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Journal of Organometallic Chemistry 689 (2004) 595–604
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Mono- and bis-(2-dimethylaminoethyl)tetramethylcyclopentadienyl zirconium(IV) complexes: synthesis and structural studies in crystalline state and in solutions

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Received 15 February 2003; accepted 10 November 2003

Abstract

A novel half-sandwich Zr(IV) complex $[\eta^5{:}\eta^1\text{-}N\text{-}C_5(CH_3)_4CH_2CH_2N(CH_3)_2]ZrCl_3$ (**6**) together with zirconocene dichlorides $[\eta^5\text{-}C_5(CH_3)_4CH_2CH_2N(CH_3)_2][\eta^5\text{-}C_5(CH_3)_5]ZrCl_2$ (**4**) and $[\eta^5\text{-}C_5(CH_3)_4CH_2CH_2N(CH_3)_2]_2ZrCl_2$ (**5**) have been prepared. Complex **6** has been isolated and characterized in three different forms, namely, as an adduct with THF **6a**, an adduct with tetrahydrothiophene **6b**, and a solvent-free form **6c**. Molecular structures of complexes **4**, **6b**, and **6c** have been established by X-ray diffraction analysis. Complex **6c** has been shown to be a monomeric solvent-free half sandwich Zr(IV) complex. The dynamic behavior of complex **6a** in a non-solvating medium (an equilibrium between **6a** and **6c** along with a degenerate interconversion of the $Zr–C_{cp}–CH_2–CH_2–N(CH_3)_2–(Zr)$ pseudo-five-member metallacycle) have been studied by the variable-temperature ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The activation parameters for the degenerate five-member cycle interconversion have been elucidated.

Keywords: Zirconium; Cyclopentadienyl ligands; Intramolecular coordination; N ligands; Dynamic behavior

1. Introduction

The organometallic chemistry of heteroelement side-chain functionalized cyclopentadienyl complexes of transition metals is now under intense development. Among these side-chain functionalized transition metal complexes, those derived from cyclopentadienyl type ligands with a pendant *n*-donor nitrogen group are of great significance. Here we present our results on the preparation and structural studies of the Zr(IV) complexes derived from $C_5(CH_3)_4CH_2CH_2N(CH_3)_2$ ligand (hereinafter Cp^{*N}). Despite the fact that the ligand itself is a well known [1] and broadly employed structural unit in modern organometallic chemistry of both transition and main Group elements (see reviews [2–4]), the Zr(IV) complexes derived from Cp^{*N} have not been reported yet. In literature, there exists the only mentioning of a pyridine adduct $\{[\eta^5\text{-}C_5(CH_3)_4CH_2CH_2N^+H(CH_3)_2]ZrCl_3\}Cl^- \cdot C_5H_5N$, unfortunately, not supported by any structural or spectral data [4]. This strange void in the Zr(IV) cyclopentadienyl chemistry enforced us to synthesize and study Zr(IV) sandwich and, especially, half-sandwich complexes derived from the Cp^{*N} ligand.

2. Results and discussion

2.1. Preparation of the Zr(IV) complexes with $C_5(CH_3)_4CH_2CH_2N(CH_3)_2$ ligand

The starting HCp^{*N} cyclopentadiene was prepared accordingly to the original procedure [1] with a small modification (see Section 4). This starting cyclopenta-

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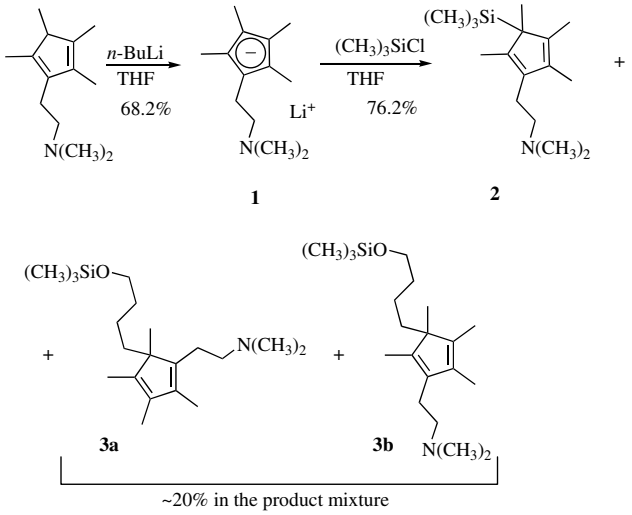
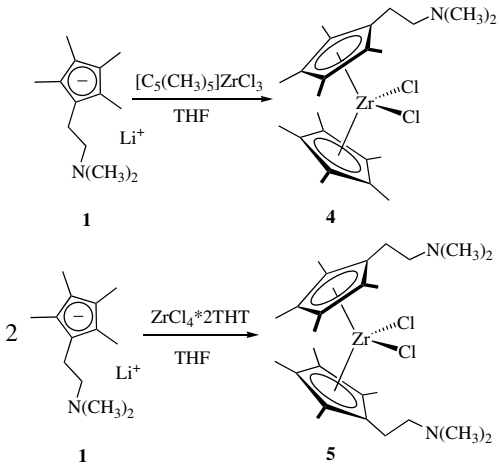
doi:10.1016/j.jorganchem.2003.11.012



Scheme 1.



Scheme 2.

diene was further consecutively converted into its lithium and trimethylsilyl derivatives **1** and **2**, respectively (see Scheme 1).

Of interest, under the reaction conditions, formation of the previously reported [5] silane **2** is accompanied by formation of a considerable amount of the side-products **3a** and **3b**. These isomeric silanes **3a** and **3b** are formed in approximately equimolar amounts (^{1}H NMR spectroscopy data). Both of them are the products of the THF ring cleavage with the lithium cyclopentadienide **1** promoted with trimethylchlorosilane. The relative rate of this side reaction is sensitive to temperature. The increase of the temperature (up to 80–90 °C) decreases the contribution of the THF cleavage side process. However, if this reaction is performed at lower temperature (0 °C or below), the molar share of silanes **3a** and **3b** in the product mixture may even exceed 50%. This fact agrees with an evident assumption, that the transition state for the side reaction requires, at least, more than two participants [i.e., cyclopentadienide **1**, THF and $(CH_3)_3SiCl$] and, this way, the side reaction possesses the higher activation entropy. All attempts to completely avoid **3a** and **3b** formation failed, with the best content of the side products achieved not less than ~20%. Application of other suitable solvents was also unsuccessful. In ether, for example, no silylation of **1** occurs even at 90 °C (sealed evacuated vessel). In ether/THF mixture (9:1), **3a** and **3b** are the only products. The THF ring cleavage products **3a** and **3b** are inseparable (at least, hardly separable) from **2**. However, the presence of **3a** and **3b** does not crucially prevent to perform the preparation and isolation procedures on the further steps of the synthesis.

Two biscyclopentadienyl complexes $Cp^*Cp^{*N}ZrCl_2$ (**4**) and $(Cp^{*N})_2ZrCl_2$ (**5**) were prepared starting from cyclopentadienide **1** and Cp^*ZrCl_3 and $ZrCl_4 \cdot 2THT$, respectively (hereinafter, THT = tetrahydrothiophene) as it is depicted in Scheme 2.

Noteworthy, both of these zirconocene dichlorides **4** and **5** are extremely sensitive to moisture. This particularity agrees with what was reported formerly for the structurally close titano- and zirconocene dichlorides with pendant nitrogen *n*-donor functionalities and is in accordance with the well known catalytic effect of tertiary amines on the hydrolysis and/or alcoholysis of the Group 4 metallocene dichlorides [3].

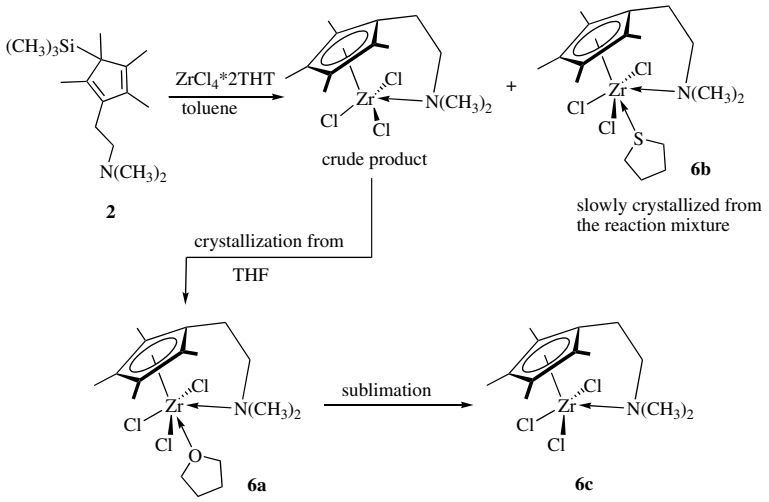
Preparation of the half-sandwich compound $[\eta^5{:}\eta^1$-*N*-$Cp^{*N}]ZrCl_3$ (**6**) was performed via silane **2** (see Scheme 3).

Compound **6** was characterized as three different complexes, **6a** (an adduct with THF), **6b** (an adduct with THT), and **6c** (a solvent-free complex), dependently upon the isolation and purification conditions. The molecular structure of complexes **6b** and **6c** was studied by X-ray diffraction analysis. The dynamic behavior of complex **6a** was investigated by the variable-temperature NMR spectroscopy in non-coordinating solvent (CD_2Cl_2).

*2.2. X-ray structural investigations of zirconocene dichloride **4** and half-sandwich complexes **6b** and **6c***

Single crystals of zirconocene dichloride **4** suitable for X-ray analysis were obtained by crystallization from ether. As expected a priori, no coordination of the amino-group to Zr(IV) was observed (see Fig. 1).

The main structural parameters of **4** are close to those observed for its S-heteroatom side-chain functionalized analogue $[\eta^5\text{-}C_5(CH_3)_4CH_2CH_2SCH_3][\eta^5\text{-}C_5(CH_3)_5]ZrCl_2$ [6] and, for instance, for similarly substituted decaalkyl zirconocene dichloride $[\eta^5\text{-}C_5(CH_3)_4CH_2CH_3]_2ZrCl_2$ [7].



Scheme 3.

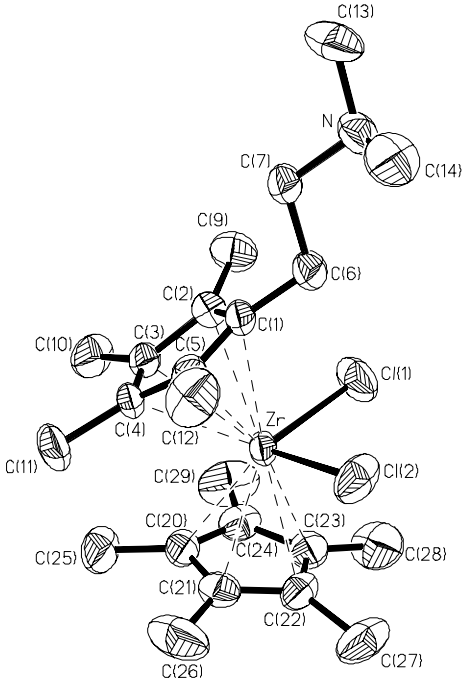


Fig. 1. Molecular structure of complex **4**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr–Cl(1) 2.438(2), Zr–Cl(2) 2.440(2), Zr–Cp_{cent}(C(1)–C(5)) 2.239, Zr–Cp_{cent}(C(20)–C(24)) 2.243, N–C(14) 1.424(9), N–C(7) 1.455(7), N–C(13) 1.464(9), Cl(1)–Zr–Cl(2) 94.8(1); C(14)–N–C(7) 110.5(6), C(14)–N–C(13) 109.3(6), C(7)–N–C(13) 109.9(6), Cp_{cent}–Zr–Cp_{cent} 136.9.

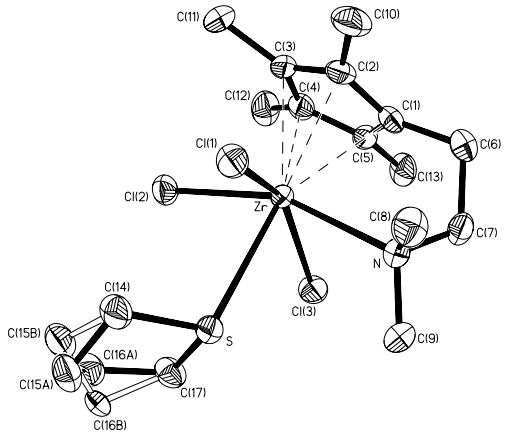


Fig. 2. Molecular structure of complex **6b**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Carbon atoms C(15) and C(16) of THT ligand are disordered over two positions with occupancy ratio 0.56/0.44. The selected bond lengths (Å) and angles (°): Zr–Cl(1) 2.470(2), Zr–Cl(2) 2.449(2), Zr–Cl(3) 2.478(2), Zr–N 2.594(3), Zr–S 2.906(2), Zr–Cp_{cent} 2.229; C(8)–N–C(7) 108.6(3), C(8)–N–C(9) 106.5(3), C(7)–N–C(9) 105.9(3), S–Zr–Cp_{cent} 178.7.

Single crystals of half sandwich **6b** were obtained by crystallization from toluene solution (the reaction mixture) containing free THT that liberated from the $ZrCl_4 \cdot 2THT$ during the course of the reaction. The Zr atom possesses pseudo-octahedron coordination environment (in an assumption that the Cp^{*N} ligand ring occupies one coordination site), with the ring and the THT molecule occupying the apical positions of the distorted tetragonal bipyramid, while the chlorine atoms and the $N(CH_3)_2$-group occupy the equatorial positions (see Fig. 2). The molecular structure of **6b** strongly resembles that of its ring non-permethylated analogue $[\eta^5{:}\eta^1\text{-}N\text{-}C_5H_4CH_2CH_2N(CH_3)_2]ZrCl_3 \cdot THF$ [8] (unfortunately, no structural parameters are presented in the communication) and to its phosphorous relative $[\eta^5{:}\eta^1\text{-}P\text{-}C_5H_4CH_2CH_2PPh_2]ZrCl_3 \cdot THF$ [9].

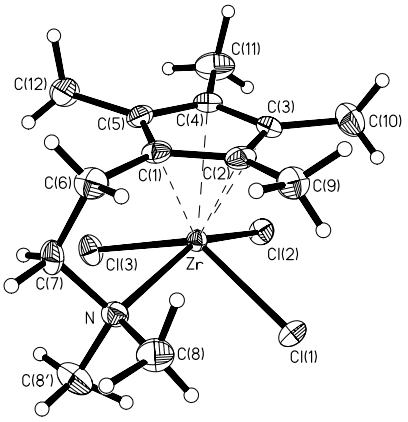


Fig. 3. Molecular structure of complex **6c**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr–Cl(1) 2.4408(9), Zr–Cl(2) 2.4502(9), Zr–Cl(3) 2.4252(9), Zr–N 2.469(3), Zr–Cp_{cent} 2.181, N–C(7) 1.507(5), N–C(8) 1.498(5), N–C(8′) 1.511(6); C(8)–N–C(7) 107.6(3), C(8)–N–C(8′) 105.5(3), C(7)–N–C(8′) 108.4(4).

The solvent-free complex **6c** and the single crystals of it were obtained by a high-vacuum sublimation of the THF-adduct **6a** (to grow up a single crystal, slow sublimation onto a "hot wall" was applied). Surprisingly, the Zr atom in **6c** is five-coordinated (assuming that the cyclopentadienyl ring occupies one position) and its coordination polyhedron is a tetragonal pyramid (see Fig. 3). Such a structural feature is rather unusual for the Zr(IV) solvent-free half-sandwiches. Contrarily, nearly all of the known solvent-free monocyclopentadienyl zirconium(IV) complexes, with even sterically crowded ones among them, exhibit a strong tendency to form double μ-Cl bridges between Zr atoms and exist as dimers [6,9–14]. Moreover, the coordination unsaturation of the Zr(IV) center is so explicit, that, in presence of the alkali metal chlorides, these dimers easily accept the third chlorine bridge atom to form complexes of general type $[CpZrCl_2–(\mu\text{-}Cl)_3–ZrCl_2Cp]^-[M(Solv)_n]^+$ [15].

As for the heteroatom side-chain functionalized Zr(IV) half sandwiches of interest, formation of $(\mu\text{-}Cl)_2$ bridged dimers is also usual. This structural motif is present, for instance, in *O*- and *S*-analogues of complex **6**, $\{[\eta^5{:}\eta^1\text{-}O\text{-}C_5(CH_3)_4CH_2CH_2OCH_3]ZrCl_2\}_2(\mu\text{-}Cl)_2$ [14] and $\{[\eta^5{:}\ \eta^1\text{-}S\text{-}C_5(CH_3)_4CH_2CH_2SCH_3]ZrCl_2\}_2(\mu\text{-}Cl)_2$ [6], (the crystallization was also performed from the gas phase). Among the known structurally characterized nitrogen side-chain functionalized analogues even sterically hindered $\{[\eta^5{:}\eta^1\text{-}N\text{-}C_5(CH_3)_4(8\text{-quinolinyl})]ZrCl_2\}_2(\mu\text{-}Cl)_2$ also crystallizes as a dimer [11]. Thus, the reasons why the monomeric structure for **6c** is preferable remain still unclear.

Comparison of the main structural parameters in **6b** and **6c** reveals that all Zr–ligand distances in **6c** are shorter than the corresponding distances in **6b**. The values of the Zr ← N coordination bond lengths in both adduct **6b** [2.594(3) Å] and solvent-free **6c** [2.469(3) Å] are in a good agreement with the ones for Zr(IV) complexes with aliphatic amines (2.400–2.603 Å) [16–22]. All three N–C bonds in both of complexes **6b** and **6c** (coordinated amino group) are reasonably longer than those in complex **4**, where the amino functionality is not

Table 1
^{1}H NMR chemical shifts (δ, ppm) for **6a**

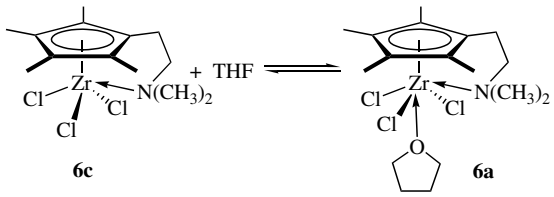
t (°C)	Solvent	CH_3(2,5)[a]	CH_3(3,4)[a]	$N(CH_3)_2$	CH_2N	CH_2CH_2N	THF
25	CD_2Cl_2	2.31	2.15	2.57	3.03	2.77	1.82
							3.74
−85	CD_2Cl_2	2.13	1.91	2.27	2.56	2.50 (2H)	1.78
		2.22	1.93	2.32	3.28		4.15
25	THF-d_8	2.26	2.03	2.40	2.83	2.59	

[a] The assignment of the signals of the methyl groups was confirmed by difference NOE experiment with the CH_2CH_2N protons irradiation.

Table 2
^{13}C NMR chemical shifts (δ, ppm) for **6a**

t (°C)	Solvent	CH_3(2–5)	$N(CH_3)_2$	CH_2CH_2N	CH_2CH_2N	C(1–5)	THF
25	CD_2Cl_2	13.19	51.72	66.11	22.89	128.64	25.88
		13.70				129.01	68.63
						132.51 [C(1)]	
−85	CD_2Cl_2	12.33	49.90	66.40	21.12	123.18	24.92
		12.39	51.13			126.92 (2C)	72.42
		13.62				128.81	
		13.72				130.84	
25	THF-d_8	13.05	51.42	67.26	22.47	126.09	
		14.25				127.54	
						130.20 [C(1)]	

coordinated. Meanwhile, the C–N–C angle values decrease from 109.3(6)–110.5(6)° in **4** (nearly tetrahedral) down to 105.9(3)–108.6(3)° in **6b** and 105.5(3)–108.4(4)° in **6c**, along with the amino group coordination. This is indicative of the greater *p*-character of the N–C bonds in the coordinated amino group in respect to the free one.



Scheme 4.

2.3. NMR spectroscopy investigations of complex *6a*

The structure of the THF adduct **6a** was studied in solutions by means of variable-temperature NMR spectroscopy. The NMR data reveal that in complex **6a** the amino group remains coordinated towards the Zr(IV) center within the entire range of the temperatures studied (see Tables 1 and 2). This fact is evident due to the distinct lower field shifting of the ^{13}C signals related to the $-NCH_2-$ and $-N(CH_3)_2$ moieties [$\delta(^{13}C) \approx 66$ and 51, respectively] for **6a** in comparison to the signals

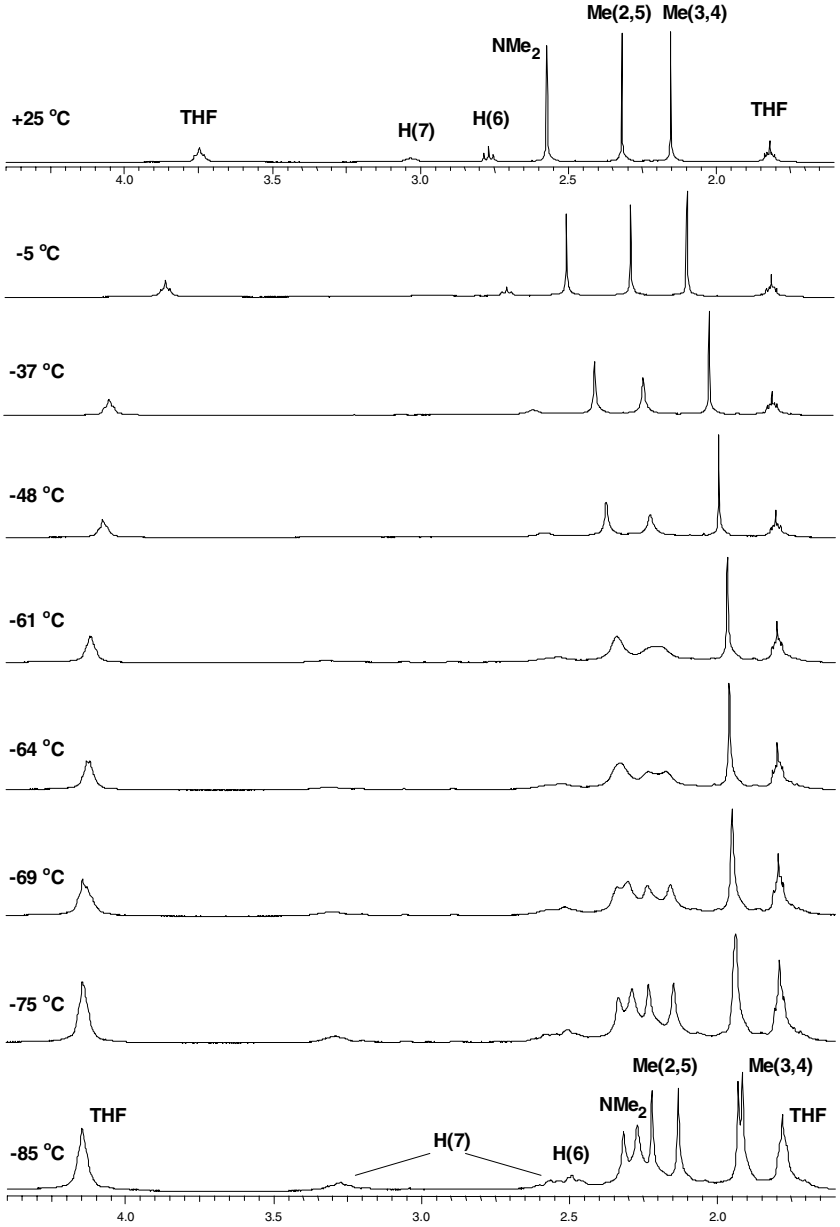


Fig. 4. Variable-temperature ^1H NMR spectra for complex **6a** (CD_2Cl_2).

of these groups in zirconocene dichlorides **4** and **5** [$\delta(^{13}C) \approx 60$ and 46]. The same happens to the values of the proton chemical shifts. However, the ^{13}C shifts are more indicative due to the lower magnetic anisotropy effects of the adjacent groups for the carbon atoms comparatively to the hydrogens. Additionally, along with this downfield shift, coordination of the amino functionality to the Zr(IV) center causes a considerable increase (≈6 Hz) of the $^{1}J_{CH}$ spin–spin coupling constants for the $-NCH_2-$ and $-N(CH_3)_2$ moieties. This effect was found previously for *S*- and *O*-analogues of complexes **4–6** [6,14] and is likely due to the increase of the *s*-character of the C–H bonds in a functionality along with the coordination of the heteroelement atom to the metal center.

Noteworthy, that the NMR data for all three forms **6a**, **6b**, and **6c** are very similar at room temperature. Moreover, the NMR data for **6a** in a THF-d_8 solution are very close to those obtained in CD_2Cl_2 (see Tables 1 and 2). Thus, there is no doubt that the $(CH_3)_2N-$ group coordination to the Zr(IV) center is retained in CD_2Cl_2 in all of the cases.

The variable temperature NMR studies reveal that in CD_2Cl_2 adduct **6a** exhibits dynamic behavior contributed by two different processes. The first process is a reversible dissociation-coordination of the THF molecule (see Scheme 4).

Along with the decrease of temperature from 25 °C down to −85 °C, the equilibrium shifts towards the adduct **6a**. This is obvious because of the downfield shift of the $-OCH_2-$ (THF) signals in both ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra (see Tables 1 and 2; the appearance of the variable-temperature ^{1}H NMR spectra is presented in Fig. 4). In $^{13}C\{^{1}H\}$ NMR spectra (see Table 2) this shift is almost +4 ppm (from 25 °C down to −85 °C).

The second exchange process reflects the loss of the pseudo-C_s symmetry of complex **6a**. At room temperature, the CH_3- groups at C(2,5), C(3,4) ring carbons and at the nitrogen atom, as well as hydrogen atoms at C(6) and C(7) bridge carbons are equivalent in pairs. Upon temperature decrease down to −85 °C, this equivalence vanishes and all these groups give the corresponding sets of signals in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra (see Tables 1, 2 and Fig. 4). The chemical shifts of two protons H(6A) and H(6B) and two quaternary carbons in the Cp-ring, as well, are occasionally close to each other.

This second exchange process can be due to either an intramolecular dissociation-coordination of the amino functionality, with the randomization taking place in an intermediate with a non-coordinated amino group, or a degenerate interconversion of the pseudo-five-member metallacycle Zr–C(1)–C(6)–C(7)–N–(Zr). However, taking into account the retention of the N→Zr coordination within the entire range of temperatures studied, the first mechanism should be excluded. An analogous pseudo-five-member metallacycle interconversion was observed previously for both *S*- and *O*-analogues of **6** [6,14]. This degenerate interconversion results in a formal reflection of the structure in respect to the Zr–C(1)–N plane.

The free energy of activation $\Delta G^{\neq}$ for this process was estimated from the coalescence temperatures measured for the protons of the methyl groups at C(2,5) and C(3,4) ring carbon atoms (212 and 198 K, respectively), and at the nitrogen atom (208 K). The obtained $\Delta G^{\neq}$ values are very close to each other, with the average value of $\Delta G^{\neq} = 43.6 \pm 0.9$ kJ/mol (10.4 ± 0.2 kcal/mol). This value is close to the one obtained for the similar process of the degenerate interconversion of a pseudo-five-member metallacycle in complex $[\eta^5{:}\eta^1\text{-}S\text{-}C_5H_4CH_2CH_2SCH_3]ZrCl_3$ $\Delta G^{\neq} = 11.2 \pm 0.2$ kcal/mol in THF-d_8 and $\Delta G^{\neq} = 10.5 \pm 0.2$ kcal/mol in CD_2Cl_2) [6].

3. Conclusion

In this paper, three novel Zr(IV) cyclopentadienyl complexes have been prepared and characterized. While the sandwich zirconocene dichlorides **4** and **5** have been shown to possess no particularities in their structure and chemical behavior, except their extreme sensitivity to hydrolysis, the half-sandwich complex **6** exhibited times more rich coordination chemistry and dynamic behavior in solutions. Thus, three forms **6a**–**6c** have been isolated and characterized, with the solvent-free form **6b** shown to be a very unusual example of a Zr(IV) monocyclopentadienyl complex monomeric in the crystalline state. For complex **6a** in a CD_2Cl_2 solution, two dynamic processes were observed: dissociation-coordination of the THF molecule and a degenerate interconversion of the pseudo-five-member Zr–C(1)–C(6)–C(7)–N–(Zr) metallacycle. However, no intramolecular dissociation-coordination of the $(CH_3)_2N-$ group in solutions was observed for **6a**–**6c**, and the amino fuctionality is always coordinated to the Zr(IV) center both in crystalline state and in solutions. In addition, within the course of the complex **6** synthesis, the difficulties in preparation of silylated cyclopentadiene **2** have been revealed, and a side reaction of THF cleavage has been observed. It should be especially underlined here that dependently upon the reaction conditions silylation of sterically hindered cyclopentadienides can proceed ambiguously and must be performed with a particular care.

4. Experimental

4.1. General remarks

All procedures were performed in sealed-off evacuated glass vessels. The employed solvents (and their

perdeuterated analogues) were dried with and distilled from conventional agents (namely: diethyl ether and THF – with sodium benzophenone ketyl; toluene, heptane and pentane – with Na–K alloy; CH_2Cl_2 – with P_2O_5 and then with CaH_2). When performing procedures in evacuated vessels, the degassed solvents were stored in evacuated reservoirs over corresponding drying agent and transferred on a high vacuum line directly into reaction vessels by trapping them with liq. N_2. Trimethylchlorosilane (*Fluka*) was refluxed with and distilled from aluminium powder (high vacuum line). THT was refluxed with and distilled from over CaH_2. $HC_5(CH_3)_4$–$CH_2CH_2N(CH_3)_2$ was prepared accordingly to the reported procedure [1]. with the minimal modification. Thus, to perform the Nazarov cyclization of carbinol $(H_3C)_2NCH_2CH_2C(OH)[C(CH_3)=CHCH_3]_2$, dimethoxyethane was used instead of ether (this made the reaction mixture homogeneous). $[\eta^5\text{-}C_5(CH_3)_5]ZrCl_3$ was prepared accordingly to the reported procedure and purified by a high-vacuum sublimation prior to use [23,24]. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer at 400 and 100 MHz, respectively. For ^1H and ^{13}C spectra, the solvent resonances [$\delta_H = 7.15$ and $\delta_C = 128.0$ (C_6D_6), $\delta_H = 5.32$ and $\delta_C = 53.8$ (CD_2Cl_2), $\delta_H = 1.73$ and $\delta_C = 25.3$ (THF-d_8)] were used as internal reference standards. For temperature calibration, the standard methanol sample was used. Mass spectra were measured on Kratos-MS-890 and Varian MAT CH7a Fa spectrometers. The elemental analyses were performed on the Carlo-Erba automated analyser.

4.2. Synthetic procedures

4.2.1. Lithium salt (*1*)

To a solution of HCp^{*N} (7.04 g, 36.4 mmol) in THF (20 mL), 2.04 M solution of *n*-BuLi in hexane (18 mL, 36.7 mmol) was added at 0 C. The mixture was allowed to warm up to room temperature and stirred during 0.5 h. The solvents were removed by trapping them into a vessel cooled with liq. N_2, the dark-red residue was washed with ether (3×10mL), recrystallized from the minimal amount of THF, washed with ether (3×10mL) again, and then dried on the high-vacuum line. White fine-crystalline powder. Yield 4.95 g, 68.2%. ^1H NMR (25 °C, THF-d_8): $\delta = 1.81$, 1.83 [each s, 6 H, $C_5(CH_3)_4$], 2.14 [s, 6 H, $N(CH_3)_2$], 2.17 (t, 2 H, $^3J_{HH} = 7.6$ Hz, CH_2N), 2.41 (t, 2 H, $^3J_{HH} = 7.6$ Hz, CH_2CH_2N). ^{13}C NMR (25 °C, THF-d_8): $\delta = 11.01$, 11.06 [each q, $^1J_{CH} = 123$ Hz, $C_5(CH_3)_4$], 25.02 (t, $^1J_{CH} = 124$ Hz, CH_2CH_2N), 46.00 [q, $^1J_{CH} = 132$ Hz, $N(CH_3)_2$], 62.80 (t, $^1J_{CH} = 133$ Hz, CH_2N), 105.98, 107.54 (each s, CCH_3), 108.75 (s, CCH_2CH_2N).

4.2.2. Trimethylsilyl substituted cyclopentadiene (*2*)

0.34 M THF solution of lithium salt **1** (40 mL, 13.5 mmol) was heated up to 70 °C and added all at once to trimethylchlorosilane (2 mL, 1.72 g, 15.8 mmol). The reaction mixture was heated at 90–100 °C during 3.5 h, the solvent was removed by trapping it into a vessel cooled with liq. N_2, the residue was taken into hexane (30 mL) and filtered through a glass filter. On removal of the solvent the residual yellow oil was distilled in high vacuum that gave the desired silane **2** (2.88 g) contaminated with approx. 20% (mol) of THF ring cleavage products **3a** and **3b** (estimated by integration of the signals related to $(CH_3)_3Si$– groups in the ^1H NMR spectrum of the product). The total yield of **2**, **3a** and **3b** is 76.2%. The corrected yield of **2** is 2.19 g (61.0%).

Analyses data for silane 2. ^1H NMR (25 °C, C_6D_6): $\delta = -0.09$ (br, $SiMe_3$), 1.17 (br, CH_3CSiMe_3), 1.79, 1.85 (each br, $=CCH_3$), 2.09, 2.18 [each br, $N(CH_3)_2$], 2.32 (br m, CH_2N), 2.54 (br, CH_2CH_2N). $^{13}C\{^1H\}$ NMR (25 °C, C_6D_6): $= -2.68$ (s, $^1J_{CSi} = 51.5$ Hz, $SiMe_3$), 11.2, 12.5, 13.7 (each br, CH_3), 25.11, 26.42 (each br s, CH_2CH_2N), 45.61, 45.77 [each br s, $N(CH_3)_2$], 53.7, 56.5 (each br, $CSiMe_3$), 60.12 (br s, CH_2N), 134.3, 135.7, 137.8, 138.7, 139.4 (each br, >C=). GC/MS EI (70 eV) *m/z* (%): 265 (5.1) $[M]^{+\cdot}$, 250 (2.1) $[M–CH_3]^+$, 207 (1.0) $[M–CH_2N(CH_3)_2]^+$, 194 (2.1) $[M–CH_2=CHN(CH_3)_2]^{+\cdot}$, 133 (17.4) $[C_7H_4(CH_3)_3]^+$, 119 (13.1) $[C_7H_5(CH_3)_2]^+$, 105 (4.5) $[C_7H_6(CH_3)]^+$, 91 (9.4) $[C_7H_7]^+$, 73 (53.6) $[Si(CH_3)_3]^+$, 59 (11.7) $[N(CH_3)_3]^{+\cdot}$, 58 (100) $[CH_2N(CH_3)_2]^+$, 42 (11.1) $[CHNCH_3]^+$.

*Analyses data for silanes **3a** and **3b** (estimated molar ratio ~1:1)*. ^1H NMR (25 °C, C_6D_6): $\delta = 0.072$, 0.076 (each s, $OSiMe_3$), 0.85 (m, CH_3CCH_2), 0.92, 0.97 (each s, CH_3CCH_2), 1.39–1.49 (m, $CH_2CH_2CH_2O$), 1.65, 1.69, 1.71, 1.72, 1.76, 1.78 (each s, $=CCH_3$), 2.17, 2.21 [each s, $N(CH_3)_2$], 2.30–2.60 (m, CH_2CH_2N), 3.458, 3.462 (each t, $^3J_{HH} = 6.6$ Hz, CH_2O). $^{13}C\{^1H\}$ NMR (25 °C, C_6D_6): $\delta = -0.31$ ($^1J_{CSi} = 58.5$ Hz, $OSiMe_3$), 9.81, 9.85, 9.89, 10.99, 11.12, 11.51 ($=CCH_3$), 20.35, 20.48 ($CH_2CH_2CH_2O$), 22.37, 22.55 (C H_3CCH_2), 24.41, 24.86 (CH_2CH_2N), 33.62, 33.73 (CH_2CH_2O), 35.36, 35.52 (CH_3CCH_2), 45.56 $[N(CH_3)_2]$, 56.14, 56.74 (CH_3CCH_2), 59.80, 60.20 (CH_2N), 62.57, 62.62 (CH_2O), 133.46, 133.75, 136.08, 137.07, 140.44, 140.76, 141.59, 142.62 (>C=). GC/MS EI (70 eV) *m/z* (%): 337 (1.1) $[M]^{+\cdot}$, 133 (2.6) $[C_7H_4(CH_3)_3]^+$, 119 (5.6) $[C_7H_5(CH_3)_2]^+$, 117 (2.4) $[CH_2CH_2OSi(CH_3)_3]^+$, 105 (2.2) $[C_7H_6(CH_3)]^+$, 103 (1.8) $[CH_2OSi(CH_3)_3]^+$, 91 (3.6) $[C_7H_7]^+$, 73 (7.2) $[Si(CH_3)_3]^+$, 59 (6.1) $[N(CH_3)_3]^{+\cdot}$, 58 (100) $[CH_2N(CH_3)_2]^+$, 42 (5.5) $[CHNCH_3]^+$.

4.2.3. Zirconocene dichloride (*4*)

$[C_5(CH_3)_5]ZrCl_3$ (0.53 g, 1.59 mmol) was added to a 0.34 M THF solution of lithium salt **1** (4.6 mL, 1.59 mmol) and the reaction mixture was heated at 80–90 °C during 6 h. The solvent was removed into a trap cooled

with liq. N_2, the residue dried on a high vacuum line and taken with toluene (10 mL). On filtering off LiCl, the solvent was removed and the residue was recrystallized from the minimal amount of ether that gave zirconocene dichloride **4** as yellow crystals (320 mg). Concentrating of the ether mother liquor allows to gain an additional portion of **4** (150 mg). Total yield 60.4%. ^{1}H NMR (25 °C, THF-d_8): $\delta = 1.97$ [s, 21 H, $C_5(CH_3)_5$, $C_5(CH_3)_4$], 2.00 [s, 6 H, $C_5(CH_3)_4$], 2.14 (m, 2 H, $^3J_{HH} = 8.2$ Hz, CH_2N), 2.20 [s, 6 H, $N(CH_3)_2$], 2.60 (m, 2 H, $^3J_{HH} = 8.2$ Hz, CH_2CH_2N). ^{13}C NMR (25 °C, THF-d_8): $\delta = 12.13$, 12.18 [each q, $^1J_{CH} = 127$ Hz, $C_5(CH_3)_4$], 12.22 [q, $^1J_{CH} = 127$ Hz, $C_5(CH_3)_5$], 26.39 (t, $^1J_{CH} = 128$ Hz, CH_2CH_2N), 45.75 [q, $^1J_{CH} = 132$ Hz, $N(CH_3)_2$], 60.13 (t, $^1J_{CH} = 133$ Hz, CH_2N), 123.49, 124.59 (each s, CCH_3), 124.12 [s, $C_5(CH_3)_5$], 126.04 (s, CCH_2CH_2N). *Anal.* Found: C, 56.56; H, 7.72; N, 2.91. Calc. for $C_{23}H_{37}Cl_2NZr$ (489.67): C, 56.42; H, 7.62; N, 2.86%. EI-MS (70 eV) m/z (%): 451 (6.5) $[M–HCl]^{+\cdot}$, 436 (11.4) $[M–HCl–CH_3]^+$, 417 (7.1) $[M–2Cl]^{+\cdot}$, 416 (3.5) $[M–HCl–Cl]^+$, 400 (11.9) $[M–HCl–Cl–CH_4]^+$, 359 (4.9) $[M–2Cl–CH_2N(CH_3)_2]^{+\cdot}$, 316 (20.3) $[M–HCl–C_5(CH_3)_5]^+$, 259 (15.8) $[(C_5(CH_3)_4CH_2)ZrCl]^+$, 192 (1.7) $[C_5(CH_3)_4CH_2CH_2N(CH_3)_2]^+$, 191 (2.5) $[C_5(CH_3)_4{=}CHCH_2N(CH_3)_2]^{+\cdot}$, 190 (1.1) $[C_7H_2(CH_3)_4N(CH_3)_2]^+$, 176 (3.6) $[C_7H_3(CH_3)_3N(CH_3)_2]^+$, 147 (2.9) $[C_7H_3(CH_3)_4]^+$, 134 (13.1) $[C_5(CH_3)_4{=}CH_2]^{+\cdot}$, 133 (14.1) $[C_7H_4(CH_3)_3]^+$, 119 (34.6) $[C_7H_5(CH_3)_2]^+$, 105 (15.8) $[C_7H_6(CH_3)]^+$, 91 (20.9) $[C_7H_7]^+$, 59 (5.7) $[N(CH_3)_3]^{+\cdot}$, 58 (100) $[CH_2N(CH_3)_2]^+$, 42 (14.0) $[CHNCH_3]^+$.

4.2.4. Zirconocene dichloride (*5*)

$ZrCl_4 \cdot 2THT$ (1.09 g, 2.66 mmol) and a 0.34 M THF solution of lithium salt **1** (15.6 mL, 5.33 mmol) were mixed and the reaction mixture was heated at 80–90 °C under stirring during 20 h. On removal of the solvent in high vacuum and drying the residue on a high-vacuum line, hexane (20 mL) was added, LiCl was filtered off, and the hexane extract was concentrated. The crude product was isolated as an orange oil (920 mg). The oil was then heated on a high vacuum line at 100 °C for 2 h, cooled down to ambient temperature and recrystallized from hexane that yielded desired complex **5** as yellow crystals (250 mg, yield 17.2%). ^{1}H NMR (25 °C, THF-d_8): $\delta = 1.97$, 2.00 (each s, 6 H, CCH_3), 2.14 (m, 2 H, $^3J_{HH} = 8.0$ Hz, CH_2N), 2.19 [s, 6 H, $N(CH_3)_2$], 2.60 (m, 2 H, $^3J_{HH} = 8.0$ Hz, CH_2CH_2N). ^{13}C NMR (25 °C, THF-d_8): $\delta = 12.19$, 12.23 (each q, $^1J_{CH} = 127$ Hz, CCH_3), 26.45 (t, $^1J_{CH} = 128$ Hz, CH_2CH_2N), 45.72 [q, $^1J_{CH} = 132$ Hz, $N(CH_3)_2$], 60.14 (t, $^1J_{CH} = 133$ Hz, CH_2N), 123.60, 124.77 (each s, CCH_3), 126.06 (s, CCH_2CH_2N). *Anal.* Found: C, 57.32; H, 8.19; N, 5.18. Calc. for $C_{23}H_{37}Cl_2NZr$ (546.77): C, 57.11; H, 8.11; N, 5.12%. EI-MS (70 eV) m/z (%): 509 (1.7) $[M–Cl]^+$, 444 (5.0) $[M–2CH_3Cl]^+$, 352 (61.0) $[M–C_5(CH_3)_4CH_2CH_2N(CH_3)_2]^+$, 336 (21.4) $[M–C_5(CH_3)_4CH_2CH_2N(CH_3)_2–CH_4]^+$, 294 (14.7) $[(C_5(CH_3)_4CH_2)ZrCl_2]^+$, 259 (6.0) $[(C_5(CH_3)_4CH_2)ZrCl]^+$, 192 (14.9) $[C_5(CH_3)_4CH_2CH_2N(CH_3)_2]^+$, 191 (7.2) $[C_5(CH_3)_4{=}CHCH_2N(CH_3)_2]^+$, 190 (9.2) $[C_7H_2(CH_3)_4N(CH_3)_2]^+$, 176 (6.0) $[C_7H_3(CH_3)_3N(CH_3)_2]^+$, 147 (8.3) $[C_7H_3(CH_3)_4]^+$, 134 (26.9) $[C_5(CH_3)_4{=}CH_2]^+$, 133 (29.4) $[C_7H_4(CH_3)_3]^+$, 119 (46.0) $[C_7H_5(CH_3)_2]^+$, 105 (13.5) $[C_7H_6(CH_3)]^+$, 91 (19.9) $[C_7H_7]^+$, 58 (100) $[CH_2N(CH_3)_2]^+$, 42 (17.5) $[CHNCH_3]^+$.

4.2.5. Half-sandwich complex (*6a, 6b and 6c*)

A solution of a mixture of **2**, **3a** and **3b** (1.12 g, contains 3.20 mmol of **2**) and a suspension of $ZrCl_4 \cdot 2THT$ (1.33 g, 3.25 mmol) in toluene (total amount 15 mL) were mixed at room temperature and then heated at 80–90 °C under stirring. After cooling down to room temperature the solution was separated from a small amount of a thin white precipitate, concentrated down to approx. 5 mL by removal the solvents into a trap cooled with liq. N_2, and left to stay at ambient temperature overnight. The white crystalline precipitate formed was filtered off washed with 5 mL of pentane and dried in high vacuum that gave crude product (690 mg). The further concentration of the mother liquor gave the THT adduct **6b** (430 mg, yield 28.1%). Recrystallization of the crude product (690 mg) from the minimal amount of hot THF gave the THF adduct **6a** (340 mg, yield 23.0%). Sublimation of **6a** (273 mg, 0.59 mmol) in high vacuum gave the solvent-free half sandwich complex **6c** (230 mg, yield 99.8% in respect to **6a**).

*Analyses data for **6b**.* ^{1}H NMR (19 °C, CD_2Cl_2): $\delta = 1.92$ (m, 4 H, CH_2CH_2S in THT), 2.14, 2.31 (each s, 6 H, CCH_3), 2.56 [s, 6 H, $N(CH_3)_2$], 2.74(t, 2 H, $^3J_{HH} = 6.2$ Hz, CH_2CH_2N), 2.86 (m, 4 H, CH_2S in THT),3.00 (br, 2 H, CH_2N). ^{13}C{^{1}H} NMR (19 °C, CD_2Cl_2): $\delta = 13.12$, 13.65 (CCH_3), 22.79 (CH_2CH_2N), 31.22 (CH_2CH_2S in THT), 32.99 (CH_2S in THT), 51.77 [$N(CH_3)_2$], 66.31 (CH_2N), 128.59, 128.79 (CCH_3), 132.10 (CCH_2CH_2N). *Anal.* Found: C, 42.54; H, 6.27; N, 2.99. Calc. for $C_{17}H_{30}Cl_3NSZr$ (478.07): C, 42.71; H, 6.33; N, 2.93%.

*Analyses data for **6a**.* ^{1}H NMR (25 °C, CD_2Cl_2): $\delta = 1.82$ (m, 4 H, CH_2CH_2O in THF), 2.15, 2.31 (each s, 6 H, CCH_3), 2.57 [s, 6 H, $N(CH_3)_2$], 2.77(t, 2 H, $^3J_{HH} = 6.4$ Hz, CH_2CH_2N), 3.03 (br, 2 H, CH_2N), 3.74 (m, 4 H, CH_2O in THF). ^{13}C NMR (25 °C, CD_2Cl_2): $\delta = 13.19$, 13.70 (each q, $^1J_{CH} = 127$ Hz, CCH_3), 22.89 (t, $^1J_{CH} = 127$ Hz, CH_2CH_2N), 25.88 (t, $^1J_{CH} = 132$ Hz, CH_2CH_2O in THF), 51.72 [q, $^1J_{CH} = 137$ Hz, $N(CH_3)_2$], 66.11 (t, $^1J_{CH} = 138$ Hz, CH_2N), 68.63 (t, $^1J_{CH} = 144$ Hz, CH_2O in THF), 128.64, 129.01 (each s, CCH_3), 132.51 (s, CCH_2CH_2N). ^{1}H NMR (25 °C, THF-d_8): $\delta = 2.03$, 2.26 (each s, 6 H, CCH_3), 2.40 [s, 6 H, $N(CH_3)_2$], 2.59(t, 2 H, $^3J_{HH} = 6.2$ Hz, CH_2CH_2N), 2.83 (br t, 2 H, CH_2N). ^{13}C{^{1}H} NMR (25 °C, THF-d_8)):

$\delta = 13.05$, 14.25 (CCH_3), 22.47 (CH_2CH_2N), 51.42 [$N(CH_3)_2$], 67.26 (CH_2N), 126.09, 127.54 (CCH_3), 130.20 (CCH_2CH_2N). *Anal*. Found: C, 43.95; H, 6.41; N, 3.12. Calc. for $C_{17}H_{30}Cl_3NOZr$ (462.01): C, 44.20; H, 6.54; N, 3.03%. EI-MS (70 eV) m/z (%): 387 (1.1) [M–THF]$^{+\cdot}$, 352 (21.2) [M–THF–Cl]$^+$, 336 (8.1) [M–THF–Cl–CH_4]$^+$, 294 (4.2) [$(C_5(CH_3)_4CH_2)ZrCl_2$]$^{+\cdot}$, 259 (3.7) [$(C_5(CH_3)_4CH_2)ZrCl$]$^+$, 192 (3.8) [$C_5(CH_3)_4CH_2CH_2N(CH_3)_2$]$^+$, 191 (12.7) [$C_5(CH_3)_4{=}CHCH_2N(CH_3)_2$]$^{+\cdot}$, 190 (6.2) [$C_7H_2(CH_3)_4N(CH_3)_2$]$^+$, 176 (10.7) [$C_7H_3(CH_3)_3N(CH_3)_2$]$^+$, 147 (15.0) [$C_7H_3(CH_3)_4$]$^+$, 134 (39.5) [$C_5(CH_3)_4{=}CH_2$]$^{+\cdot}$, 133 (49.9) [$C_7H_4(CH_3)_3$]$^+$, 119 (69.2) [$C_7H_5(CH_3)_2$]$^+$, 105 (36.6) [$C_7H_6(CH_3)$]$^+$, 91 (41.0) [$C_7H_7$]$^+$, 59 (36.9) [$N(CH_3)_3$]$^{+\cdot}$, 58 (100) [$CH_2N(CH_3)_2$]$^+$.

Analyses data for ***6c***. ^{1}H NMR (25 °C, CD_2Cl_2): $\delta =$ 2.18, 2.33 (each s, 6 H, CCH_3), 2.60 [s, 6 H, $N(CH_3)_2$], 2.79(t, 2 H, $^3J_{HH} = 6.2$ Hz, CH_2CH_2N), 3.06 (br, 2 H, CH_2N). ^{13}C NMR (25 °C, CD_2Cl_2): $\delta = 13.26$, 13.65 (each q, $^1J_{CH} = 127$ Hz, CCH_3), 23.01 (t, $^1J_{CH} = 127$ Hz, CH_2CH_2N), 51.81 [q, $^1J_{CH} = 137$ Hz, $N(CH_3)_2$], 65.97 (t, $^1J_{CH} = 138$ Hz, CH_2N), 128.39, 129.43 (each s,CCH_3), 133.15 (s, CCH_2CH_2N).

4.3. X-ray crystallographic study

CCDC-197627 (compound **4**), CCDC-197628 (compound **6b**) and CCDC-197629 (compound **6c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at

Table 3
Crystal data, data collection, structure solution and refinement parameters for **4**, **6b** and **6c**

Compound	**4**	**6b**	**6c**
Empirical formula	$C_{23}H_{37}Cl_2N_1Zr_1$	$C_{17}H_{30}Cl_3N_1S_1Zr_1$	$C_{13}H_{22}Cl_3N_1Zr_1$
Formula weight	489.66	478.05	389.89
Colour, habit	Colorless prism	Colorless block	Colorless block
Crystal size (mm)	$0.4 \times 0.3 \times 0.3$	$0.5\ 0.4 \times 0.4$	$0.3 \times 0.2 \times 0.1$
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
Unit cell dimensions			
a [Å]	9.596(6)	15.750(7)	8.4341(4)
b [Å]	17.260(7)	8.219(8)	12.8151(6)
c [Å]	14.845(13)	15.984(7)	14.8220(7)
β [°]	99.87(7)	93.26(4)	–
Volume (Å^3)	2422(3)	2066(2)	1602.0(1)
Z	4	4	4
Density (calculated) (g cm^{-3})	1.343	1.537	1.617
Absorption coefficient (mm^{-1})	0.683	1.020	1.170
$F(000)$	1024	984	792
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Bruker SMART CCD
Temperature (K)	293	293	110.0(2)
Radiation (λ, Å)	Graphite-monochromated Mo-Kα (0.71073)		
θ range (°)	2.36 to 24.99	2.55 to 24.97	2.10 to 27.00
Index ranges	$-11 \leqslant h \leqslant 11$	$-18 \leqslant h \leqslant 10$	$-8 \leqslant h \leqslant 11$
	$-3 \leqslant k \leqslant 20$	$-2 \leqslant k \leqslant 9$	$-17 \leqslant k \leqslant 17$
	$-2 \leqslant l \leqslant 17$	$-3 \leqslant l \leqslant 18$	$-20 \leqslant l \leqslant 20$
Reflections collected	6251	5019	11,242
Independent reflections	4266 [$R_{int} = 0.1217$]	3319 [$R_{int} = 0.0439$]	3495 [$R_{int} = 0.0393$]
Data reduction	XCAD4 [25]	XCAD4 [25]	Bruker SAINT [26]
Absorbtion correction type	–	Empirical [27]	Empirical (SADABS) [28]
Min. and Max. transmission	–	0.3318 and 0.5970	0.6941 and 1.0000
Solution method	Direct methods (SHELXS-93) [29]		
Refinement method	Full-matrix least-squares on F^2 (SHELXL-93) [30]		
Data/restraints/parameters	3975/0/255	3056/0/233	3468/0/251
Reflections with $I > 2\sigma(I)$	3213	2522	3302
Goodness-of-fit on F^2 1.056	1.024	1.109	
Final R indices [$I > 2\sigma(I)$]			
R_1	0.0838	0.0422	0.0351
wR_2	0.2092	0.1048	0.0872
R indices (all data)			
R_1	0.1072	0.0656	0.0371
wR_2	0.2430	0.1180	0.0887
Absolute structure parameter	–	–	−0.04(6)
Extinction coefficient	–	0.0017(5)	–
Largest difference peak and hole (e Å^{-3})	1.836 and −1.342	1.264 and −1.236	1.437 and −0.603

www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Crystal data, data collection, structure solution and refinement parameters for compounds **4, 6b** and **6c** are presented in Table 3. For all structures non-hydrogen atoms were refined in anisotropic approximation. In the structures of **4** and **6b**, hydrogen atoms were placed in calculated positions and refined using a riding model. As for **6c**, all hydrogen atoms were found from difference Fourier synthesis and refined with isotropic thermal parameters.

Acknowledgements

Authors greatly acknowledge the Russian Foundation for Basic Research for CCSD licence payment (Grant 02-07-90322) and financial support for A.V.C. (Grant 01-03-32474).

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