



1-Methylimidazolin-2-yl functionalized cyclopentadienyl complexes of titanium and zirconium. Crystal structure of $\{[\eta^5:\eta^1-\kappa N-C_5H_4CPh_2CH_2-(1-Me-C_3H_4N_2)]ZrCl_2\}_2(\mu-Cl)_2$

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ABSTRACT

The novel bidentate ligand, $C_5H_4CPh_2CH_2-(1-Me-C_3H_4N_2)$ (**3**), has been prepared and characterized as its lithium salt $LiC_5H_4CPh_2CH_2-(1-Me-C_3H_4N_2)$ (**3-Li**). Cyclopentadiene $HC_5H_4CPh_2CH_2-(1-Me-C_3H_4N_2)$ (**3-H**) has been obtained from 6,6-diphenylfulvene and 1,2-dimethylimidazoline (**1**). In THF-*d*₈ solution in the presence of **1**, (1-methylimidazolin-2-yl)methyl lithium (**2**) has been proved to undergo gradual conversion into a dilithium derivative of *N*¹-methyl-*N*²-[(1*E*,2*E*)-1-methyl-2-(1-methylimidazolidine-2-ylidene)ethylidene]ethane-1,2-diamine (**2a**). In a solution, cyclopentadiene **3-H** has been shown to undergo isomerization into 3-*N*-[2-(*N*-methylamino)ethyl]amino-1,1-diphenyl-1,2-dihydropentalene (**4**) and, further, into a mixture of **4** and two rotameric 3-*N*-[2-(*N*-methylamino)ethyl]amino-1,1-diphenyl-1,2-dihydropentalenes (**5a**) and (**5b**). Treatment of the lithium salt **3-Li** with Me_3SiCl has led to 3-*N*-[2-(*N*-trimethylsilylamino)ethyl]amino-1,1-diphenyl-1,2-dihydropentalene (**6**) as the dominant component in the reaction mixture. In the latter case the expected $Me_3Si-C_5H_4CPh_2CH_2-(1-Me-C_3H_4N_2)$ (**3-Si**) was not observed. Stannylation of **3-Li** with 1 equiv. of Me_3SnCl has resulted in formation of a mixture of $Me_3Sn-C_5H_4CPh_2CH_2-(1-Me-C_3H_4N_2)$ (**3-Sn**), $(Me_3Sn)_2-C_5H_3CPh_2CH_2-(1-Me-C_3H_4N_2)$ (**3-Sn**₂), and cyclopentadiene **3-H** in a ca. 2:1:1 molar ratio. Monocyclopentadienyl complexes $\{[\eta^5:\eta^1-\kappa N-C_5H_4CPh_2CH_2-(1-Me-C_3H_4N_2)]MCl_3$ (*M* = Ti (**7**), Zr (**8**)) have been prepared starting from the organotin and organolithium compounds **3-Sn** and **3-Li**, respectively. The dynamic behavior of complexes **7** and **8** has been investigated by means of variable-temperature NMR spectroscopy in solutions. The molecular structures of the dihydropentalene **4**, binuclear complex $\{[\eta^5:\eta^1-\kappa N-C_5H_4CPh_2CH_2-(1-Me-C_3H_4N_2)]-ZrCl_2\}_2(\mu-Cl)_2$ **8**, and a coordination dimer of the dilithium salt **2a** have been established by X-ray diffraction analysis. In the crystal structure of the **2a**-dimer, the shortest known Li–Li contact has been found.

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1. Introduction

The Group 4 transition metal complexes with cyclopentadienyl ligands bearing a nitrogen-containing *n*-donor moiety in the side chain have been extensively studied (see reviews [1–3]) and still attract considerable attention [4–14]. In the most complexes of this type, the nitrogen atom is bound to aliphatic substituents

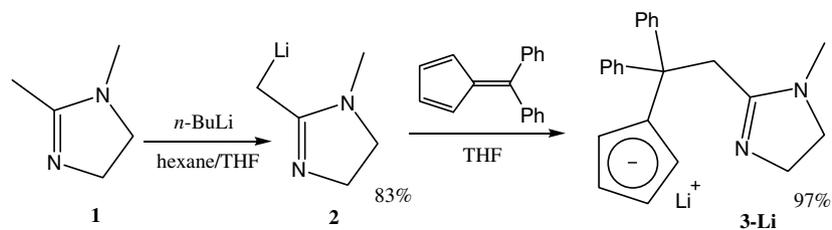
and is either in an sp^3 -hybridized state ($N \rightarrow M$ coordination bond) or in an sp^2 -hybridized state due to additional donation of the lone electron pair to the metal atom (so-called geometry constrained complexes). Complexes in which the $N \rightarrow M$ coordination is provided by an sp^2 -hybridized nitrogen atom (aromatic or related azaheterocycle) are few and limited to pyridine or quinoline systems [9,15–24] (i.e., to monoaza aromatic systems).

Consideration of 1,3-diazoles in this context seems to be top intriguing. The presence of the second “external” nitrogen atom, which is conjugated to the metal-linked nitrogen atom, provides additional possibilities for control of the nitrogen–metal interactions (for example, toggling between sp^2 - and sp^3 -hybridization modes) and “fine tuning” of the π -donor–acceptor and σ -donor properties of the coordinating nitrogen atom.

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Scheme 1.

1,3-Diazoles seldom occur as N-donor ligands in organometallic chemistry of the Group 4 metals (Arduengo carbenes are not considered in this context). The earliest works dating back to the 1960s [25,26] report preparation of 1:1 and 1:2 adducts of substituted imidazoles and benzimidazoles with MCl_4 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Th}$). Later in the middle of the 1980s a series of 1:1 binuclear imidazole adducts $[\text{MX}_4-(2\text{-R-C}_3\text{H}_2\text{N}_2)]_2$ ($\text{M} = \text{Ti}, \text{Zr}, \text{R} = \text{H}, \text{Me}$) was prepared [27]. However, no structural data on these complexes are available. The first structurally characterized complexes of Ti and Zr with imidazole-type ligands appeared comparatively recently. These were a dimeric dititanium complex $[\kappa\text{N}(3)-(1\text{-Me}_3\text{Si-C}_3\text{H}_2\text{N}_2)\text{TiCl}_3]_2(\mu\text{-Cl})_2$ [28] and dizirconium dihydroxyl bridged zwitterionic complex $[\kappa\text{N}(3)-(1-(\text{C}_6\text{F}_5)_3\text{B}^--\text{C}_3\text{H}_2\text{N}_2)(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}^+]_2(\mu\text{-OH})_2$ prepared by hydrolysis from monomeric precursor $[\kappa\text{N}(3)-(1-(\text{C}_6\text{F}_5)_3\text{B}^--\text{C}_3\text{H}_2\text{N}_2)(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}^+\text{Me}]$ [29]. In the latter publication the authors used imidazole moiety as a “spacer” between cationic and anionic centers of the zwitterionic system. 2-Methylimidazole was also applied as a ligand that successfully competes for a coordination place even with a THF molecule for isolation purposes (complexes $[\eta^5:\eta^1\text{-}\kappa\text{P-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{P}(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)][\kappa\text{N}(3)-(1\text{-Me}_3\text{Si-C}_3\text{H}_2\text{N}_2)]\text{MCl}_2$ ($\text{M} = \text{Zr}, \text{Hf}$) [30]).

In our recent paper we reported preparation of the first imidazole side chain functionalized cyclopentadienyl ligand $\text{C}_5\text{H}_4\text{CPh}_2\text{CH}_2(1\text{-Me-C}_3\text{H}_2\text{N}_2)$ in the forms of its Li-salt, CH-acid, and trimethylsilyl-derivative along with two monocyclopentadienyl titanium and zirconium complexes derived from it [31].

However, while complexes of the Group 4 metals with imidazoles or related systems as N-ligands are known, imidazolines have never been applied in this area of organometallic chemistry. Meanwhile, the known greater basicity of imidazolines ($\text{pK}_{\text{a}}^{25}(2\text{-Me-C}_3\text{H}_6\text{N}^+) 11.1$ [32]) comparatively to imidazoles ($\text{pK}_{\text{a}}^{25}(2\text{-Me-C}_3\text{H}_4\text{N}^+) 8.02$ [33]), on one hand, and the greater reactivity of the imidazoline moiety (possibility to accept nucleophilic attacks at the 2nd position and ring-opening reactions), on the other, make them even somewhat more attractive than imidazoles for the purposes of coordination and organometallic chemistry of the Group 4 elements.

This paper describes preparation of the first imidazoline side-chain functionalized ligand $\text{C}_5\text{H}_4\text{CPh}_2\text{CH}_2(1\text{-Me-C}_3\text{H}_4\text{N}_2)$ (**3**), its non-trivial properties and synthesis and structural investigations of the half-sandwich complexes of titanium and zirconium complexes based on it.

2. Results and discussion

2.1. Ligand synthesis

The functionalized cyclopentadienyl ligand **3** was prepared as its lithium salt **3-Li** by metallation of 1,2-dimethylimidazoline (**1**) with *n*-BuLi in THF/hexane followed by a reaction of (1-methylimidazoline-2-yl)methyl lithium (**2**) with 6,6-diphenylfulvene (Scheme 1). As for the imidazole analogue of **3-Li** [31], both salts **2** and **3-Li** were isolated in pure state and characterized by ^1H and ^{13}C NMR spectroscopy.

To perform more detailed description of the ligand **3**, the lithium salt **3-Li** was converted into cyclopentadiene **3-H** by treatment with methanol at 0–20 °C. As well as its imidazole analog [31], **3-H** represents a mixture of two isomers on positioning of the double bonds in respect to the substituent (**3-Ha:3-Hb** = 1:1.3, see Scheme 2). However, the other chemical features of **3-H** differ markedly from those of its imidazole analogue. Thus, in its ^1H NMR spectrum, the signals related to the Cp-ring hydrogens of the isomer **3-Ha** are considerably broadened. This can be explained by the reversible intramolecular deprotonation of the Cp-ring in **3-Ha** with the strongly basic imidazoline nitrogen (for **3-Hb** such a process can be realized with difficulty, if at all).

Moreover, the cyclopentadiene **3-H** is unstable thermally and, if heated above 40 °C, turns quantitatively into substituted 1,2-dihydropentalene **4**. On further staying in a solution at room temperature, compound **4** reversibly isomerizes into a mixture of 1,2-dihydropentalenes **5a** and **5b**, with the equilibrium establishing after two weeks. Compounds **5a** and **5b** are rotamers in respect to spinning around the C(3)–N bond which is cumbed due to conjugation of the nitrogen lone pair with the C=C bond. Of interest, both NMR (carbons C(3) and C(3a) are the quaternary ones) and X-ray data (*vide infra*) indicate that dihydropentalene **4** exists exclusively as an enamine. That may be due to the thermodynamic preference of the fulvene-type system. For compound **4**, rotamerism around C(3)–N bond is not observed. All isomeric dihydropentalenes **4**, **5a** and **5b** at room temperature are in an equilibrium one with each other, with molar ratio **4:5a:5b** being equal to 3.0:1.5:1 (NMR spectroscopy data).

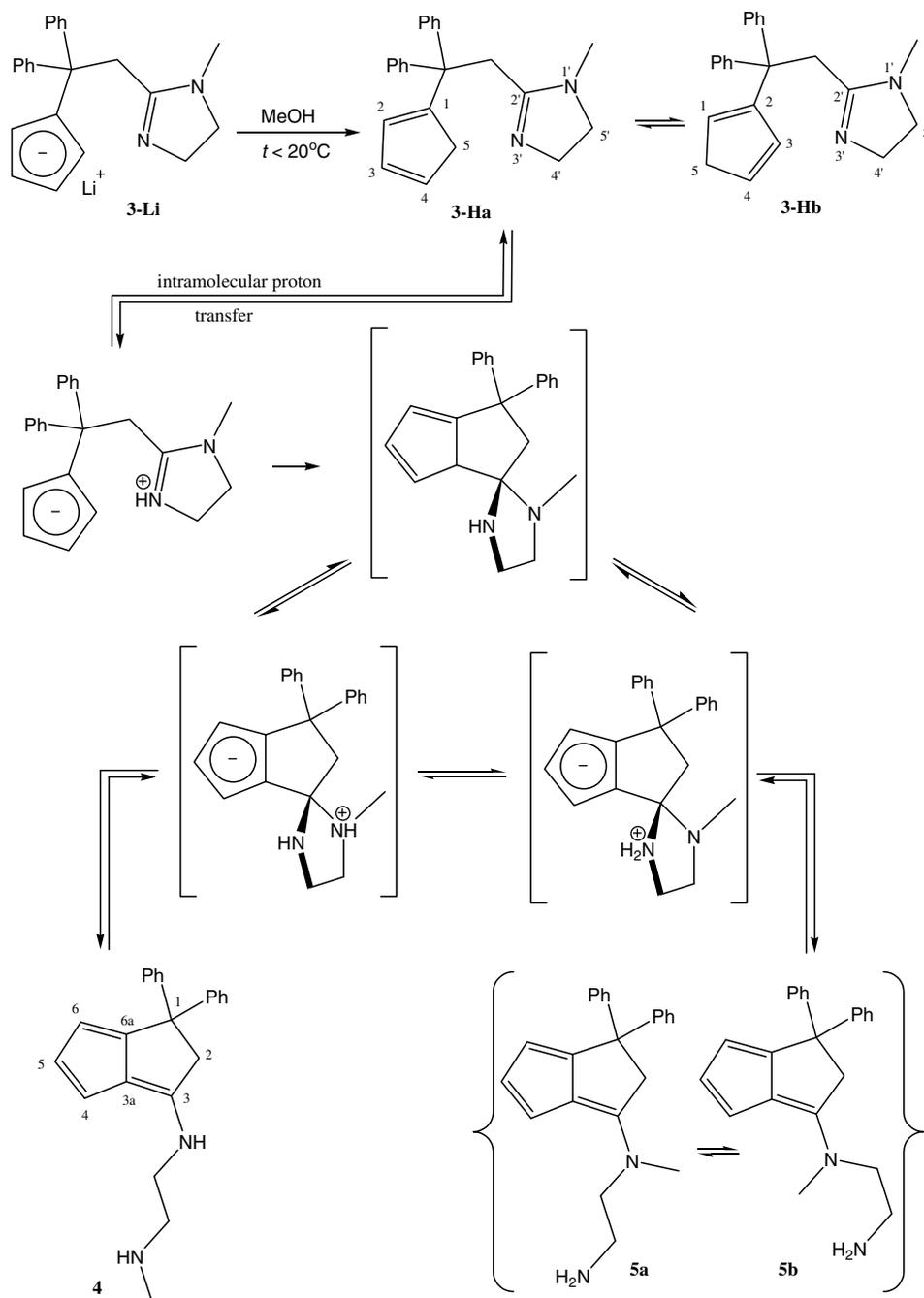
2.2. Crystal structure of 3-[N-[2-(N-methylamino)ethyl]amino]-1,1-diphenyl-1,2-dihydropentalene (**4**)

Compound **4** was crystallized from a hexane solution of its equilibrium mixture with **5a,b** containing a small amount of methanol as an adduct with one molecule of CH_3OH . Molecular structure of **4** is depicted in Fig. 1, crystal structure of the adduct is presented in Fig. 2. The selected bond lengths and angles are listed in Table 1.²

Both phenyl rings in **4** are disordered over several positions. The cyclopentadienyl fragment C(4)–C(8) is planar within 0.005 Å, the fulvene fragment C(1),C(4)–C(8) is planar within 0.006 Å. The nitrogen atom N(1) is sp^2 -hybridized [valency angle sum at N(1) equals $360(4)^\circ$]. The bond lengths C(1)–C(8) and C(1)–N(1) (1.379(5) and 1.321(5) Å, respectively) indicates the enamine nature of **4** what is in a complete agreement with the NMR data for solutions of **4**.

In crystal, the molecules of compound **4** and methanol assemble in chains by the $\text{H}(1)\cdots\text{O}(1)$ and $\text{H}(3)\cdots\text{N}(2\text{A})$ hydrogen bonds. Likely, it is the presence of methanol in mother solution that provides the preference of the Z-conformer crystallization. Evidently,

² Numbering of atoms in the crystallographic section does not match the IUPAC rules. For other sections of this paper the atom numbering given in corresponding schemes is used.



the tendency of **4** to capture and retain methanol caused unsatisfactory elemental analysis results obtained for **4**.

2.3. Imidazoline ring-opening degradation of compound **2** and crystal structure of the diamido-type product **2a**

If not free from 1,2-dimethylimidazoline **1**, organolithium compound **2** in a THF- d_8 solution gradually undergoes degradation and interconverts into its formal dimer **2a** (3 months, room temperature). As far as it is hardly believable that the C2 carbon in **2** can accept any nucleophilic attacks this process of the imidazoline ring opening, supposedly, may occur as it is depicted in Scheme 3 and is catalyzed with non-deprotonated **1**. Indeed, if presence of even the traces of **1** is excluded, THF solutions of organolithium compound **2** are stable and no ring cleavage occurs.

Single crystal of compound **2a** was grown up from the THF- d_8 solution of organolithium compound **2** containing trace amounts of imidazoline **1** in an NMR tube. Molecular structure of compound **2a** was established by X-ray diffraction analysis and is presented in Fig. 3 (ORTEP drawing). In Fig. 4, ball-and-stick drawing of **2a** is provided for clarification. The selected bond lengths and angles for **2a** are listed in Table 2.

In crystalline state, diamide **2a** represents a centrosymmetric coordination dimer and exists as an adduct with two molecules of THF(- d_8). In respect to each Li-atom, the organic part of the molecule serves as an $\eta^3\text{-}\kappa\text{N,N,N}$ -ligand, with the methyl group protected nitrogen of the imidazoline moiety not participating in the coordination. Binding of the two parts of the molecule is provided by bonds N(4)–Li(2) and N(4A)–Li(2A). The lithium atoms Li(1) and Li(2A) are positioned on the opposite sides of the N(2),N(3),N(4) plane

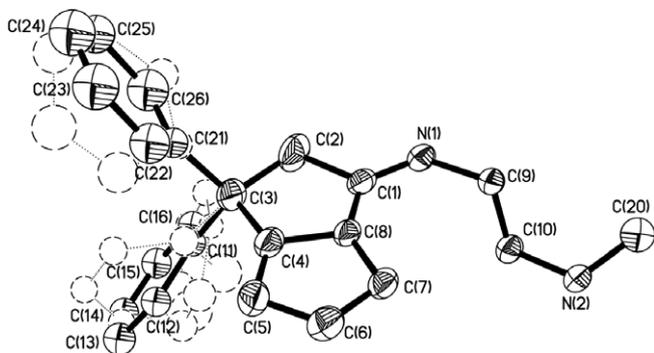


Fig. 1. Molecular structure of compound **4** (adduct with CH_3OH 1:1). The methanol molecule and hydrogen atoms are omitted for clarity.

(PL1), with the distance $\text{Li}(1)\text{--PL1}$ being *ca.* 0.05 Å shorter than $\text{Li}(2\text{A})\text{--PL1}$ [1.075(4) vs. 1.125(3) Å, respectively]. The “outer” $\text{Li}(1)$ atom is coordinated with an $\text{O}(1)$ atom of the THF molecule. In respect to electronegative atoms (O, N) all Li atoms exhibit $\text{CN} = 4$, with $\text{Li}(1)$ and $\text{Li}(2\text{A})$ sited very close to one of the faces of the respective distorted tetrahedra [$\text{N}(2), \text{N}(3), \text{N}(4), \text{O}(1)$; deviation of $\text{Li}(1)$ from $\text{N}(2), \text{N}(4), \text{O}(1)$ plane 0.2891(40) Å; $\text{N}(2), \text{N}(3), \text{N}(4), \text{N}(4\text{A})$; deviation of $\text{Li}(2\text{A})$ from $\text{N}(2), \text{N}(4), \text{N}(4\text{A})$ plane 0.2781(35) Å].

The presence of extremely close lithium–lithium contacts [$\text{Li}(1)\text{--Li}(2\text{A})$ 2.201(5) Å and $\text{Li}(2)\text{--Li}(2\text{A})$ 2.396(6) Å] is the most

remarkable feature of the **2a** molecule. Analysis of the Cambridge Structural Database (release: August 2007; 60 entries, 160 fragments, Li–Li distance range 2.232–2.499 Å) [34] reveals that $\text{Li}(1)\text{--Li}(2\text{A})$ contact is the shortest among ever observed. This contact is remarkably shorter than the Li–Li distances in organolithium clusters [Cambridge Structural Database (release: August 2007; 21 entries, 78 fragments, Li–Li distance range 2.342–2.489 Å) [34]] and in earlier reported ($\mu^3\text{-Me}$) $_4\text{Li}_4$ (2.56 Å) [35] and closer to what is observed in lithium amides and polyamides (2.252 Å [36], 2.281, 2.301 Å [37]; 2.232 Å [38]; 2.280 Å [39]). However, it is considerably greater than the sum of the ionic radii of two Li^+ cations (1.18 Å for $\text{CN}_{\text{Li}} = 4$) [40]. The fragment $\text{Li}(1), \text{Li}(2), \text{Li}(1\text{A}), \text{Li}(2\text{A}), \text{N}(4), \text{N}(4\text{A})$ (mean plane PL2) is planar within 0.05 Å, with the $\text{Li}(1)$ and $\text{Li}(1\text{A})$ atoms deviating the most. Similar assembling of lithium atoms and strongly electronegative heteroatoms (O, N, F) into a nearly planar moieties was observed earlier [36–39,41,42].

As for the organic part of the molecule, the fragment $\text{N}(1), \text{N}(2), \text{C}(1), \text{C}(2)$ (mean plane PL3) is planar within 0.005 Å, with the sum of the angles at $\text{C}(1)$ being 359.99(54)°. Carbon atom $\text{C}(3)$ only slightly deviates from PL3 [0.0076(44) Å], while $\text{C}(2)\text{--PL3}$ and $\text{C}(5)\text{--PL3}$ distances are considerably large [0.4291(51) and 0.4202(46) Å]. Thus, the imidazoline moieties of the molecule are essentially non-planar and are in envelope conformations.

Carbon atom $\text{C}(11)$ is also very close to the PL3 [0.0278(39) Å], with the dihedral angle $\text{N}(2)\text{--C}(1)\text{--C}(4)\text{--C}(11)$ being equal to

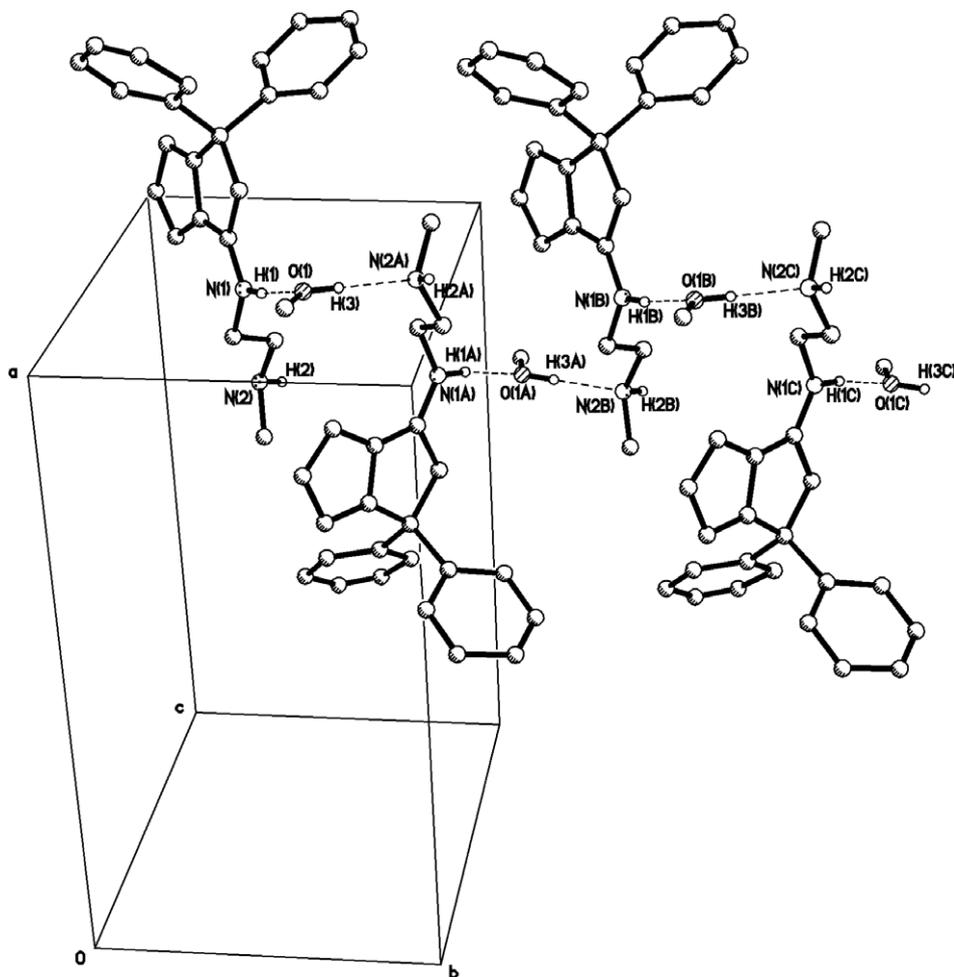


Fig. 2. Crystal structure of the adduct of **4** with one molecule of methanol. Hydrogen bonds are drawn as dashed lines. Hydrogen atoms linked to carbons are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for compound **4**

N(1)–C(1)	1.321(5)	C(1)–N(1)–C(9)	123.5(3)
N(1)–C(9)	1.461(4)	C(1)–N(1)–H(1)	116(2)
N(1)–H(1)	0.91(4)	C(9)–N(1)–H(1)	121(2)
N(2)–C(20)	1.468(5)	C(20)–N(2)–C(10)	113.2(3)
N(2)–C(10)	1.470(4)	C(20)–N(2)–H(2)	104(2)
N(2)–H(2)	0.91(4)	C(10)–N(2)–H(2)	111(2)
C(1)–C(8)	1.379(5)	N(1)–C(1)–C(8)	130.9(3)
C(1)–C(2)	1.507(5)	N(1)–C(1)–C(2)	119.7(3)
C(2)–C(3)	1.555(6)	C(8)–C(1)–C(2)	109.4(3)
C(3)–C(4)	1.506(5)	C(41)–C(3)–C(31)	93.2(8)
C(4)–C(5)	1.377(6)	C(5)–C(4)–C(8)	107.6(3)
C(4)–C(8)	1.434(5)	C(5)–C(4)–C(3)	140.1(3)
C(5)–C(6)	1.430(5)	C(8)–C(4)–C(3)	112.3(3)
C(6)–C(7)	1.367(5)	C(1)–C(8)–C(7)	142.1(3)
C(7)–C(8)	1.431(5)	C(1)–C(8)–C(4)	109.5(3)
C(9)–C(10)	1.517(5)	C(7)–C(8)–C(4)	108.3(3)
		N(1)–C(9)–C(10)	111.7(3)

0.5(4)° only. The next by the chain torsion angle C(1)–C(4)–C(11)–N(3) is also small [9.13(35)°]. The C(11)–N(3) bond length [1.300(2)] indicates its double nature. The bond lengths N(2)–C(1), C(1)–C(4), C(4)–C(11) [1.330(2), 1.401(3), and 1.395(3) Å, respectively] are in a range between single and double bond lengths that is typical for conjugated systems with delocalized negative charge.

As for the THF fragment, carbon atom C(22) and hydrogen atoms H(22A,B), H(21A,B), and H(23A,B) (not depicted in Figs. 3 and 4) are disordered between two positions with the occupancies 0.44 (envelope conformation) and 0.56 (twisted conformation).

In THF-*d*₈ solution, compound **2a** exhibits dynamic behavior, probably, due to monomerization–dimerization processes. Indeed, in both ¹H and ¹³C NMR spectra, the signals related to the end-of-chain CH₃–N–CH₂ amido-moiety are broadened the most (this made accurate measurement of the ¹J_{CH} constants for C(7') and C(5') impossible). All ¹J_{CH} constants for C(8'), C(5), and C(4') are of the normal value (135, 137, and 137 Hz, respectively), while the ones for C(4) (129 Hz) and C(7') (126 Hz; measured as difference between the ¹³C satellites in ¹H NMR spectrum) are considerably lower. Both ¹H and ¹³C chemical shifts for C(1') (3.78 and 73.86, respectively) along with rather high ¹J_{CH} (154 Hz) are in an agreement with the retention of the chelating structure of the **2a** in a THF solution, as well.

2.4. Trimethylsilylation and –stannylation reactions of lithium salt **3-Li**

Conversion of alkali-metal cyclopentadienides into corresponding trialkylsilyl and/or –stannyl derivatives is nowadays a routine

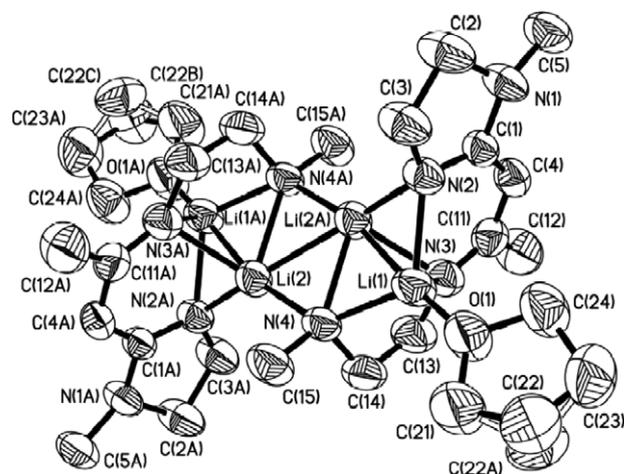
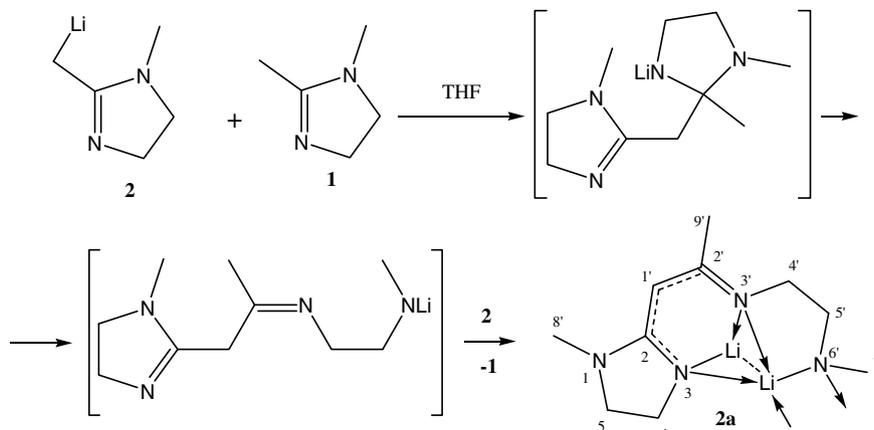


Fig. 3. Molecular structure of a dimer of **2a** (adduct with 2 molecules of THF-*d*₈). All hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at 50% probability level.

and conventional intermediate step in the Group 4 metal organo-element chemistry. However, while the imidazole analogue of salt **3-Li**, LiC₅H₄CPh₂CH₂–(1-Me–C₃H₂N₂), gives the target silane Me₃Si–C₅H₄CPh₂CH₂–(1-Me–C₃H₂N₂) in an excellent yield [31], cyclopentadienide **3-Li** reacted with Me₃SiCl in an absolutely different manner and the desired silane **3-Si** was not even observed in the reaction mixture. The main product of this reaction is the substituted 1,2-dihydropentalene **6** (ca. 60% in the isolated mixture of the products, see Scheme 4). The suggested mechanism for formation of **6** is given in Scheme 4, as well. The structure of dihydropentalene **6** was established by ¹H and ¹³C NMR spectroscopy and mass spectrometry.

Trimethylstannylation of **3-Li** with Me₃SnCl (1:1 molar ratio) also proceeds in a non-trivial manner and along with expected stannane **3-Sn** (ca. 50 mol.%) equimolar amounts of distannylation (!) cyclopentadiene **3-Sn**₂ and cyclopentadiene **3-H** (25 and 25 mol.%, NMR data, see Scheme 4). 1,2-Dihydropentalene-type products analogous to **4, 5a, b** and **6** were not observed. Monostannylation compound **3-Sn** was isolated in a mixture with **3-Sn**₂ and **3-H** as yellow oil and this mixture was used for the further purposes without the component separation.

The structure of the distannylation compound **3-Sn**₂ was established by ¹H and ¹³C NMR spectroscopy (**3-Sn**, **3-Sn**₂ and **3-H** mixture was investigated). The subspectra (both ¹H and ¹³C) of monostannylation cyclopentadiene **3-Sn** exhibit all features typical for monostannylation cyclopentadienes, with the signals related to



Scheme 3.

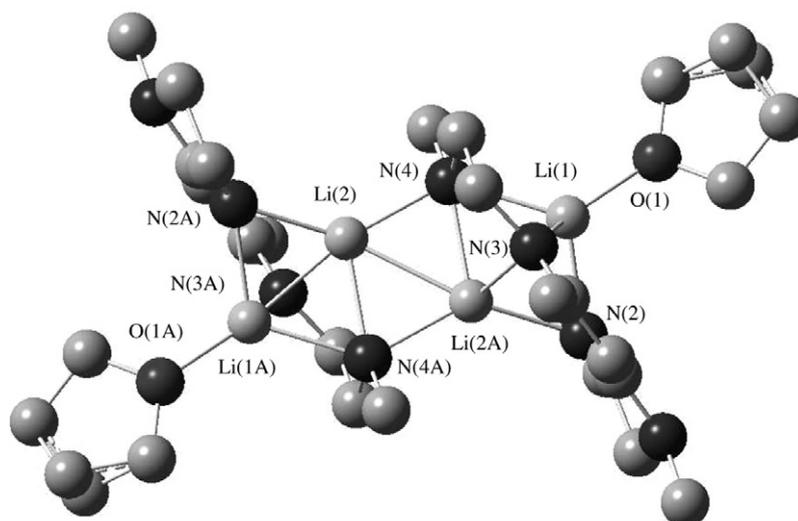


Fig. 4. Ball-and-stick drawing of a dimer of **2a** (adduct with two molecules of THF- d_8). All hydrogen atoms are omitted for clarity. Only the atoms participating in the coordination interaction are labeled. View normal to PL2 [mean plane of the Li(1),Li(2),Li(1A),Li(2A),N(4),N(4A) fragment].

Table 2
The selected bond lengths (Å) and angles (°) for compound **2a**

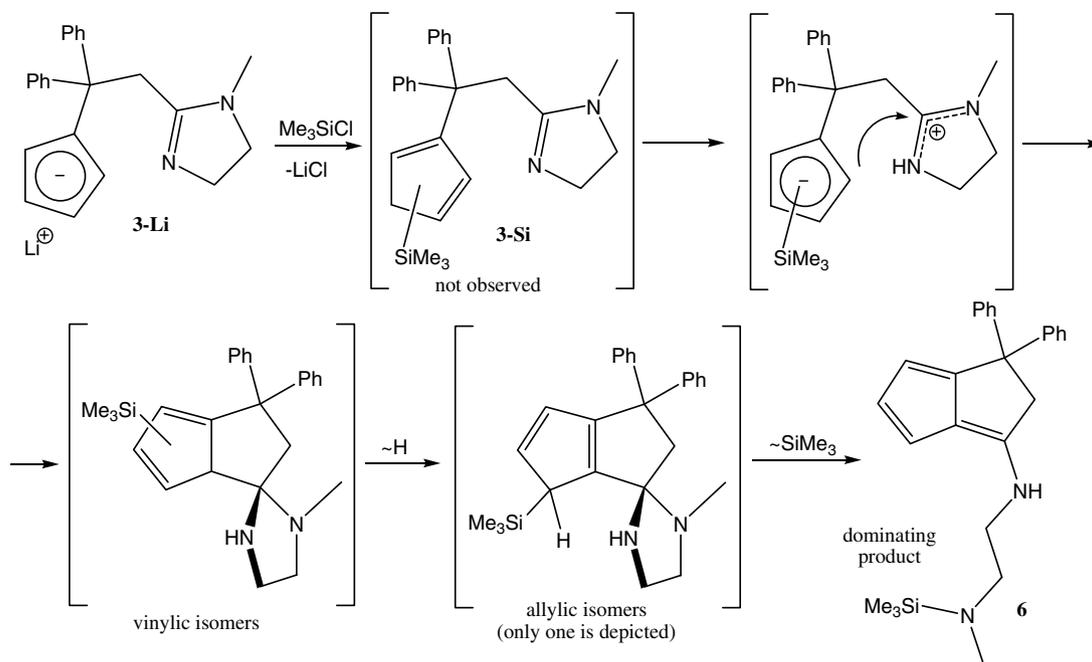
N(1)–C(1)	1.393(2)	C(1)–N(1)–C(2)	107.35(18)	N(1)–C(2)–C(3)	101.3(2)
N(1)–C(2)	1.442(3)	C(1)–N(2)–C(3)	107.30(17)	N(2)–C(3)–C(2)	104.6(2)
N(1)–C(5)	1.445(3)	C(1)–N(2)–Li(1)	117.29(17)	C(11)–C(4)–C(1)	124.24(19)
N(2)–C(1)	1.330(2)	C(3)–N(2)–Li(1)	125.13(17)	N(3)–C(11)–C(4)	120.8(2)
N(2)–C(3)	1.464(3)	C(1)–N(2)–Li(2A)	110.22(15)	N(3)–C(11)–C(12)	121.3(2)
N(2)–Li(1)	2.052(4)	C(3)–N(2)–Li(2A)	127.2(2)	C(4)–C(11)–C(12)	118.0(2)
N(2)–Li(2A)	2.083(4)	Li(1)–N(2)–Li(2A)	64.34(14)	N(3)–C(13)–C(14)	106.5(2)
N(3)–C(11)	1.300(2)	C(11)–N(3)–C(13)	123.9(2)	N(4)–C(14)–C(13)	110.6(2)
N(3)–C(13)	1.450(3)	C(11)–N(3)–Li(1)	126.79(18)	O(1)–Li(1)–Li(2A)	169.2(2)
N(3)–Li(1)	2.028(4)	C(13)–N(3)–Li(1)	108.20(18)	N(3)–Li(1)–Li(2A)	60.01(14)
N(3)–Li(2A)	2.120(4)	C(11)–N(3)–Li(2A)	110.08(17)	N(2)–Li(1)–Li(2A)	58.52(14)
N(4)–C(14)	1.445(3)	C(13)–N(3)–Li(2A)	102.42(18)	N(4)–Li(1)–Li(2A)	58.46(13)
N(4)–C(15)	1.448(3)	Li(1)–N(3)–Li(2A)	64.06(15)	N(4)–Li(2)–N(2A)	132.58(19)
N(4)–Li(2)	2.012(4)	C(14)–N(4)–C(15)	108.6(2)	N(4)–Li(2)–N(4A)	108.87(15)
N(4)–Li(2A)	2.105(4)	C(14)–N(4)–Li(2)	110.87(18)	N(2A)–Li(2)–N(4A)	112.99(16)
N(4)–Li(1)	2.107(4)	C(15)–N(4)–Li(2)	97.68(17)	N(4)–Li(2)–N(3A)	129.02(19)
C(1)–C(4)	1.401(3)	C(14)–N(4)–Li(2A)	111.69(17)	N(2A)–Li(2)–N(3A)	81.91(13)
C(2)–C(3)	1.514(3)	C(15)–N(4)–Li(2A)	139.5(2)	N(4A)–Li(2)–N(3A)	77.57(14)
C(4)–C(11)	1.395(3)	Li(2)–N(4)–Li(2A)	71.13(15)	N(4)–Li(2)–Li(1A)	166.7(2)
C(11)–C(12)	1.515(4)	C(14)–N(4)–Li(1)	90.68(17)	N(2A)–Li(2)–Li(1A)	57.15(13)
C(13)–C(14)	1.527(4)	C(15)–N(4)–Li(1)	113.78(18)	N(4A)–Li(2)–Li(1A)	58.52(13)
Li(1)–Li(2A)	2.201(5)	Li(2)–N(4)–Li(1)	133.92(16)	N(3A)–Li(2)–Li(1A)	55.93(14)
Li(2)–Li(2A)	2.396(6)	Li(2A)–N(4)–Li(1)	63.02(13)	N(4)–Li(2)–Li(2A)	56.25(14)
O(1)–Li(1)	1.908(4)	N(2)–C(1)–N(1)	111.81(18)	N(2A)–Li(2)–Li(2A)	155.7(3)
		N(2)–C(1)–C(4)	126.80(19)	N(4A)–Li(2)–Li(2A)	52.62(13)
		N(1)–C(1)–C(4)	121.38(17)	N(3A)–Li(2)–Li(2A)	109.9(2)
				Li(1A)–Li(2)–Li(2A)	111.0(2)

Symmetry transformations used to generate equivalent atoms: $-x + 2, -y, -z + 1$.

the Cp-ring $-\text{CH}=\text{}$ fragments averaged (AA'BB') spin system, for more detailed information on monostannylated cyclopentadienes see review [43] and references cited therein). In the subspectra of **3-Sn₂**, all signals related to the Cp-ring $-\text{CH}=\text{}$ fragments are different. The relative peak intensities of the $^{117/119}\text{Sn}$ satellites (except those of the Me_3Sn -groups signals) in ^{13}C NMR spectrum for the signals of **3-Sn₂** are approximately two times greater than those for the signals related to **3-Sn** (the signal to noise ratio was not high enough to make quantitative integration possible). For the ^{13}C NMR signal of the Me_3Sn -group in **3-Sn₂**, two pairs of satellites are observed ($^1J(\text{C}-^{119}\text{Sn}) = 339 \text{ Hz}$, $^3J(\text{C}-^{119}\text{Sn}) = 4.3 \text{ Hz}$, SnMe_3). For compound **3-Sn₂**, the signal of the quaternary carbon of the Cp-ring possesses a pair of satellites $^{117/119}\text{Sn}$ ($\delta = 51.37 \text{ ppm}$,

$^1J(\text{C}-^{119}\text{Sn}) = 198 \text{ Hz}$). In the ^1H and ^{13}C NMR subspectra of **3-Sn₂**, the observed relative intensity of the Me_3Sn -group signals also matches the presence of two trimethylstannyl moieties.

The formation of distannylated cyclopentadiene **3-Sn₂**, especially in such considerable amounts, is rather surprising. First of all, it is a "sterically overhindered" molecule. Secondly, the mechanism of **3-Sn₂** formation is not evident. In literature, no examples of deprotonation of stannylated cyclopentadienes are known. Di- and polystannylated cyclopentadienes can be prepared by a reaction of stannylamines $\text{R}_3\text{Sn}-\text{NR}'_2$ with corresponding CH-acidic cyclopentadienes [44]. Consideration of these facts allows to suggest the mechanism for the compound **3-Sn₂** formation, as depicted in Scheme 5.



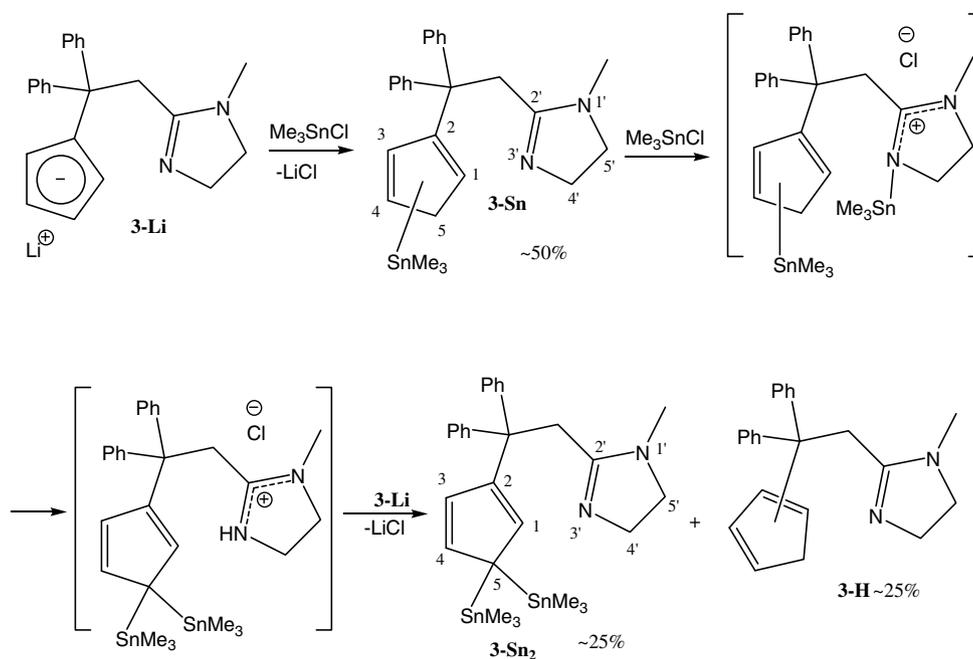
It is worth mentioning here that compounds **4**, **5a,b** and **6** themselves can serve as precursors of new polydentate ligands for organometallic chemistry. However, this should be a subject for further investigations.

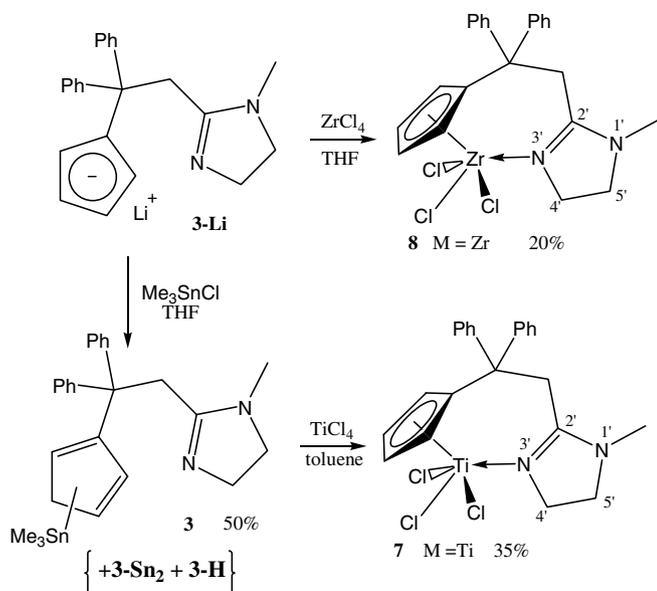
2.5. Preparation of titanium(IV) and zirconium(IV) monocyclopentadienyl complexes **7** and **8**

Unlike in case of the imidazole analogue of ligand **3** [31], synthesis of complexes $[\eta^5:\eta^1-\kappa N-C_5H_4CPh_2CH_2-(1-MeC_3H_4N_2)]TiCl_3$ (**7**) and $[\eta^5:\eta^1-\kappa N-C_5H_4CPh_2CH_2-(1-MeC_3H_4N_2)]ZrCl_3$ (**8**) met cer-

tain problems due to unavailability of silane **3-Si**. Titanium and zirconium complexes **7** and **8** were, however, prepared, starting from **3-Sn** (a 2:1:1 mixture with **3-Sn₂** and **3-H**) and **3-Li**, respectively (see Scheme 6). As it was expected, the yields of **7** and **8** were lower than formerly observed for their imidazole analogues $[\eta^5:\eta^1-\kappa N-C_5H_4CPh_2CH_2-(1-MeC_3H_2N_2)]MCl_3$ (M = Ti, Zr) [31] what once more illustrates the efficiency of application of the silylated cyclopentadienes for preparation of monocyclopentadienyl complexes of titanium and zirconium.

Compounds **7** and **8** are both crystalline solids. Titanium complex **7** is red to orange (dependently on the size of the crystalline grains)





Scheme 6.

while the zirconium complex **8** is nearly colorless. Formation of stable adducts with THF was not observed neither for **7** nor for **8**.

2.6. Crystal structure of complex **8**

Complex **8** is a centrosymmetric dimer with the Zr centers linked one to another with two bridging chlorine atoms. The molecular structure of **8** is depicted in Fig. 5. The selected bond lengths and angles are listed in Table 3.

The coordination environment of the zirconium center is a distorted octahedron (in an assumption that the Cp-ligand occupies one coordination place). Three chlorine atoms and the non-methylated nitrogen atom of the imidazoline moiety occupy the equatorial positions while the Cp-ligand and one of chlorine atoms from the environment of another Zr-center are located in the axial positions. This structural motif is rather typical for *n*-donor solvent free zirconium half-sandwich cyclopentadienyl complexes [45–48]. In general, complex **8** exhibits no remarkable quantitative or qualitative structural particularities (CCDC, release August 2007 [34]).

2.7. NMR-studies of the fluxional behavior for complexes **7** and **8** in solutions

The fluxional behavior of complexes **7** and **8** in solutions was studied by variable-temperature NMR spectroscopy. The tempera-

Table 3
Selected bond lengths (Å) and angles (°) for compound **8**

Zr(1)–N(1)	2.281(10)	N(1)–Zr(1)–Cl(3)	84.4(3)
Zr(1)–Cl(3)	2.466(4)	N(1)–Zr(1)–Cl(2)	154.6(3)
Zr(1)–Cl(2)	2.520(3)	N(1)–Zr(1)–Cl(1)	83.2(3)
Zr(1)–Cl(1)	2.592(4)	Cl(3)–Zr(1)–Cl(1)	153.76(13)
Zr(1)–Cl(1A)	2.724(4)	Cl(2)–Zr(1)–Cl(1)	90.78(13)
N(1)–C(8)	1.278(15)	Cl(3)–Zr(1)–Cl(2)	90.58(13)
N(2)–C(8)	1.334(17)	N(1)–Zr(1)–Cl(1A)	78.6(3)
Zr(1)–PL ^a	2.205(6)	Cl(3)–Zr(1)–Cl(1A)	80.78(12)
		Cl(2)–Zr(1)–Cl(1A)	76.09(12)
		Cl(1)–Zr(1)–Cl(1A)	74.14(13)
		Zr(1)–Cl(1)–Zr(1A)	105.86(13)
		C(8)–N(1)–C(9)	105.8(11)
		C(8)–N(1)–Zr(1)	131.8(9)
		C(9)–N(1)–Zr(1)	122.4(8)
		N(1)–C(8)–N(2)	117.0(12)

^a PL – mean plane of the Cp-ring.

ture-dependant ^1H NMR spectra for **7** in CD_2Cl_2 and **8** in $\text{THF-}d_8$ are presented in Figs. 6 and 7, respectively.

Zirconium complex **8** in a $\text{THF-}d_8$ solution exhibits dynamic behavior similar to what observed formerly for its imidazole analogue $[\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CPh}_2\text{CH}_2\text{-}(1\text{-MeC}_3\text{H}_2\text{N}_2)]\text{ZrCl}_3$ [31]. At 55 °C, compound **8** possesses the pseudo- C_5 symmetry that vanishes along with the temperature decrease due to slowing of the six-member metallacycle $-\text{Zr}-\text{Cp}-\text{CPh}_2-\text{CH}_2-\text{C}-\text{N}-(\text{Zr})$ interconversion. Analogous processes were observed previously for $(\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{SMe})\text{ZrCl}_3$ [45] and $(\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{NMe}_2)\text{ZrCl}_3$ [12]. At –60 °C (the low-rate exchange limit), two pairs of the Cp-ring protons, two pairs of the CH_2-CH_2 protons, bridge methylene group protons and phenyl groups become non-equivalent. In ^{13}C NMR spectrum (–60 °C), Cp-ring carbons CH(2,5) and CH(3,4) and the phenyl group carbons also become non-equivalent.

Within the range of –60 through +55 °C, the temperature drift of the ^{13}C NMR signals, except that for CH(2,5) cyclopentadienyl carbons, does not exceed 0.5 ppm (at –60 °C the average shifts for the corresponding pairs of the signals were considered). For CH(2,5) cyclopentadienyl carbons the magnitude of this drift is ca. 1 ppm that is also a regular value for the temperature drifts. This agrees with the retention of the $\text{N} \rightarrow \text{Zr}$ coordination within all the temperature range studied.

The metallacycle inversion barrier for **8** was estimated by measuring the coalescence temperatures for CH(2,5) [$\Delta G^\ddagger = 49.6 (\pm 0.9)$ (kJ/mol) = 11.9 (± 0.2) (kCal/mol), $T_{\text{coal}} = -13$ °C], CH(3,4) [$\Delta G^\ddagger = 50.1 (\pm 0.9)$ (kJ/mol) = 12.0 (± 0.2) (kCal/mol), $T_{\text{coal}} = -25$ °C], $\text{CH}_2(4')$ [$\Delta G^\ddagger = 49.7 (\pm 0.9)$ (kJ/mol) = 11.9 (± 0.2) (kCal/mol), $T_{\text{coal}} = -17$ °C] and $\text{CH}_2(5')$ [$\Delta G^\ddagger = 49.6 (\pm 0.9)$ (kJ/mol) = 11.9 (± 0.2) (kCal/mol), $T_{\text{coal}} = -20$ °C]. The average value $\Delta G^\ddagger = 49.8 (\pm 0.9)$ (kJ/mol) = 11.9 (± 0.2) (kCal/mol). This is by 0.7 kCal/mol lower than

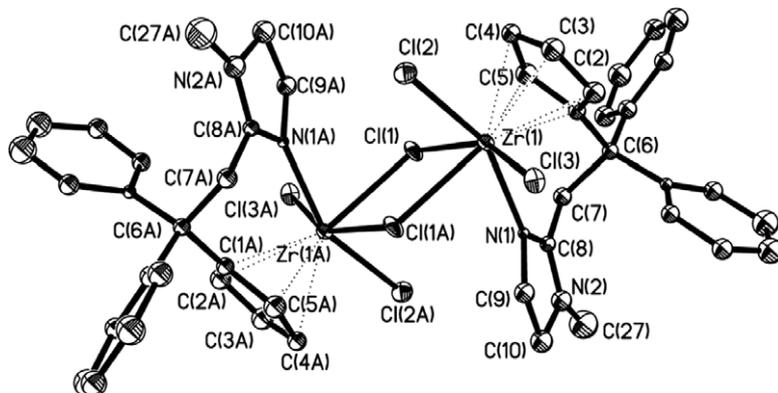


Fig. 5. Molecular structure of complex **8**. All hydrogen atoms are omitted for clarity.

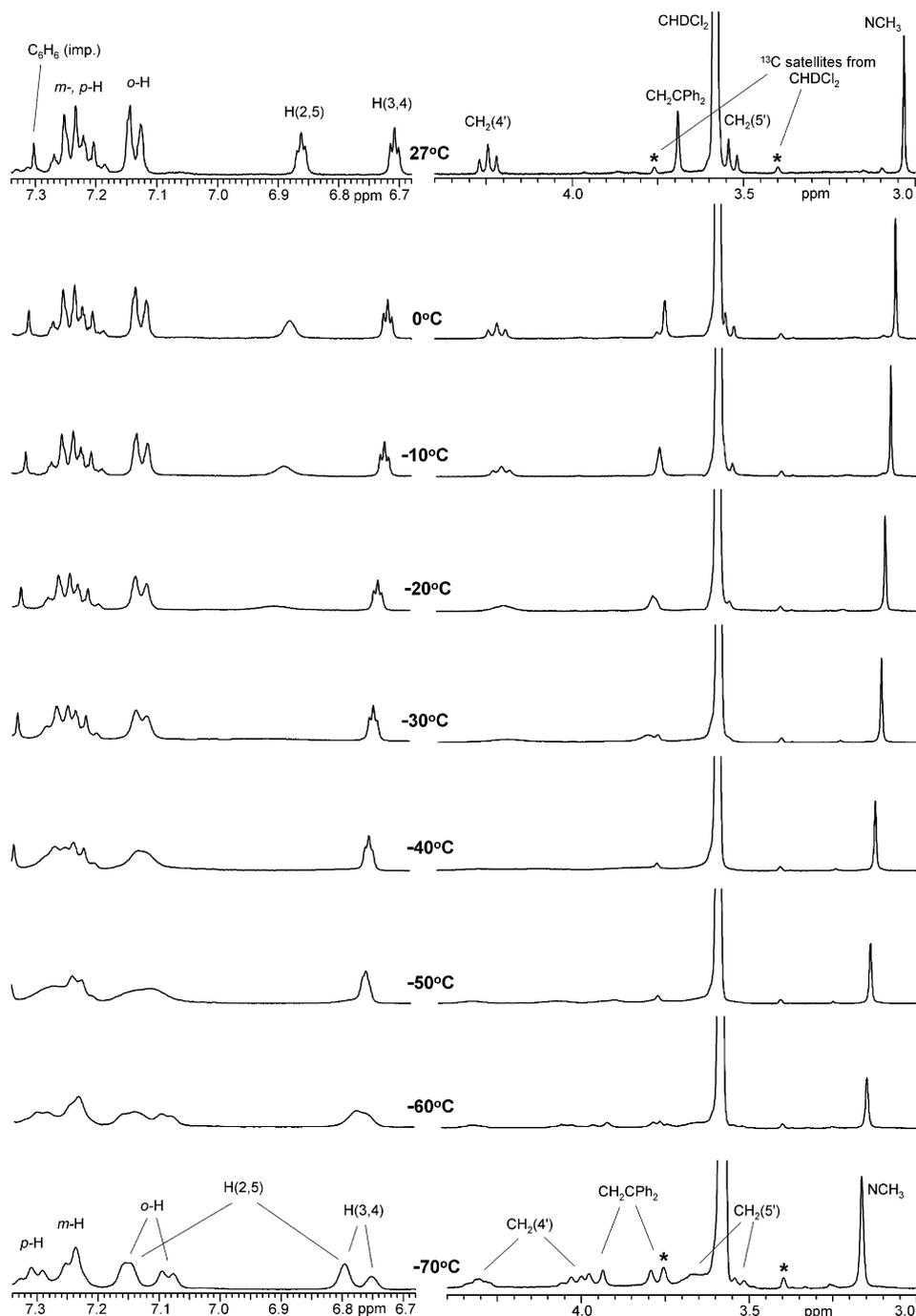


Fig. 6. Fluxional behavior of $[\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CPh}_2\text{CH}_2\text{-}(1\text{-methylimidazolin-2-yl})\text{TiCl}_3$ (**7**) in a CD_2Cl_2 solution.

observed previously for the imidazole analogue of **8** [31]. The interpretation of the cyclopentadienyl parts of the NMR spectra was performed similarly to how it was done earlier [31].

Titanium complex **7**, unlike its imidazole counterpart $[\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CPh}_2\text{CH}_2\text{-}(1\text{-MeC}_3\text{H}_2\text{N}_2)]\text{TiCl}_3$ [31], does not exhibit the reversible intramolecular coordination–dissociation of the imidazoline functionality towards the metal center in a solvating solvent (THF- d_8). Thus, its dynamic behavior in THF- d_8 is fully analogous to that of **8**.

The metallacycle inversion barrier for **7** was estimated by measuring the coalescence temperatures for $\text{CH}(2,5)$ [$\Delta G^\ddagger = 46.4$ (± 0.9) (kJ/mol) = 11.1 (± 0.2) (kCal/mol), $T_{\text{coal}} = -35$ °C], $\text{CH}_2(4')$ [$\Delta G^\ddagger = 46.4$ (± 0.9) (kJ/mol) = 11.1 (± 0.2) (kCal/mol), $T_{\text{coal}} = -37$ °C]

and CH_2CPh_2 [$\Delta G^\ddagger = 46.8$ (± 0.9) (kJ/mol) = 11.2 (± 0.2) (kCal/mol), $T_{\text{coal}} = -40$ °C]. The average value $\Delta G^\ddagger = 46.5$ (± 0.9) (kJ/mol) = 11.1 (± 0.2) (kCal/mol). This value is by 0.8 kCal/mol lower than for **8** and by 0.3 kCal/mol lower than observed previously for the imidazole analogue of **7** in CD_2Cl_2 [31]. The low solubility of **7** even in THF did not allow us to gain its ^{13}C NMR spectrum.

3. Experimental

3.1. General remarks

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



Fig. 7. Fluxional behavior of $[\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CPh}_2\text{CH}_2\text{-(1-methylimidazolin-2-yl)}]\text{ZrCl}_3$ (**8**) in a THF- d_8 solution.

logues) were dried with and distilled from conventional agents (namely: diethyl ether and THF, with sodium benzophenone ketyl, benzene, toluene and hexane, with Na–K alloy, CH_2Cl_2 and with CaH_2). The degassed solvents were stored in evacuated reservoirs over corresponding drying agent and transferred on a high-vacuum line (the residual pressure of non-condensable gases of 10^{-3} torr order) directly into reaction vessels by trapping them with liq. N_2 . The operations with volatile reagents were performed similarly [Me_3SiCl (over Al powder), MeOH (over $(\text{MeO})_2\text{Mg}$), 6,6-Diphenylfulvene was prepared as described previously [49], 1,2-Dimethylimidazoline (**1**) was prepared from *N*-methylethylenediamine by an analogy to [50]. TiCl_4 was distilled under dry Ar atmosphere, heated under

reflux with freshly prepared reduced copper powder, degassed on the high-vacuum line and packed by recondensation into weighed-up glass receivers, that were then sealed off (Teflon grease for joints was applied). ZrCl_4 was sublimed in the stream of dry hydrogen prior to use. For all compounds except **2a**, ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400 and 100 MHz, respectively. ^1H and ^{13}C NMR spectra for compound **2a** were measured on a Bruker Avance 500 instrument at 500 and 125 MHz, respectively. For ^1H and ^{13}C spectra, the solvent resonances [$\delta_{\text{H}} = 7.15$ and $\delta_{\text{C}} = 128.0$ (C_6D_6), $\delta_{\text{H}} = 1.73$ and $\delta_{\text{C}} = 25.3$ (THF- d_8), and $\delta_{\text{H}} = 5.32$ and $\delta_{\text{C}} = 53.8$ (CD_2Cl_2)] were used as internal reference standards. The calibration of the temperature controller

was performed by measuring the standard methanol sample spectra. Mass spectra were measured on Finnigan MAT SSQ 7000 chromatograph-mass spectrometer. The elemental analyses were performed on the Carlo-Erba automated analyser.

3.2. (1-Methylimidazolin-2-yl)methyl lithium (**2**)

To a solution of 1,2-dimethylimidazoline (**1**) (1.77 g, 18.0 mmol) in THF (10 mL), *n*-BuLi (10 mL of 2.45 M solution in hexane, 24.5 mmol, 35% excess) and diethyl ether (15 mL) were added at -20°C and vigorous shaking of the reaction mixture that caused nearly immediate formation of white thin-crystalline voluminous precipitate. The reaction mixture was allowed to warm up to room temperature, stirred at room temperature for 4 h and left to stay overnight. The yellow liquor was removed by filtering, the white precipitate was washed on a filter with ether (3×10 mL) and dried in high vacuum that gave 0.64 g of the organolithium compound **2** as white crystalline powder. Concentrating of the mother liquor and ethereal washings allowed to isolate additionally 0.93 g of the product. Total yield 1.57 g (83.4%). NMR ^1H (THF- d_8 , 30°C): $\delta = 1.93$ (broad s, 2H, CH_2Li), 2.56 (s, 3H, NCH_3), 2.88, 3.26 (both t, 2H, $^3J_{\text{HH}} = 6.5$ Hz, $\text{NCH}_2\text{CH}_2\text{N}$). ^{13}C (THF- d_8 , 30°C): $\delta = 35.94$ (q, $^1J_{\text{CH}} = 133$ Hz, NCH_3), 36.46 (t, $^1J_{\text{CH}} = 152$ Hz, CH_2Li), 49.70 [t, $^1J_{\text{CH}} = 136$ Hz, $\text{NCH}_2(4)$], 56.47 [tq, $^1J_{\text{CH}} = 136$ Hz, $\text{NCH}_2(5)$], 172.91 (s, =NCN).

3.3. Dilithium salt of N^1 -methyl- N^2 -[(1*E*,2*E*)-1-methyl-2-(1-methylimidazolidine-2-ylidene)ethylidene]-ethane-1,2-diamine (**2a**)

A solution of **2** in THF- d_8 containing small amount of non-deprotonated imidazoline **1** was kept at an ambient temperature (25 – 35°C) in sealed-off evacuated NMR tubes for 3 months. Well-formed colorless single crystals grew on the bottom of the tube. The first NMR tube was opened in a glove box under Ar atmosphere, the single crystal for X-ray analysis was picked up and mounted inside a Lindemann glass capillary that was sealed off. The second tube was opened under high vacuum, the mother liquor was removed from the crystals of **2a** by decantation, the crystals were washed with THF- d_8 , re-dissolved in the same THF- d_8 (THF- d_8 was transferred by re-condensations) and the solution was placed into the new NMR tube that was sealed off. Numbering of atoms in **2a** is provided in Scheme 3. NMR ^1H (THF- d_8 , 25°C): $\delta = 1.79$ (broadened s, 3H, $^1J_{\text{CH}} = 125$ Hz, $\text{CH}_3(9')$), 2.59 (broad s, 3H, $^1J_{\text{CH}} = 126$ Hz, $\text{CH}_3(7')$), 2.61 (broadened s, 3H, $^1J_{\text{CH}} = 132$ Hz, $\text{CH}_3(8')$), 2.83 (broadened t, 2H, $^3J_{\text{HH}} = 4.7$ Hz, $\text{CH}_2(5')$), 2.94 (t, 2H, $^3J_{\text{HH}} = 8.0$ Hz, $\text{CH}_2(4')$), 3.30–3.39 (overlapped broadened t, 2H + 2H, $\text{CH}_2(5)$ and $\text{CH}_2(4')$), 3.78 (broadened s, 1H, $^1J_{\text{CH}} = 154$ Hz, $\text{CH}(1')$). ^{13}C (THF- d_8 , 25°C): $\delta = 19.91$ (q, $^1J_{\text{CH}} = 126$ Hz, $\text{CH}_3(9')$), 35.17 (q, $^1J_{\text{CH}} = 135$ Hz, $\text{C}(8')$), 44.03 (broad q, $\text{C}(7')$), 50.68 (t, $^1J_{\text{CH}} = 137$ Hz, $\text{C}(5)$), 50.94 (t, $^1J_{\text{CH}} = 129$ Hz, $\text{C}(4)$), 54.63 (t, $^1J_{\text{CH}} = 137$ Hz, $\text{C}(4')$), 62.70 (broad t, $\text{C}(5')$), 73.86 (d, $^1J_{\text{CH}} = 154$ Hz, $\text{C}(1')$), 167.64, 171.80 ($\text{C}(2)$, $\text{C}(2')$).

3.4. Lithium [2-(1-methylimidazolin-2-yl)-1,1-diphenylethyl]cyclopentadienide (**3-Li**)

To a red solution of 6,6-diphenylfulvene (1.43 g, 6.21 mmol) in THF (20 mL), the lithium salt **2** (0.63 g, 6.05 mmol) was added under vigorous shaking and cooling at 0°C . The color of the reaction mixture immediately changed to dark-green. The solution was heated at 35 – 45°C for 2 days. The completeness of the reaction was monitored by measuring the ^1H NMR spectra of the control sample in THF- d_8 . Concentrating of the solution till dryness gave the crude product as green solidified foam soluble in ether and toluene. To remove THF completely, the product was dissolved in toluene (20 mL) and the resultant solution was evaporated till

dryness once more. The product was washed with hexane (3×20 mL) and dried on the high vacuum line. Light-green powder. Yield 1.98 g (96.9%). ^1H NMR (THF- d_8 , 30°C): $\delta = 2.63$ (s, 3H, NCH_3), 3.14, 3.35 (both t, 2H, $^3J_{\text{HH}} = 9.6$ Hz, $\text{NCH}_2\text{CH}_2\text{N}$), 3.23 [s, 2H, $\text{CH}_2(7)$], 5.51, 5.68 (both virt. t, 2H, $^{3+4}J_{\text{HH}} = 5.4$ Hz, C_5H_4), 7.01 (m, 2H, *p*-CH), 7.09 (m, 4H, *m*-CH), 7.23 (m, 4H, *o*-CH). ^{13}C - $\{^1\text{H}\}$ NMR (THF- d_8 , 30°C): $\delta = 33.36$ (NCH_3), 40.07 [$\text{CH}_2(7)$], 51.98, 52.80 ($\text{NCH}_2\text{CH}_2\text{N}$), 54.17 (CPh_2), 103.29, 104.78 (CH in C_5H_4), 121.75 (C in C_5H_4), 125.58 (*p*-CH), 127.50 (*m*-CH), 130.06 (*o*-CH), 152.22 (*i*-C), 169.81 (=NCN).

3.5. [2-(1-Methylimidazolin-2-yl)-1,1-diphenylethyl]cyclopentadiene (**3-H**) (a mixture of isomers.)

Salt **3-Li** (0.59 g, 1.76 mmol) was dissolved in a small amount of methanol (5 mL). Methanol was removed by trapping into a vessel cooled with liq. N_2 , the residue was extracted with hexane (3×5 mL) and the hexane extract was evaporated and dried on the high-vacuum line that gave **3-H** as a yellow crystalline solid in an almost quantitative yield. At all steps of the reaction and isolation procedure the temperature was kept below 20°C . ^1H NMR (C_6D_6 , 30°C): $\delta = 1.63$ [s, $\text{NCH}_3(\mathbf{a})$], 1.79 [s, $\text{NCH}_3(\mathbf{b})$], 2.54, 3.42 [both t, $^3J_{\text{HH}} = 9.6$ Hz, $\text{NCH}_2\text{CH}_2\text{N}(\mathbf{b})$], 2.55, 3.45 [both t, $^3J_{\text{HH}} = 9.6$ Hz, $\text{NCH}_2\text{CH}_2\text{N}(\mathbf{a})$], 2.75 [q, $^3J_{\text{HH}} = ^4J_{\text{HH}} = 1.5$ Hz, $\text{CH}_2(5)(\mathbf{b})$], 3.18 [br s, $\text{CH}_2(7)(\mathbf{a})$], 3.19 [s, $\text{CH}_2(5)(\mathbf{a})$], 3.32 [s, $\text{CH}_2(7)(\mathbf{b})$], 6.19 (2H, 6.54 (1H) [both m, =CH(1, 3, 4)(**b**)], 6.25, 6.39, 6.45 [all br m, =CH(2, 3, 4)(**a**)], 7.00–7.16 [a set of m, *m*-, *p*-CH(**a**, **b**)], 7.38 [m, *o*-CH(**a**)], 7.51 [m, *o*-CH(**b**)]. ^{13}C - $\{^1\text{H}\}$ NMR (C_6D_6 , 30°C): $\delta = 32.52$ [$\text{NCH}_3(\mathbf{a})$], 33.02 [$\text{NCH}_3(\mathbf{b})$], 36.55 [$\text{CH}_2(7)(\mathbf{b})$], 36.95 [$\text{CH}_2(7)(\mathbf{a})$], 40.92 [$\text{CH}_2(5)(\mathbf{b})$], 43.05 [$\text{CH}_2(5)(\mathbf{a})$], 52.58, 52.71, 52.80 (2C) [$\text{NCH}_2\text{CH}_2\text{N}(\mathbf{a}$, **b**)], 54.29 [$\text{CPh}_2(\mathbf{b})$], 55.33 [$\text{CPh}_2(\mathbf{a})$], 126.35 [*p*-CH(**a**, **b**)], 127.69 [*m*-CH(**a**, **b**)], 128.05, 132.47, 135.47 [=CH(1, 3, 4)(**b**)], 129.61, 131.62, 132.87 [=CH(2, 3, 4)(**a**)], 129.77 [*o*-CH(**a**)], 130.04 [*o*-CH(**b**)], 146.05 [*i*-C(**b**)], 147.14 [*i*-C(**a**)], 153.10 [=C(2)(**b**)], 155.05 [=C(1)(**a**)], 163.78 [=NCN(**b**)], 163.82 [=NCN(**a**)]. Isomer ratio **3-Hb**:**3-Ha** is 1.3. The numbering is given in Scheme 2. GC/MS (EI, 70 eV, 70 – 290°C), *m/z* (%): 328 [$\text{M}]^+$ (0.4), 231 [$\text{C}_5\text{H}_5\text{CPh}_2]^+$ (18.6), 230 [$\text{C}_5\text{H}_4\text{CPh}_2]^+$ (100), 153 [$\text{C}_5\text{H}_4\text{CPh}]^+$ (7.2), 84 [$\text{C}_3\text{N}_2\text{H}_5\text{Me}]^+$ (7.5), 77 [$\text{Ph}]^+$ (3.3). Calc. for $\text{C}_{23}\text{H}_{24}\text{N}_2$: C, 84.11; H, 7.36; N, 8.53. Found: C, 82.00; H, 7.81; N, 8.05%. The lower content of carbon and the higher content of hydrogen can be explained by the presence of methanol. Thus, calc. for a 1:1 adduct $\text{C}_{23}\text{H}_{24}\text{N}_2 \cdot \text{CH}_3\text{OH}$: C, 79.96; H, 7.83; N, 7.77 element content is in better agreement with the found values.

3.6. The 1,2-dihydropentalene-type products of cyclopentadiene **3-H** rearrangement (a mixture of isomeric **4**, **5a** and **5b**)

Heating of the cyclopentadiene **3-H** solution in C_6D_6 above 40°C for 20 min afforded quantitative formation of substituted 1,2-dihydropentalene **4**. On further staying in the solution at room temperature, compound **4** reversibly isomerized into a mixture of 1,2-dihydropentalenes **5a** and **5b**, with the equilibrium established after two weeks. The numbering of atoms in the dihydropentalene moiety is given in Scheme 2. Isomer **4** ^1H NMR (C_6D_6 , 27°C): $\delta = 0.04$ (broad, 1H, NHCH_3), 1.92 [s, 3H, NHCH_3], 2.14 (broadened s, 2H, CH_3NHCH_2), 3.04 [broadened s, 2H, $\text{CH}_2\text{NHC}(3)$], 3.42 (s, 2H, CH_2CPh_2), 5.39 [broad, 1H, $\text{HNC}(3)$], 6.30 [s, 1H, $\text{H}(6)$], 6.42 [d, 1H, $^3J_{\text{HH}} = 4.4$ Hz, $\text{H}(4$ or $5)$], 7.14 [1H, overlaps with *m*-CH and $\text{C}_6\text{D}_5\text{H}$, $\text{H}(5$ or $4)$], 7.01 (m, 2H, *p*-CH), 7.12 (m, 4H, *m*-CH), 7.45 (d, 4H, $^3J_{\text{HH}} = 7.6$ Hz, *o*-CH). ^{13}C NMR (C_6D_6 , 27°C): $\delta = 35.64$ (q, $^1J_{\text{CH}} = 133$ Hz, NCH_3), 44.46, 49.31 (both t, $^1J_{\text{CH}} = 139$ Hz, $\text{NCH}_2\text{CH}_2\text{N}$), 54.53 (s, CPh_2), 57.00 [t, $^1J_{\text{CH}} = 130$ Hz, CH_2CPh_2], 107.22 (d, $^1J_{\text{CH}} = 167$ Hz), 112.01 (d, $^1J_{\text{CH}} = 164$ Hz), 131.59 (d, $^1J_{\text{CH}} = 160$ Hz) [$\text{CH}(4, 5, 6)$], 121.44 [s, $\text{C}(3a)$], 125.90 (d, $^1J_{\text{CH}} = 160$ Hz, *p*-CH), 128.23, 128.28 (both d, $^1J_{\text{CH}} = 158$ Hz, *m*-, *o*-CH), 149.48 (s, *i*-C),

153.40, 157.14 [both s, C(3, 6a)]. Isomers **5a** and **5b** in a mixture with **4** (aliphatic part of the spectra; the low-field signals of **5a** and **5b** overlap with those of **4**). ^1H NMR (C_6D_6 , 27 °C): δ = 0.11 [broad, NH_2 (**5a**)]; 0.32 [broad, NH_2 (**5b**)]; 2.07 [broadened. quint, $^3J_{\text{HH}} = 6.0$ Hz, CH_2NH_2 (**5a**)]; 2.22 [c, NCH_3 (**5b**)]; 2.48 [broadened t, $^3J_{\text{HH}} = 6.0$ Hz, CH_2NCH_3 (**5a**)]; 2.54 [broad, CH_2NH_2 (**5b**)]; 2.65 [s, NCH_3 (**5a**)]; 3.05 [overlaps with $\text{CH}_2\text{NHC}(3)$ of **4**, CH_2NCH_3 (**5a**)]; 3.61 [s, CH_2CPh_2 (**5b**)]; 3.76 [s, CH_2CPh_2 (**5a**)].

3.7. Silylation of cyclopentadienide **3-Li** (1,2-dihydropentalene-type product **6**)

To a solution of Me_3SiCl (0.34 mL, 0.27 g, 2.69 mmol) in THF (20 mL) kept at -20 °C, the lithium salt **3-Li** (0.90 g, 2.69 mmol) was added. The resultant red slurry was allowed to warm up to room temperature, stirred for 2 h and left to stay overnight. The solvent was removed by trapping into a vessel cooled with liq. N_2 , the residual red foam was extracted with hexane (15 mL), the extract was concentrated and dried on the high-vacuum line that gave 0.88 g (82%) of **6** along with its minor isomers (^1H NMR estimated content of **6** is ca. 60%). The numbering of the atoms in the dihydropentalene moiety is given in Scheme 2. ^1H NMR (C_6D_6 , 27 °C): δ = 0.04 (s, 9H, SiMe_3), 2.17 (s, 3H, NCH_3), 2.61 (t, 2H, $^3J_{\text{HH}} = 6.0$ Hz, CH_2NCH_3), 3.18 (q, 2H, $^3J_{\text{HH}} = 6.0$ Hz, CH_2NH), 3.55 (s, 2H, CH_2CPh_2), 4.98 (broadened t, 1H, $^3J_{\text{HH}} = 5.0$ Hz, NH), 6.26 [broadened s, 1H, CH(6)], 6.48 [d, 1H, $^3J_{\text{HH}} = 4.3$ Hz, CH(4 or 5)], 7.08 [overlaps with the signals of Ph, 1H, CH(5 or 4)], 7.00–7.16 (a set of m, 6H, *m*-, *p*-CH), 7.47 (m, 4H, *o*-CH). ^{13}C NMR (C_6D_6 , 27 °C): δ = 0.88 (q, $^1J_{\text{CH}} = 118$ Hz, $^1J_{\text{CSi}} = 56.8$ Hz, SiMe_3), 33.83 (q, $^1J_{\text{CH}} = 134$ Hz, NCH_3), 43.25 (t, $^1J_{\text{CH}} = 138$ Hz, CH_2N), 48.27 (t, $^1J_{\text{CH}} = 134$ Hz, CH_2N), 54.51 (s, CPh_2), 57.48 (t, $^1J_{\text{CH}} = 130$ Hz, CH_2CPh_2), 107.17 (d, $^1J_{\text{CH}} = 167$ Hz), 111.94 (d, $^1J_{\text{CH}} = 164$ Hz), 131.85 (d, $^1J_{\text{CH}} = 160$ Hz) [CH(4, 5, 6)], 121.25 [s, C(3a)], 125.95 (d, $^1J_{\text{CH}} = 160$ Hz, *p*-CH), 128.22, 128.28 (both d, $^1J_{\text{CH}} = 159$ Hz, *m*-, *o*-CH), 149.39 (s, *i*-C), 153.63, 156.94 [both s, C(3, 6a)]. GC/MS (EI, 70 eV, 70–290 °C), *m/z* (%): 401 [M] $^+$ (0.1), 328 [M– SiMe_3] $^+$ (2.0), 303 [M– $\text{Me}_2\text{SiCH}_2\text{–C}_2\text{H}_2$] $^+$ (27.3), 302 [M– $\text{SiMe}_3\text{–C}_2\text{H}_2$] $^+$ (83.9), 288 [M– $\text{Me}_2\text{SiCH}_2\text{–C}_2\text{H}_2\text{–CH}_3$] $^+$ (19.4), 287 [M– $\text{SiMe}_3\text{–C}_2\text{H}_2\text{–CH}_3$] $^+$ (67.9), 231 [C $_5\text{H}_5\text{CPh}_2$] $^+$ (11.0), 230 [C $_5\text{H}_4\text{CPh}_2$] $^+$ (52.2), 147 [(SiMe $_3$) $_2\text{H}$] $^+$ (100), 91 [C $_7\text{H}_7$] $^+$ (62.9), 73 [Me $_3\text{Si}$] $^+$ (29.9), 59 [Me $_2\text{SiH}$] $^+$ (8.2).

3.8. Stannylation of cyclopentadienide **3-Li** (mono- and distannylated compounds **3-Sn** and **3-Sn₂**)

To a solution of the salt **3-Li** (0.25 g, 0.75 mmol) in diethyl ether (15 mL), Me_3SnCl (0.14 g, 0.70 mmol) was added and the reaction mixture was stirred at room temperature for 1 h. The brownish-red solution was decanted from the precipitated LiCl, ether was removed by trapping into a liq. N_2 cooled vessel and the residual oil was dried on the high-vacuum line that gave red solidified foam (0.21 g, 61%). The NMR spectroscopy data indicate the presence of mono- and distannylated derivatives **3-Sn** and **3-Sn₂** along with cyclopentadiene **3-H** in a ca. 2:1:1 ratio. The numbering is given in Scheme 5. Compounds **3-Sn** and **3-Sn₂**. ^1H NMR (C_6D_6 , 27 °C): δ = -0.13 [s, $^2J_{\text{HSn}} = 53.0$ Hz, SnMe_3 (**3-Sn**)], 0.04 [s, $^2J_{\text{HSn}} = 53.0$ Hz, SnMe_3 (**3-Sn**)], 1.77 [s, NCH_3 (**3-Sn**, **3-Sn₂**)], 2.55 [t, $^3J_{\text{HH}} = 9.6$ Hz, $\text{NCH}_2(5')$ (**3-Sn**, **3-Sn₂**)], 3.45 [m, $\text{NCH}_2(4')$, CH_2CPh_2 (**3-Sn**, **3-Sn₂**)], 5.12 [broadened s, $^2J_{\text{HSn}} = 45$ Hz, CH(4, 5) (**3-Sn**)], 6.41 [dd, $^3J_{\text{HH}} = 4.5$ Hz, $^4J_{\text{HH}} = 2.6$ Hz, CH(4) (**3-Sn**)], 6.58 [broadened s, CH(1, 3) (**3-Sn**)], CH(1) (**3-Sn₂**)], 6.84 [dd, $^3J_{\text{HH}} = 4.5$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, $^4J_{\text{HSn}} = 9.0$ Hz, CH(3) (**3-Sn₂**)], 7.04 [m, *p*-CH (**3-Sn**, **3-Sn₂**)], 7.15 [m, *m*-CH (**3-Sn**, **3-Sn₂**)], 7.61 [m, *o*-CH (**3-Sn**, **3-Sn₂**)]. ^{13}C – $\{^1\text{H}\}$ NMR (C_6D_6 , 27 °C): δ = -8.46 [$^1J_{\text{C–}^{119}\text{Sn}} = 339$ Hz, $^3J_{\text{CSn}} = 4.3$ Hz, SnMe_3 (**3-Sn₂**)], -8.30 [$^1J_{\text{C–}^{119}\text{Sn}} = 335$ Hz, SnMe_3 (**3-Sn**)], 33.01 [NCH $_3$ (**3-Sn**)], 33.10 [NCH $_3$ (**3-Sn₂**)], 36.91 [CH $_2\text{CPh}_2$ (**3-Sn**)], 37.31 [CH $_2\text{CPh}_2$ (**3-Sn₂**)], 51.37 [$^1J_{\text{C–}^{119}\text{Sn}} = 198$ Hz, C(5)

(**3-Sn₂**)], 52.75, 52.90 [NCH $_2\text{CH}_2\text{N}$ (**3-Sn**)], 52.93, 52.95 [NCH $_2\text{CH}_2\text{N}$ (**3-Sn₂**)], 54.57 [CPh $_2$ (**3-Sn**)], 54.63 [CPh $_2$ (**3-Sn₂**)], 90.91 [broadened s, $^1J_{\text{CSn}} = 55$ Hz, CH(4, 5) (**3-Sn**)], 125.96 [*p*-CH (**3-Sn₂**)], 126.03 [*p*-CH (**3-Sn**)], 127.44 [*m*-CH (**3-Sn**, **3-Sn₂**)], 127.91 [CH(1, 3) (**3-Sn**)], 129.44 [$^3J_{\text{CSn}} = 25$ Hz, CH(3) (**3-Sn₂**)], 130.24 [*o*-CH (**3-Sn₂**)], 130.36 [*o*-CH (**3-Sn**)], 132.80 ($^2J_{\text{CSn}} = 12$ Hz), 135.03 ($^2J_{\text{CSn}} = 11$ Hz) [CH(1, 4) (**3-Sn₂**)], 147.75 [*i*-C (**3-Sn**)], 148.25 [*i*-C (**3-Sn₂**)], 148.70 [$^3J_{\text{CSn}} = 24$ Hz, C(2) (**3-Sn**)], 149.00 [$^3J_{\text{CSn}} = 27$ Hz, C(2) (**3-Sn₂**)], 163.87 [=NCN (**3-Sn**)], 163.92 [=NCN (**3-Sn₂**)].

3.9. [η^5 : η^1 -C $_5\text{H}_4\text{CPh}_2\text{CH}_2(1\text{-MeC}_3\text{H}_4\text{N}_2)$] TiCl_3 (**7**)

To a solution of a mixture of **3-Sn**, **3-Sn₂** and **3-H** (molar ratio 2:1:1, total amount 0.21 g, 0.43 mmol of stannanes) in toluene (7 mL), a solution of TiCl_4 in toluene (0.7 mL containing 0.06 g, 0.32 mmol of TiCl_4) was added at room temperature. The color of the solution turned dark-green. In a day, the color of the reaction mixture changed to orange-red and orange precipitate formed. The reaction mixture was stirred at room temperature for 3 additional days, the mother liquor was decanted, the precipitate was washed with toluene (3×7 mL) and dried on the high-vacuum line that gave 0.1 g (65%) of a crude product. Double recrystallization from THF (ca. 5 mL) gave 0.06 g (39%) of pure **7**. Fine-crystalline powder. The numbering is given in Scheme 6. ^1H NMR (THF- d_8 , 27 °C): δ = 3.03 (s, 3H, NCH_3), 3.54 [t, 2H, $^3J_{\text{HH}} = 10.0$ Hz, $\text{CH}_2(5')$], 3.69 (s, 2H, CH_2CPh_2), 4.24 [t, 2H, $^3J_{\text{HH}} = 10.0$ Hz, $\text{CH}_2(4')$], 6.71 [virtual t, 2H, $^{3+4}J_{\text{HH}} = 5.5$ Hz, CH(3, 4)], 6.86 [virtual t, 2H, $^{3+4}J_{\text{HH}} = 5.5$ Hz, CH(2, 5)], 7.13 (m, 4H, *o*-CH), 7.23 (m, 6H, *m*-, *p*-CH). ^1H NMR (THF- d_8 , -70 °C): δ = 3.15 (s, 3H, NCH_3), 3.52, 3.66 [both broadened m, 1H, $\text{CH}_2(5')$], 3.76 (A-part of an AB-system, 1H, $^2J_{\text{HH}} = 15.0$ Hz, CHHCPh_2), 3.95 (B-part of an AB-system, 1H, $^2J_{\text{HH}} = 15.0$ Hz, CHHCPh_2), 4.00, 4.30 [both broadened m, 1H, $\text{CH}_2(4')$], 6.74 [broadened s, 1H, CH(4)], 6.79 [broadened s, 2H, CH(3), CH(5)], 7.07 [broadened d, 2H, $^3J_{\text{HH}} = 7.6$ Hz, *o*-CH], 7.14 [broadened m, 3H, *o*-CH, CH(2)], 7.23 (broadened m, 4H, *m*-CH), 7.30 (broadened m, 2H, *p*-CH). Calc. for C $_{23}\text{H}_{23}\text{Cl}_3\text{N}_2\text{Ti}$: C, 57.35; H, 4.81; N, 5.82. Found: C, 57.54; H, 4.71; N, 6.02%.

3.10. [η^5 : η^1 -C $_5\text{H}_4\text{CPh}_2\text{CH}_2(1\text{-MeC}_3\text{H}_4\text{N}_2)$] ZrCl_3 (**8**)

To a solution of $\text{ZrCl}_4 \cdot 2\text{THF}$ (0.50 g, 1.33 mmol) in THF (40 mL), a solution of the lithium salt **3-Li** (0.46 g, 1.38 mmol) in THF (30 mL) was added during 15 min under vigorous stirring and cooling (-10 °C). The reaction mixture was then kept in a refrigerator at -18 °C for 15 h. The solution was decanted from the white precipitate and concentrated that gave a yellow oil. On drying of the oil was on the high-vacuum line, toluene (0.5 mL) was added, the mixture was homogenized and the solvent was removed in high vacuum. The dry residue (a yellow powdered solid foam) was washed with toluene (4×15 mL) and dried on the high-vacuum line that gave 0.43 g of crude product. Recrystallization from dichloromethane (10 mL) gave 0.14 g (20%) of pure compound **8** as yellow crystals. The numbering is provided in Scheme 6. ^1H NMR (THF- d_8 , 55 °C): δ = 2.40 (s, 3H, NCH_3), 3.29 [t, 2H, $^3J_{\text{HH}} = 10.3$ Hz, $\text{CH}_2(5')$], 3.63 (s, 2H, CH_2CPh_2), 4.05 [t, 2H, $^3J_{\text{HH}} = 10.3$ Hz, $\text{CH}_2(4')$], 6.40 [virtual t, 2H, $^{3+4}J_{\text{HH}} = 5.7$ Hz, CH(3, 4)], 6.57 [virtual t, 2H, $^{3+4}J_{\text{HH}} = 5.7$ Hz, CH(2, 5)], 7.18–7.29 (a set of m, 10H, Ph). ^{13}C – $\{^1\text{H}\}$ NMR (THF- d_8 , 55 °C): δ = 32.85 (NCH $_3$), 39.02 (CH $_2\text{CPh}_2$), 52.20, 54.10 (NCH $_2\text{CH}_2\text{N}$), 52.28 (CPh $_2$), 116.92 [CH(3, 4)], 123.53 [CH(2, 5)], 127.55 (*p*-CH), 128.78 (*m*-CH), 129.45 (*o*-CH), 133.32 [C(1)], 147.07 (*i*-C), 170.44 (=NCN). ^1H NMR (THF- d_8 , -60 °C): δ = 2.16 (s, 3H, NCH_3), 3.07, 3.41 [both broadened m, 1H, $\text{CH}_2(5')$], 3.62 (AB-system, 2H, $^2J_{\text{HH}} = 13.0$ Hz, CH_2CPh_2), 3.76, 4.19 [both broadened m, 1H, $\text{CH}_2(4')$], 6.23 [broadened s, 2H, CH(4), CH(5)], 6.40 [broadened s, 1H, CH(3)], 6.89 [broadened s, 1H, CH(2)], 7.24–7.36 (a set of m,

10H, Ph). ^{13}C - $\{^1\text{H}\}$ NMR (THF- d_8 , -60°C): $\delta = 32.49$ (NCH₃), 38.77 (CH₂CPh₂), 51.99 (CPh₂), 52.03, 54.52 (NCH₂CH₂N), 114.19, 118.41 [CH(3, 4)], 122.21, 126.88 [CH(2, 5)], 127.41, 128.19 (*p*-CH), 128.77 (*m*-CH), 129.22, 130.33 (*o*-CH), 133.07 [C(1)], 144.43, 149.39 (*i*-C), 170.93 (=NCN). ^1H NMR (CD₂Cl₂, 27°C): $\delta = 2.86$ (s, 3H, NCH₃); 3.52 (s, 2H, CH₂CPh₂); 3.55 [t, 2H, $^3J_{\text{HH}} = 10.1$ Hz, CH₂(5')]; 4.13 [t, 2H, $^3J_{\text{HH}} = 10.1$ Hz, CH₂(4')]; 6.56, 6.72 [both virtual t, 2H, $^3+4J_{\text{HH}} = 5.6$ Hz, CH(2-5)]; 7.07 (m, 4H, *o*-CH); 7.29 (m, 6H, *m*-, *p*-CH). ^{13}C - $\{^1\text{H}\}$ NMR (CD₂Cl₂, 27°C): $\delta = 33.79$ (NCH₃); 38.80 (CH₂CPh₂); 51.29 (CPh₂); 52.34 (2C, NCH₂CH₂N); 118.26, 118.34 [CH(2-5)]; 127.65 (*p*-CH); 128.46, 128.78 (*o*-, *m*-CH); 136.25 [C(1)]; 145.86 (*i*-C); 168.60 (=NCN).

3.11. X-ray crystallographic study

The single crystal of compound **4** suitable for X-ray diffraction analysis was grown up from a hexane solution that contained a small amount of methanol. The single crystal of complex **8** was grown up from a dichloromethane solution. The single crystal of compound **2a** was grown up from THF- d_8 (within the course of its formation from **2**, inside an NMR sample tube). X-ray data for **4** and **8** were collected on a Bruker SMART 6K diffractometer (graphite-monochromatized Mo K α radiation, 0.71073 Å) using ω scan mode at 120 K. X-ray data for **2a** were collected on a Bruker SMART APEX diffractometer (graphite-monochromatized Mo K α radiation, 0.71073 Å) using ω scan mode at 293 K. The crystal of **8** exhibited twin behavior and the data for it was treated using GEMINI software [51]. In all cases, the absorption corrections were performed semi-

empirically from equivalents [52]. All structures were solved by direct methods [53] and refined by full matrix least-squares on F^2 [54]. In the structure of **4**, all non-hydrogen atoms (except disordered phenyl groups) were refined anisotropically. In **8**, only Zr and chlorine atoms were refined anisotropically due to the lack of data (HKL 5). In case of compound **4**, amine hydrogen atoms were found from difference Fourier synthesis and refined in an isotropic approximation; all others were refined using a riding model. In case of complex **8**, all hydrogen atoms were placed in calculated positions and refined using a riding model. In case of lithium salt **2a**, all hydrogen atoms except those of disordered THF were found from difference Fourier synthesis and refined in an isotropic approximation; hydrogen atoms of the disordered THF molecule were placed in calculated positions and refined using a riding model. The rest of the crystal and structure refinement data is listed in Table 4.

4. Supplementary material

CCDC 667529, 667530 and 668555 contain the supplementary crystallographic data for **4**, **8**, and **2a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 4

Crystal and structure refinement data for **4** · CH₃OH, **8** (dimer), and **2a** (dimer, 1:1 adduct with THF- d_8)

	4	8	2a
Empirical formula	C ₂₄ H ₂₈ N ₂ O	C ₄₆ H ₄₆ Cl ₆ N ₄ Zr ₂	C ₂₈ H ₅₂ Li ₄ N ₈ O ₂
Formula weight	360.48	1050.01	560.54
Color, habit	Yellow block	Colorless block	Colorless block
Crystal size (mm)	0.20 × 0.15 × 0.15	0.15 × 0.03 × 0.02	0.41 × 0.35 × 0.21
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
Cell dimensions			
<i>a</i> (Å)	16.8122(13)	9.972(3)	8.6775(10)
<i>b</i> (Å)	9.1808(7)	9.520(3)	9.8895(11)
<i>c</i> (Å)	12.9098(10)	23.344(8)	10.8199(13)
α (°)	90.00	90.00	97.506(2)
β (°)	94.489(2)	99.625(8)	90.229(2)
γ (°)	90.00	90.00	110.682(2)
Volume (Å ³)	1986.5(3)	2184.9(13)	859.98(17)
<i>Z</i>	4	2	1
<i>D</i> _{calc.} (g cm ⁻³)	1.205	1.596	1.082
Absorption coefficient μ (mm ⁻¹)	0.074	0.883	0.068
<i>F</i> (000)	776	1064	304
θ Range (°)	2.73 < θ < 26.00	1.77 < θ < 26.00	1.77 < θ < 26.00
Index ranges	-20 ≤ <i>h</i> ≤ 20, -10 ≤ <i>k</i> ≤ 11, -8 ≤ <i>l</i> ≤ 15	-10 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 11, -28 ≤ <i>l</i> ≤ 28	-8 ≤ <i>h</i> ≤ 10, -12 ≤ <i>k</i> ≤ 11, -12 ≤ <i>l</i> ≤ 13
Reflections collected	9406	3003	4726
Independent reflections (<i>R</i> _{int})	3897 (0.0489)	3050 (0.0000)	3307 (0.0453)
Reflections with <i>I</i> > 2 σ (<i>I</i>)	2250	2154	1773
Data/restraints/parameters	3897/0/256	3050/0/139	3307/0/271
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0932, <i>wR</i> ₂ = 0.2012	<i>R</i> ₁ = 0.0823, <i>wR</i> ₂ = 0.1778	<i>R</i> ₁ = 0.0574, <i>wR</i> ₂ = 0.1346
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1627, <i>wR</i> ₂ = 0.2233	<i>R</i> ₁ = 0.1185, <i>wR</i> ₂ = 0.1937	<i>R</i> ₁ = 0.1011, <i>wR</i> ₂ = 0.1525
Largest difference in hole/peak (e Å ⁻³)	-0.562/0.918	-0.528/0.538	-0.151/0.156

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