, the Cl–Zr–Cl′ bond angle is 98.6° and the C_g–Zr–C'_g angle is 125.0° (C_g defines the centers of gravity of the five-membered rings of the corresponding tetrahydroindenyl systems) [17]. In *rac*-**3a** the corresponding angles are RHN–Zr–N′H′R′ = 105.9°, and C_g–Zr–C'_g = 123.7°. Furthermore, *rac*-**3a** can be compared with the related compound (EBTHI)$Zr(CH_2\text{–}Ph)_2$ which lacks the 2,6-dimethyl substitution and shows a C–Zr–C′ angle of only 94.7°, and a C_g–Zr–C'_g angle of 124.4° [18]. In particular, the fact that the RHN–Zr–N‘H‘R bond angle in *rac*-**3a** is more than 7° bigger than in the related chloro or benzyl compound shows that *rac*-**3a** suffers from large steric strain. Due to this high steric strain it is likely to predict an easy loss of amine from *rac*-**3a** and its enantiomerically pure counterpart which should possess analogous properties. This should give access to a reactive and potential chiral imidocomplex under relatively mild conditions.

3. Conclusion

Novel C_2-symmetric and potential chiral [14] *ansa*-zirconocene bisamides bearing the ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)-ligand (EBTHI)$Zr(NHR)_2$ *rac*-**3a**–**c** (R = Ph, 2,6-$Me_2C_6H_3$, C_6F_5) are accessible for the first time from *rac*-1,2-bis(η^5-4,5,6,7-tetrahydro-

Table 1
Atomic coordinates and equivalent isotropic thermal parameters of *rac*-**3a**

Atom	*x*	*y*	*z*	U_{eq} (Å^2)
Zr(1)	0.5000	0.25337(4)	0.2500	0.0408(1)
N(1)	0.6398(2)	0.1659(2)	0.22486(17)	0.0462(10)
C(1)	0.4547(3)	0.3963(2)	0.1728(3)	0.0567(14)
C(2)	0.5508(4)	0.3537(3)	0.1390(3)	0.0700(19)
C(3)	0.5139(5)	0.2733(3)	0.1018(2)	0.0703(18)
C(3a)	0.3963(4)	0.2650(3)	0.1119(2)	0.0617(16)
C(4)	0.3135(5)	0.1994(3)	0.0746(3)	0.091(2)
C(5)	0.1921(5)	0.2178(4)	0.0975(4)	0.122(3)
C(6)	0.1648(4)	0.3084(3)	0.1083(4)	0.106(3)
C(7)	0.2366(3)	0.3634(3)	0.1663(2)	0.0683(16)
C(7a)	0.3600(3)	0.3408(3)	0.1561(2)	0.0530(14)
C(8)	0.4532(3)	0.4841(2)	0.2187(3)	0.0743(19)
C(9)	0.6877(3)	0.1194(3)	0.1593(2)	0.0470(12)
C(10)	0.6301(3)	0.0477(3)	0.1223(3)	0.0607(16)
C(11)	0.6801(5)	0.0017(3)	0.0597(3)	0.086(2)
C(12)	0.7845(5)	0.0217(4)	0.0323(3)	0.099(3)
C(13)	0.8432(4)	0.0927(3)	0.0670(3)	0.084(2)
C(14)	0.7962(3)	0.1416(3)	0.1301(3)	0.0613(16)
C(15)	0.5139(4)	0.0165(3)	0.1483(3)	0.0890(19)
C(16)	0.8598(3)	0.2208(3)	0.1646(3)	0.092(2)

1-indenyl)-zirconium dichloride and lithium amides. In connection with our efforts in developing an efficient catalytic hydroamination process for alkenes based on transitionmetal imidocomplexes as catalysts, we consider these novel complexes as possible chiral catalyst precursors. Investigations concerning the reactivity of the described compounds towards the hydroamination of alkynes compared with $Cp_2Zr(NHR)_2$ and an extension to alkene substrates are underway in our laboratories and will be published in due course.

4. Experimental

4.1. General procedures

All reactions were carried out under an inert atmosphere of argon in flame-dried glassware. Toluene, THF, Et_2O and hexane were distiled from sodium benzophenone ketyl under argon. 2,6-Dimethylaniline and aniline were distiled from sodium under argon. 2,3,4,5,6-Pentafluoroaniline was purchased from Acros Organics and used without further purification. *rac*-(EBTHI)$ZrCl_2$ was purchased from Witco and used without further purification. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Mass spectra were measured on a Finnigan MAT 312 spectrometer. Elemental analyses were recorded on an elementar vario EL machine.

4.1.1. *rac-bis(2,6-dimethylphenylamido)-[Ethylene-1,2-bis(η⁵-4,5,6,7-tetrahydro-1-indenyl)] zirconium (rac-**3a**)*

To a solution of 2,6-dimethylaniline (0.33 ml, 2.67 mmol) in THF (10 ml), 1.6 M *n*-BuLi in hexane (1.54 ml, 2.46 mmol) was added dropwise at 25°C. After the solution was stirred for 30 min, solid *rac*-(EBTHI)$ZrCl_2$ (0.5 g, 1.17 mmol) was added in one portion. The reaction mixture turned yellow. The solution was stirred for 6 h at 25°C. Then the volatile materials were removed under reduced pressure. Toluene (20 ml) was added to the residue and the mixture was stirred for 12 h at 25°C. The slurry was filtered. The toluene was removed under reduced pressure. The remaining yellow solid was washed with Et_2O (4×10 ml) and dried under vacuum. The obtained yellow powder (0.54 g, 0.91 mmol, 77%) was pure by ^{1}H-NMR. Crystals for X-ray analysis were obtained by layering a THF solution of *rac*-**3a** with hexane and cooling the resulting mixture to -30°C. Yellow crystals formed over several days. ^{1}H-NMR: (400 MHz, C_6D_6): $\delta = 7.17$ (d, $^3J(H,H) = 7.4$ Hz, 4H, Ar–H), 6.92 (t, $^3J(H,H) = 7.4$ Hz, 2H, Ar–H), 5.57 (d, $^3J(H,H) = 3.0$ Hz, 2H, Cp–H), 5.40 (sbr, 2H, NH), 5.30 (d, $^3J(H,H) = 3.0$ Hz, 2H, Cp–H), 2.74–2.26 (m, 24H), 1.75–1.52 (m, 4H), 1.40–1.26 (m, 4H) ppm; ^{13}C-NMR (100.6 MHz, DEPT, C_6D_6): $\delta = 155.5$ (C), 129.4 (C), 129.4 (C), 119.7 (CH), 119.4 (C), 112.7 (CH), 106.5 (CH), 28.5 (CH_2), 24.1 (CH_2), 24.0 (CH_2), 23.3 (CH_2), 22.8 (CH_2), 21.5 (CH_3) ppm; MS (EI, 150°C): *m*/*z* (%): 594 ([M^+], 3), 474 ([M^+–NH–2,6-$Me_2C_6H_3$], 44), 347 (25), 121 ([NH_2–2,6-$Me_2C_6H_3$], 100), 106 (62); $C_{36}H_{44}N_2Zr$ (595.98): Calc. C 72.55, H 7.44, N 4.70; found C 72.18, H 7.42, N 4.56.

4.1.2. *rac-bis(phenylamido)[Ethylene-1,2-bis-(η⁵-4,5,6,7-tetrahydro-1-indenyl)]zirconium (rac-**3b**)*

To a solution of aniline (0.24 ml, 2.67 mmol) in THF (10 ml), 1.6 M *n*-BuLi in hexane (1.54 ml, 2.46 mmol) was added dropwise at 25°C. After the solution was stirred for 30 min, solid *rac*-(EBTHI)$ZrCl_2$ (0.5 g, 1.17 mmol) was added in one portion. The reaction mixture turned yellow. The solution was stirred for 6 h at 25°C. Then the volatile materials were removed under reduced pressure. Toluene (20 ml) was added to the residue and the mixture was stirred for 12 h at 25°C. The slurry was filtered. The toluene was removed under reduced pressure. The remaining yellow solid was washed with Et_2O (4×10 ml) and dried under vacuum. The obtained yellow powder (0.44 g, 0.81 mmol, 69%) was pure by ^{1}H-NMR. ^{1}H-NMR: (400 MHz, C_6D_6): $\delta = 7.20$ (tt, $^3J(H,H) = 7.4$, 1.9 Hz, 4H, Ar–H), 6.88 (dt, $^3J(H,H) = 7.5$, 1.0 Hz, 4H, Ar–H), 6.80 (tt, $^3J(H,H) = 7.3$, 1.1 Hz, 2H, Ar–H), 6.01 (sbr, 2H, NH), 5.90 (d, $^3J(H,H) = 3.0$ Hz, 2H, Cp–H), 5.13 ($^3J(H,H) = 3.0$ Hz, 2H, Cp–H), 2.94–2.85 (m, 2H), 2.67–2.47 (m, 6H), 2.42–2.28 (m, 4H), 1.83–1.70 (m, 4H), 1.60–1.43 (m, 4H) ppm; ^{13}C-NMR (100.6 MHz, DEPT, C_6D_6): $\delta = 156.5$ (C), 129.0 (CH), 128.7 (C), 128.1 (C), 119.5 (C), 118.7 (CH), 117.9 (CH), 110.4 (CH), 103.9 (CH), 27.5 (CH_2), 24.3 (CH_2), 23.7 (CH_2), 23.3 (CH_2), 23.3 (CH_2) ppm; MS (EI, 130°C): *m*/*z* (%): 538 ([M^+], 5), 446 ([M–NH–Ph], 52), 147 (29), 134 (100), 117 (28), 93 (NH_2–Ph, 80).

4.1.3. *rac-bis(2,3,4,5,6-pentafluorophenylamido)-[Ethylene-1,2-bis(η⁵-4,5,6,7-tetrahydro-1-indenyl)]-zirconium (rac-**3c**)*

To a solution of 2,3,4,5,6-pentafluoroaniline (0.24 g, 1.33 mmol) in THF (5 ml), 1.6 M *n*-BuLi in hexane (0.77 ml, 1.23 mmol) was added dropwise at room temperature. After the solution was stirred for 30 min at room temperature, solid *rac*-(EBTHI)$ZrCl_2$ (0.25 g, 0.59 mmol) was added in one portion. The reaction mixture turned yellow brown. The solution was stirred for 6 h at 25°C. Then the volatile materials were removed under reduced pressure. Toluene (20 ml) was added to the residue and the mixture was stirred for 12 h at 25°C. The slurry was filtered. The toluene was removed under reduced pressure. The remaining gray-brown solid was washed with Et_2O (1×5 ml), hexane (1×5 ml) and cold toluene (1×1 ml) and dried under vacuum. The remaining yellow solid (0.285 g, 0.40 mmol, 68%) was pure by ^{1}H-NMR. ^{1}H-NMR (400 MHz, C_6D_6): $\delta = 5.71$ (m, 2H, Cp–H), 5.13 (d, $^3J(HH) = 3.1$ Hz, 2H, Cp–H), 5.0 (sbr, 2H, NH), 2.71–2.38 (m, 8H), 2.37–2.22 (m, 4H), 1.80–1.66 (m, 4H), 1.52–1.34 (m, 4H) ppm; ^{13}C-NMR (100.6 MHz, C_6D_6): $\delta = 138.9$ (d, $^1J(CF) = 233.6$ Hz, CF), 138.5 (d, $^1J(CF) = 245.4$ Hz, CF), 131.0, 130.9, 121.9, 111.8, 106.1, 27.6, 23.9, 23.2, 22.8, 22.6 ppm; The two missing signals for the 2,3,4,5,6-pentafluorophenylamido ligand could not be detected, probably due to their low intensity.

4.1.4. Crystal structure determination of *rac*-**3a**

X-ray structure of *rac*-**3a**: formula $C_{36}H_{44}N_2Zr$ formula weight, 595.98; crystal system, orthorhombic; space group, *Pbcn* (No. 60); $a = 1181.6(1)$; $b = 1471.6(2)$; $c = 1688.2(2)$ pm; $\alpha = 90°$; $\beta = 90°$; $\gamma = 90°$; $V = 2935.5(6) \times 10^6$ pm^3; $Z = 4$; $\rho_{calc} = 1.349$ g cm^{-1}; $F_{000} = 1256$; $\mu = 4.0$ cm^{-1}; crystal size, 0.37 × 0.37 × 0.52 mm; diffractometer type, STOE IPDS; graphite monochromated Mo–K_α, 71.073 pm; measurement at 300 K; range of measurement, $4.4° < 2\Theta < 48.2°$; *h,k,l* range, −13/13, −16/16, −19/19; 22439 measured reflections; 2308 unique reflections; 1159 observed reflections ($I_0 > 2.0\sigma(I_0)$); $R_1(F_0 > 4.0\sigma(F_0)) = 0.0304$; $wR_2 = 0.0654$; GOF = 0.84; number of refined parameters, 181; $(\Delta\rho)_{min} = -0.22$ e Å^{-3}; $(\Delta\rho)_{max} = 0.22$ e Å^{-3}; programs used, SHELXS-86, SHELXL-93, PLATON.

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[14] For economical reasons we started our project using the less expensive *rac*-(EBTHI)$ZrCl_2$ instead of the enantiomeric pure compound.

[15] This moisture sensitivity and the lack of equipment for preparing samples for elemental analysis under an inert atmosphere in our laboratorium are the reasons why elemental analysis could not be determined reproducible for the very sensitive compounds **3b** and **3c**.

[16] Unfortunately, a comparison with $Cp_2Zr(NH–2,6\text{-}Me_2C_6H_3)_2$ is not possible because crystallographic data for this compound are not published yet.

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