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Complexes of titanium and zirconium based on $[C_5Me_4CH_2\text{-}(2\text{-}C_5H_4N)]$ ligand

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Abstract

Half-sandwich $[\eta^5:\eta^1\text{-}\kappa N\text{-}C_5Me_4CH_2\text{-}(2\text{-}C_5H_4N)]MCl_3$ (M = Ti (**4**), Zr (**5**)) and sandwich $[\eta^5\text{-}C_5Me_4CH_2\text{-}(2\text{-}C_5H_4N)][\eta^5\text{-}C_5Me_5]ZrCl_2$ (**6**) ring-peralkylated complexes have been prepared and characterized. Evidence of the intramolecular coordination of the side-chain pyridyl group both in **4** and **5** in solutions is provided by NMR spectroscopy data. Crystal structure of an adduct **5-py** with one molecule of pyridine has been established by X-ray diffraction analysis.

Keywords: Zirconium; Titanium; Cyclopentadienyl ligands; Oxidative addition; Reduction; N Ligands

1. Introduction

In recent years the Group 4 metal complexes prepared from linked cyclopentadienyl–(*N*-aromatic heterocycle) bidentate ligands attract considerable attention [1–8]. However, only few complexes of the type containing ring-peralkylated Cp-moiety were reported [2,8]. This arises from the certain difficulties met in preparation of the Cp-ring peralkylated ligands in comparison with their ring non-peralkylated counterparts. Indeed, despite the synthetic approaches to the HC_5Me_4–(short hydrocarbyl link)–(*N*-aromatic heterocycle) type compounds were in general developed [2,8–13], most of them still remain not so readily available.

In course of our current research we were interested in synthesis of the Zr and Ti complexes based on HC_5Me_4–CH_2–(2-pyridyl) ligand [9], studies of their structure in crystalline state and in solutions, and the principal features of their chemical behavior, especially red–ox transformations of the Zr biscyclopentadienyl complexes. This paper reports recent results obtained in this area.

2. Results and discussion

2.1. Synthesis of the $HC_5Me_5CH_2(2\text{-}C_5H_4N)$ ligand (1)

Preparation of $HC_5Me_5CH_2(2\text{-}C_5H_4N)$ (**1**) starting from lithium tetramethylcyclopentadienide and (2-chloromethyl)pyridine was previously described in patent literature [9] (see Scheme 1). Unfortunately, the spectral data for compound **1** presented in [11] seem to be rather poor to judge upon its actual purity. However, previous data for similar alkylations of LiC_5HMe_4 and $LiC_5(SiMe_3)Me_4$ revealed that regioselectivity of these electrophilic attacks is rather ambiguous [14,15]. This forced us to perform more thorough investigation of this reaction.

The interaction between LiC_5HMe_4 and (2-chloromethyl)pyridine was carried out in THF at −20, 0 and 20 °C. The times required for reaction completeness

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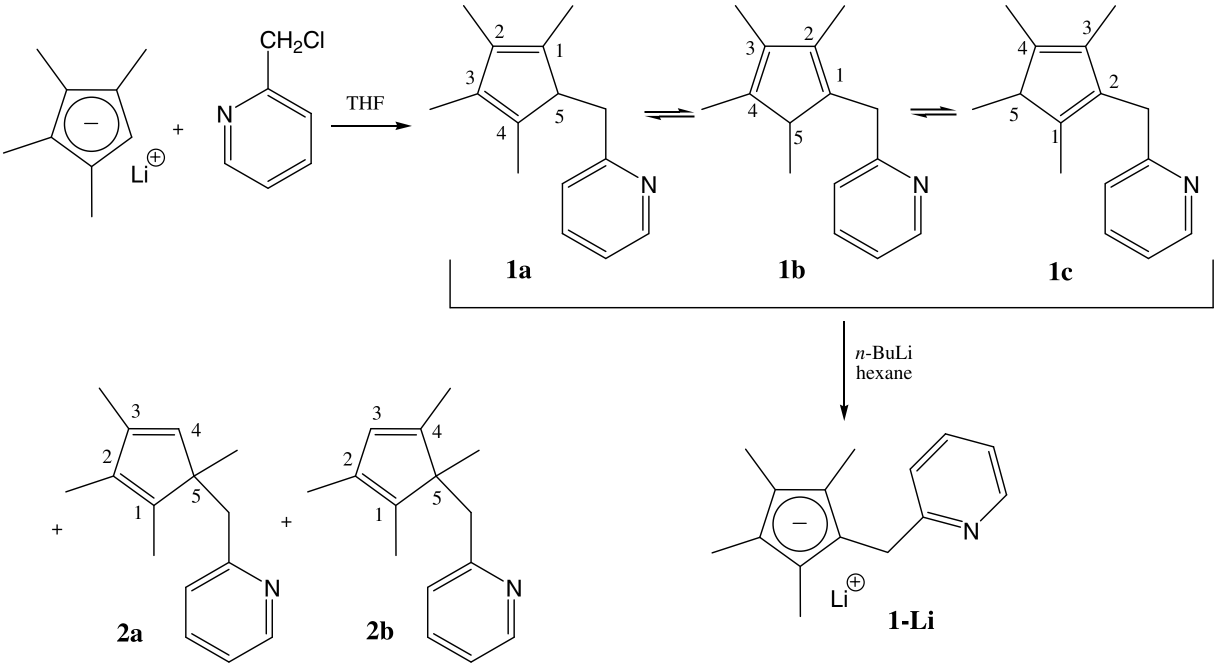


Scheme 1.

(dissolution of LiC_5HMe_4) were 7 days, 1 day, and 1 h, respectively. The NMR spectroscopy data revealed that the relative content of the target compound **1a**–**c** under the applied reaction temperatures was 51%, 52%, and 68%, respectively. NMR-monitoring of the reaction mixture (C_6D_6, room temperature) also indicated that the relative ratio of the isomers **1a**–**c** gradually changed, with the content of the initially dominant isomer **1a** decreased. In 5 months at ambient temperature the equilibrium is achieved and the estimated molar ratio of **1a**:**1b**:**1c** equals to 1.0:3.4:2.9. The chance to observe the product mixture at various relative ratios of the components **1a**–**c** along with a series of NOE measurements allowed us to perform almost complete assignment of the signals in both ^1H and ^{13}C NMR spectra even for this complicated mixture of five isomeric compounds.

The increase of the yield of compound **1** along with the growth of the temperature may be explained by the increase of the content of the contact ion pairs $\{Li^+ \cdots C_5HMe_4^-\}$ due to the destruction of rather unstable $\{Li^+ \cdots n\text{-THF}\}$ solvates. Analogous tendencies were observed earlier [15,16].

After addition of corresponding amount of *n*-BuLi compound **1** was separated from **2** as lithium salt **1-Li**. Pure compound **1a**–**c** free of *gem*-dialkyl substituted co-products **2a**,**b** was obtained by quenching salt **1-Li** with methanol.

An alternative approach to ligand **1a**–**c** starting from 1,2,3,4-tetramethylfulvene [17] and 2-pyridylmagnesium bromide failed, with no reaction observed after prolonged (15 h) heating in THF at 50 °C (80% of initial fulvene recovered). Reaction with 2-lithiopyridine was also unsuccessful what agrees with the literature data [10].

2.2. Synthesis of half-sandwich complexes of Ti(IV) (*4*) and Zr(IV) (*5*) and Metallocene Zr(IV) complex (*6*) derived from ligand *1*

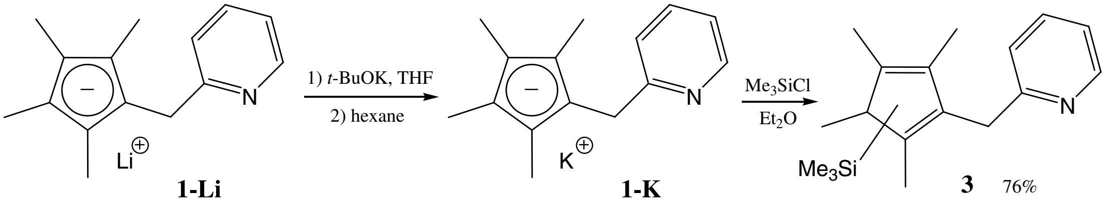
Half-sandwich complexes **4** and **5** were prepared according to Scheme 2. To increase the reactivity of cyclopentadienide, **1-Li** was converted into potassium salt **1-K**. Unlike lithium derivative, potassium salt reacts with Me_3SiCl in ether. This allows to avoid usage of THF at this step, excluding, this way, formation of the THF ring cleavage products [18], and to increase the yield and the purity grade of silane **3**.

Transformation of the silane **3** into half-sandwich complexes **4** and **5** is depicted in Scheme 3.

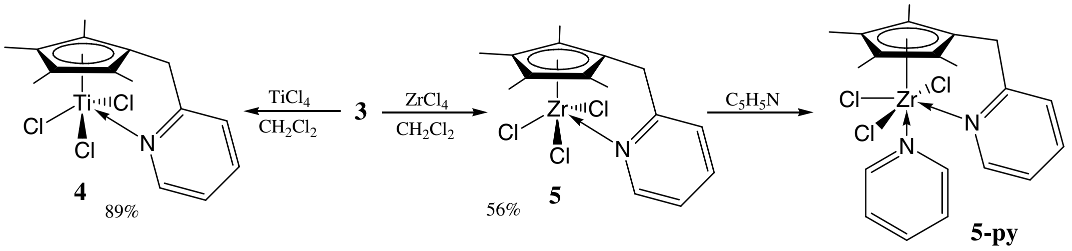
The work-up of complex **5** with THF does not afford formation of any stable adduct. However, recrystallization of **5** from pyridine gives adduct **5-py** as well-formed crystals suitable for X-ray analysis (vide infra).

Zirconocene dichloride **6** was prepared from salt **1-Li** and $C_5Me_5ZrCl_3$ in THF in good yield as depicted in Scheme 4. To complete this reaction, the mixture was heated at 100 °C for several days. Compound **6** was additionally purified by crystallization from diethyl ether.

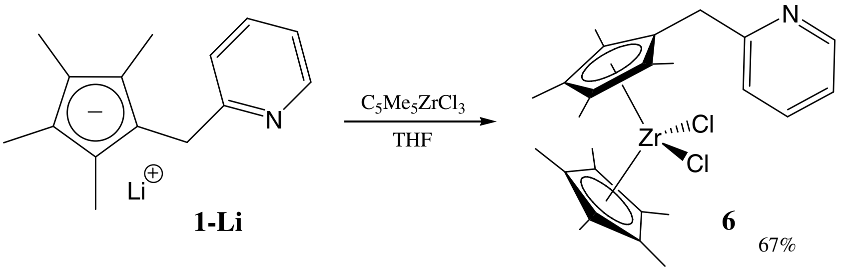
Reduction of the α-picolyl functionalized zirconocene dichloride **6** in THF with Mg/Hg either in presence of excess of PMe_3 or without any additive reactant lead to a non-identifiable mixture of products. This result of the reduction of **6** is unlike to what was observed formerly for $[\eta^5\text{-}C_5Me_4CH_2CH_2NMe_2][\eta^5\text{-}C_5Me_5]ZrCl_2$ [19] and recently for the reduction of decamethylzirconocene dichloride with Mg/Hg in pyridine [20]. In these cases, reduction of the metal center was followed by selective



Scheme 2.



Scheme 3.



Scheme 4.

oxidative addition of C–H bond to the Zr-atom (NCH_2–H and *ortho*-C–H bond in pyridine molecule, respectively).

2.3. X-ray structural investigation of half-sandwich complex **5-py**

The molecular structure of complex **5-py** along with the selected bond lengths and angles is presented in Fig. 1. The Zr-atom possesses a distorted octahedron coordination environment (C_5-ring centroid (Cp_{cent}) is assumed to occupy one coordination place) with three chlorine atoms and the nitrogen atom of the linked pyridyl group taking the pseudo-equatorial positions. This structural motif is very typical for Zr(IV) half-sandwich complexes bearing two n-donor ligands linked or non-linked to the cyclopentadienyl group (for the data on the closest analogues see [12,18,21–26]).

The C(1)–C(5) ring in **5-py** is planar within 0.016(1) Å. The methyl group carbon atoms C(9)–C(12) are declined 0.057(3)–0.206(3) Å from the Cp-ring mean plane outwards from the Zr-atom. At the same time the methylene group carbon atom C(6) is shifted 0.075(3) Å in the opposite direction. This may be due to the evident geometry constriction of the pseudo-five member metallacycle Zr(1)–C(1)–C(6)–C(7)–N(1)–[Zr(1)].

Analysis of the Cambridge Structural Database (release: January 2004) [27] reveals that the Zr–Cl bond lengths (2.4728(4)–2.5009(4) Å) are within the range typical for the terminal Zr–Cl bonds (2.357–2.542 Å).

Both of the pyridine moieties in **5-py** are planar within 0.010(1) Å, with the deviation of the Zr(1) atom out of the mean planes not exceeding 0.118(3) Å. The Zr–N–C angles are within 118.5(1)–124.8(1)° that is indicative of the true sp^2-hybridization of both nitrogen atoms. Noteworthy, the apical Zr(1)–N(2) bond is considerably longer than the equatorial Zr(1)–N(1) one (2.514(1) versus 2.431(1) Å, respectively). Similar tendency was observed for $[CpB(C_6F_5)_2Py]ZrCl_3(C_5H_5N)_2$ (2.492(2) and 2.494(2) versus 2.412(2) and 2.418(2) Å) [28] and for Zr–O(THF) distances in $(C_5H_4R)ZrCl_3 \cdot 2THF$ (R=H, Me, $-CH{=}CH_2$, $-CMe{=}CH_2$) [29,30].

3. Experimental

3.1. General remarks

All procedures were performed in sealed-off evacuated glass vessels. All solvents (and their perdeuterated analogs) were dried with and distilled from conventional agents (namely: diethyl ether and THF – with sodium benzophenone ketyl; hydrocarbons – with Na–K alloy; pyridine – 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

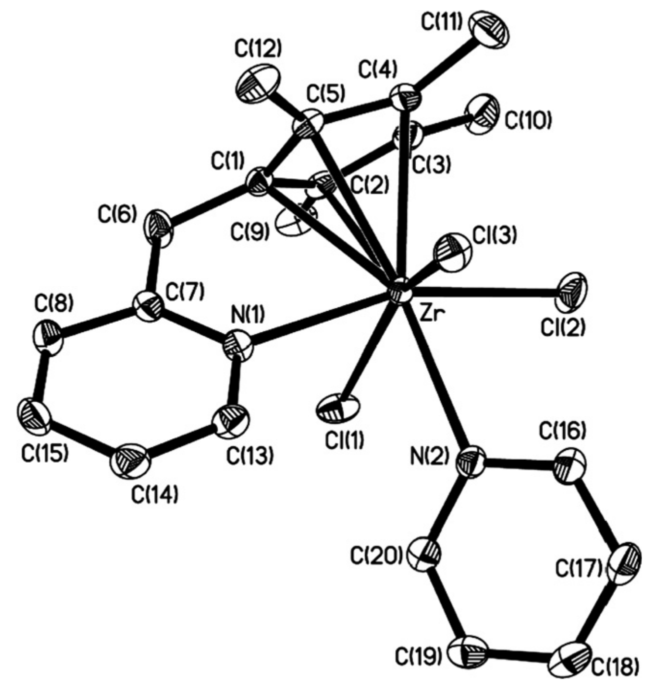


Fig. 1. Molecular structure of complex **5-py**; displacement ellipsoids are shown at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr–N(1) 2.4310(13), Zr–N(2) 2.5135(14), Zr–Cl(1) 2.4975(4), Zr–Cl(2) 2.4728(4), Zr–Cl(3) 2.5009(4), Zr–C(1) 2.4728(15), Zr–C(2) 2.5623(16), Zr–C(3) 2.5972(16), Zr–C(4) 2.5595(16), Zr–C(5) 2.5192(15), Zr–PL(1) 2.2341(7); N(1)–Zr–Cl(2) 161.74(3), N(1)–Zr–Cl(1) 79.62(3), Cl(2)–Zr–Cl(1) 94.433(18), N(1)–Zr–Cl(3) 80.63(3), Cl(2)–Zr–Cl(3) 96.384(17), Cl(1)–Zr–Cl(3) 147.633(15), N(1)–Zr–N(2) 84.50(4), Cl(2)–Zr–N(2) 77.34(3), Cl(1)–Zr–N(2) 77.62(3), Cl(3)–Zr–N(2) 75.18(3), C(7)–N(1)–C(13) 117.35(14), C(7)–N(1)–Zr 120.40(10), C(13)–N(1)–Zr 122.24(11), C(20)–N(2)–C(16) 116.63(14), C(20)–N(2)–Zr 124.84(11), C(16)–N(2)–Zr 118.47(11), C(1)–C(6)–C(7) 112.22(14), N(1)–C(7)–C(6) 117.79(14).

vacuum line directly into reaction vessels by re-condensations (trapping with liq. N_2). Amalgamated magnesium [31], 2-(chloromethyl)pyridine [32], and pyridylmagnesium bromide [33–35] were prepared accordingly to the reported procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400 and 100 MHz, respectively. For ^{1}H and ^{13}C spectra, the solvent resonances [$\delta_H = 7.15$ and $\delta_C = 128.0$ (C_6D_6), $\delta_H = 1.73$ and $\delta_C = 25.3$ (THF-d_8), $\delta_H = 5.32$ and $\delta_C = 53.8$ (CD_2Cl_2), $\delta_H = 7.19$ and $\delta_C = 123.5$ (C_5D_5N), $\delta_H = 7.24$ and $\delta_C = 77.0$ ($CDCl_3$)] were used as internal reference standards. Mass spectra were measured on Bruker Autoflex spectrometer (N_2 laser, 337 nm). Chromato-mass measurements were performed on Finningan MAT SSQ 7000 (EI 70 eV, 70–290 °C) instrument. The elemental analyses were performed on the Carlo-Erba automated analyser.

3.2. $HC_5Me_4CH_2(2\text{-}C_5H_4N)$ (*1*)

3.2.1. A mixture of ***1a–c***, ***2a***, and ***2b***

2-(Chloromethyl)pyridine (3.92 g, 30.7 mmol) and lithium tetramethylcyclopentadienide (3.94 g, 30.7 mmol) were mixed in THF (50 mL) and the slurry was stirred until the complete dissolution of the precipitate. The solvent was removed by trapping with liq. N_2, the residue taken into hexane (50 mL), the solution filtered off and used at the next step without further purification. Small portions of the solution were dried on the high-vacuum line (yellow oil), dissolved in C_6D_6 and the ratios of the isomeric **1a–c**, **2a** and **2b** were measured by integrating ^{1}H NMR spectra (see below). The reaction was run at −20, 0, and 20 °C. The relative content of the target **1a–c** was 51%, 52%, and 68%, respectively. ^{1}H NMR (30 °C, C_6D_6): $\delta = 0.98$ [d, $^3J_{HH} = 7.6$ Hz, $CHCH_3$ (**1c**)], 1.01 [s, $CH_3(5)$ (**2b**)], 1.05 [d, $^3J_{HH} = 7.6$ Hz, $CHCH_3$ (**1b**)], 1.12 [s, $CH_3(5)$ (**2a**)], 1.58–1.96 {=CCH_3; assigned from NOE experiments: 1.59 [s, $CH_3(2)$ (**2b**)], 1.70 [s, $CH_3(3)$ (**2a**)], 1.71 [s, $CH_3(4)$ (**1b**)], 1.73, 1.82, [each s, $CH_3(1, 4)$ (**1c**)], 1.81 [s, $CH_3(1)$ (**2a**)], 1.84 [s, $CH_3(1)$ (**2b**)], 1.96 [s, $CH_3(4)$ (**2b**)]}, 2.46 [q, $^3J_{HH} = 7.6$ Hz, CH (**1c**)], 2.63 [q, $^3J_{HH} = 7.6$ Hz, CH (**1b**)], 2.77 [A-part of AB-pattern, $^2J_{HH} = 12.5$ Hz, C*H*H (**2a**)], 2.96 [s, CH_2 (**2b**)], 3.01 [B-part of AB-pattern, $^2J_{HH} = 12.5$ Hz, CH*H* (**2a**)], 3.01 [d, $^3J_{HH} = 6.4$ Hz, CH_2 (**1a**)], 3.25 [t, $^3J_{HH} = 6.4$ Hz, CH (**1a**)], 3.79 [A-part of AB-pattern, $^2J_{HH} = 15.1$ Hz, C*H*H (**1b**)], 3.90 [s, CH_2 (**1c**)], 3.95 [B-part of AB-pattern, $^2J_{HH} = 15.1$ Hz, CH*H* (**1b**)], 5.61 [q, $^4J_{HH} = 1.6$ Hz, =CH (**2b**)], 5.97 [q, $^4J_{HH} = 1.4$ Hz, =CH (**2a**)], 6.54–6.64 (set of m, H^5 in py), 6.70–6.90 {set of d, H^3 in py; assigned from NOE experiments: 6.79 [d, $^3J_{HH} = 7.8$ Hz, H^3 (**2a**)], 6.83 [d, $^3J_{HH} = 7.8$ Hz, H^3 (**1b**)]}, 6.96–7.09 (set of m, H^4 in py), 8.30–8.49 (set of m, H^6 in py). $^{13}C\{^1H\}$ NMR (30 °C, C_6D_6): $\delta = 10.22$, 10.77, 13.97, [=CCH_3 (**2a**)], 10.43, 12.47, 13.13 [=CCH_3 (**2b**)], 11.16 (2C), 11.46, 11.52, 11.72 (2C), 11.95, 12.49 [=CCH_3, (**1a–c**)], 14.30 [$CHCH_3$ (**1b**)], 14.35 [$CHCH_3$ (**1c**)], 20.89 [$CH_3(5)$ (**2a**)], 22.37 [$CH_3(5)$ (**2b**)], 35.41 [CH_2 (**1c**)], 36.06 [CH_2 (**1b**)], 37.98 [CH_2 (**1a**)], 44.02 [CH_2 (**2b**)], 45.28 [CH_2 (**2a**)], 50.24 [CH (**1b**)], 52.00 [CH (**1c**)], 55.22 [C(5) (**2a**)], 56.54 [CH (**1a**)], 57.75 [C(5) (**2b**)], 120.70 [CH^5 (**2b**) in py], 120.77 [CH^5 (**1c**) in py], 120.79 [CH^5 (**2a**) in py], 120.88 [CH^5 (**1a**) in py], 120.94 [CH^5 (**1b**) in py], 121.95 [CH^3 (**1c**) in py], 122.29 [CH^3 (**2b**) in py], 122.46 [CH^3 (**1b**) in py], 122.95 [CH^3 (**1a**) in py], 123.61 [CH^3 (**2a**) in py], 129.95 [=CH (**2a** or **2b**), second =CH is obscured by C_6D_6], 132.68, 133.41, 134.15, 134.24, 135.63, 135.83, 136.06, 136.51, 136.76, 138.27, 139.21, 139.92, 139.99, 140.36, 140.40, 144.31 [=CCH_3, =CCH_2 (**2a**, **2b**, **1a–c**)], 134.70 [CH^4 (**2a**, **2b**) in py], 135.24 [CH^4 (**1a**) in py], 135.78 [CH^4 (**1b**) in py], 136.10 [CH^4 (**1c**) in py], 148.67 [CH^6 (**2b**) in py], 148.89 [CH^6 (**2a**) in py], 149.26 [CH^6 (**1a**) in py], 149.56 [CH^6 (**1b**) in py], 149.59 [CH^6 (**1c**) in py], 158.99 [C^2 (**2b**) in py], 160.23 [C^2 (**2a**) in py], 160.95 [C^2 (**1a**) in py], 161.72 [C^2 (**1c**) in py], 162.26 [C^2 (**1b**) in py]. NOE data: $\eta_{Me(5)(\mathbf{2a})}$(=CH (**2a**)) = 0.6%, $\eta_{Me(3)(\mathbf{2a})}$(=CH (**2a**)) = 0.9%, $\eta_{CH2(\mathbf{2a})}$(=CH (**2a**)) = 1.1%, $\eta_{H(3)(\mathbf{2a})}$(=CH (**2a**)) = 2.1%, $\eta_{Me(2)(\mathbf{2b})}$(=CH (**2b**)) = 0.6%, $\eta_{Me(4)(\mathbf{2b})}$(=CH (**2b**)) = 0.7% $\eta_{Me(5)(\mathbf{1}b)}$(CH (**1b**)) = 1.5%, $\eta_{Me(4)(\mathbf{1}b)}$(CH (**1b**)) = 1.0%, $\eta_{CH2(\mathbf{1}b)}$(CH (**1b**)) = 0.6%, $\eta_{H(3)(\mathbf{1}b)}$(CH (**1b**)) = 0.8% $\eta_{Me(5)(\mathbf{1}c)}$(CH (**1c**)) = 1.3%, $\eta_{Me(1,4)(\mathbf{1}c)}$(CH (**1c**))

$= 0.7\%$, $\eta_{\mathrm{Me(1)(\mathbf{2a})}}((5)\ (\mathbf{2a})) = 1.3\%$, $\eta_{\mathrm{CH2(\mathbf{2a})}}(\mathrm{Me}(5)\ (\mathbf{2a})) = 3.6\%$, $\eta_{\mathrm{=CH(\mathbf{2a})}}(\mathrm{Me}(5)\ (\mathbf{2a})) = 4.0\%$. $\eta_{\mathrm{Me(1)(\mathbf{2b})}}(\mathrm{Me}(5)\ (\mathbf{2b})) = 0.8\%$, $\eta_{\mathrm{Me(4)(\mathbf{2b})}}(\mathrm{Me}(5)\ (\mathbf{2b})) = 0.7\%$, $\eta_{\mathrm{CH2(\mathbf{2b})}}$-$(\mathrm{Me}(5)\ (\mathbf{2b})) = 4.8\%$. Molar ratios of isomers **2a**:**2b** = 1.0:0.6; **1a**:**1b**:**1c** = 1.0:3.4:2.9. Here and below the numbering of groups and atoms corresponds to that given in Scheme 1.

3.2.2. *Lithium salt (**1-Li**)*

To a solution of **1a**–**c**, **2a**, and **2b** in hexane (50 mL, ^{1}H NMR estimated content of **1a**–**c** 16.1 mmol), a solution of *n*-BuLi in hexane (2.45 m, 6.3 mL, 16.2 mmol) was added. The red precipitate was washed on a glass frit with hexane (10 mL), recrystallized from ether (10 mL), and dried on the high-vacuum line. Brownish-red powder. Yield 1.9 g (28% in respect to lithium tetramethylcyclopentadienide). ^{1}H NMR (30 °C, THF-d_8): $\delta = 1.80$, 1.97 [each s, 6H, $C_5(CH_3)_4$], 3.97 (s, 2H, CH_2), 6.98 (dd, 1H, $^3J_{HH} = 7.7$ Hz, $^3J_{HH} = 4.9$ Hz, H^5), 7.21 (d, 1H, $^3J_{HH} = 7.7$ Hz, H^3), 7.55 (td, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.8$ Hz, H^4), 8.12 (d, 1H, $^3J_{HH} = 4.9$ Hz, H^6). ^{13}C NMR (30 °C, THF-d_8): $\delta = 10.91$, 11.36 [each q, $^1J_{CH} = 123$ Hz, $C_5(\mathit{C}H_3)_4$], 34.52 (t, $^1J_{CH} = 124$ Hz, CH_2), 106.19, 108.06 (each s, *C*CH$_3$), 106.32 [s, *C*CH$_2$ in $C_5(CH_3)_4$], 121.07 (d, $^1J_{CH} = 164$ Hz, CH^5), 123.95 (d, $^1J_{CH} = 161$ Hz, CH^3), 137.05 (d, $^1J_{CH} = 161$ Hz, CH^4), 148.78 (d, $^1J_{CH} = 176$ Hz, CH^6), 166.89 (s, C^2).

3.2.3. *Pure ligand **1a**–**c***

A small amount of the lithium salt **1-Li** (100 mg) was quenched with excess of methanol (1 mL). Methanol was removed on a high-vacuum line, the residue was taken into hexane (2 mL), the solution filtered off and dried under high vacuum. The yield is nearly quantitative. Yellow oil. ^{1}H NMR (30 °C, CDCl$_3$): $\delta = 1.01$ [d, $^3J_{HH} = 7.7$ Hz, CHC*H*$_3$ (**1b**)], 1.08 [d, $^3J_{HH} = 7.7$ Hz, CHC*H*$_3$ (**1c**)], 1.64, 1.71, 1.72, 1.80, 1.82, 1.88, 1.89 [each s, =CCH$_3$ (**1a**–**c**)], 2.60 [m, CH (**1b**,**c**)], 2.98 [d, $^3J_{HH} = 6.6$ Hz, CH$_2$ (**1a**)], 3.14 [t, $^3J_{HH} = 6.6$ Hz, CH (**1a**)], 3.69 [A-part of AB-pattern, $^2J_{HH} = 15.5$ Hz, C*H*H (**1b**)], 3.81 [s, CH$_2$ (**1c**)], 3.92 [B-part of AB-pattern, $^2J_{HH} = 15.5$ Hz, CH*H* (**1b**)], 6.94–7.07 (m, H^3, H^5 in py), 7.45–7.54 (m, H^4 in py), 8.51 (m, H^6 in py). ^{13}C{^{1}H} NMR (30 °C, CDCl$_3$): $\delta = 10.93$, 10.98, 11.09, 11.36, 11.54 (2C), 11.77, 12.16 (=C*C*H$_3$),14.04 [CHC*H*$_3$ (**1b**)], 14.35 [CH*C*H$_3$ (**1c**)], 34.78 [CH$_2$ (**1c**)], 35.51 [CH$_2$ (**1b**)], 37.77 [CH$_2$ (**1a**)], 49.81 [CH (**1b**)], 51.70 [CH (**1c**)], 56.07 [CH (**1a**)], 120.65 [CH^5 (**1b**) in py], 120.71 [CH^5 (**1c**) in py], 120.86 [CH^5 (**1a**) in py], 121.84 [CH^3 (**1c**) in py], 122.48 [CH^3 (**1b**) in py], 123.01 [CH^3 (**1a**) in py], 133.57, 133.88, 135.52, 135.66, 135.89, 136.69, 138.53, 139.08, 139.38, 140.77 (=*C*CH$_3$, =*C*CH$_2$), 135.62 [CH^4 (**1a**) in py], 136.10 [CH^4 (**1b**) in py], 136.22 [CH^4 (**1c**) in py], 148.80 [CH^6 (**1a**) in py], 148.99 [CH^6 (**1c**) in py], 149.04 [CH^6 (**1b**) in py], 160.57 [C^2 (**1a**) in py], 161.07 [C^2 (**1c**) in py], 161.67 [C^2 (**1b**) in py]. Molar ratios of isomers **1a**:**1b**:**1c** = 1.0:2.9:2.1. Calc. for $C_{15}H_{19}N$: C, 84.46; H, 8.98, N, 6.57. Found: C, 84.34, H, 8.89, N, 6.69%.

3.3. *(Me_3Si)$C_5Me_4CH_2$(2-C_5H_4N) (**3**)*

3.3.1. *Potassium salt **1-K***

Lithium derivative **1-Li** (450 mg, 2.1 mmol) was dissolved in THF (20 mL) and *t*-BuOK (400 mg, 3.6 mmol, sublimed under high vacuum prior to use) was entered. The formed solution was concentrated up to dryness and hexane (20 mL) was added. The dark-red precipitate was filtered off, washed on a glass filter with hexane (3 × 5 mL), dried and used at the next step without further purification.

3.3.2. *(Me_3Si)$C_5Me_4CH_2$(2-;C_5H_4N)(**3**)*

To a suspension of **1-K** in diethyl ether (40 mL), trimethylchlorosilane (0.3 mL, 260 mg, 2.4 mmol) was added and the mixture was heated under stirring at 65 °C for 5 h. Ether was removed under high vacuum and hexane (40 ml) entered. The solution was filtered, concentrated and the residual pale-yellow oil was distilled under high vacuum (pressure $< 10^{-2}$ Torr). Yield 450 mg (76% in respect to **1-Li**). ^{1}H NMR (30 °C, C$_6$D$_6$): $\delta = -0.10$ (s, SiMe$_3$), 1.20 (br, C*H*$_3$CSiMe$_3$), 1.76, 1.85 (each br s, =CCH$_3$), 3.60 (br, C*H*$_2$CSiMe$_3$), 3.96 (br s, =CCH$_2$), 6.59 (br m, H^5 in py), 6.92 (br m, H^3 in py), 7.04 (br m, H^4 in py), 8.47 (br m, H^6 in py). ^{13}C{^{1}H} NMR (30 °C, C$_6$D$_6$): $\delta = -2.58$ (s, SiMe$_3$), 11.71, 12.86, 13.95 (each br s, C*C*H$_3$), 35.72, 36.26 (each br s, CH$_2$), 54.0 (br, *C*SiMe$_3$), 120.69 (s, CH^5 in py), 122.15 (s, CH^3 in py), 135.59 (s, CH^4 in py), 149.51 (s, CH^6 in py), 161.97 (s, C^2 in py). GC/MS EI (70 eV) *m*/*z*(%): 285 (75.7) [M]$^+$, 270 (45.7) [M − CH$_3$]$^+$, 212 (24.7) [M − SiMe$_3$]$^+$, 196 (38.3) [M − SiMe$_3$− CH$_4$]$^+$, 119 (33.8) [$C_7H_5(CH_3)_2$]$^+$, 105 (7.3) [$C_7H_6(CH_3)$]$^+$, 93 (100) [C_5H_4(2-CH_3)N]$^+$, 91 (8.6) [C_7H_7]$^+$, 73 (68.8) [SiMe$_3$]$^+$. Calc. for $C_{18}H_{27}NSi$: C, 75.72; H, 9.53; N, 4.91; Si, 9.84. Found: C, 75.53; H, 9.48; N, 5.02; Si, 10.04%.

3.4. *[η^5:η^1-κN- $C_5Me_4CH_2$-(2-C_5H_4N)]$TiCl_3$ (**4**)*

Solutions of silylated cyclopentadiene **3** (350 mg, 1.23 mmol) and TiCl$_4$ (230 mg, 1.22 mmol) in CH$_2$Cl$_2$ (total amount 20 mL) were mixed at room temperature that resulted in a nearly immediate formation of red precipitate. The precipitate was filtered off, washed on a filter with cold dichloromethane (3 × 3 mL) and dried on a high-vacuum line. Yield 402 mg (89%). ^{1}H NMR (30 °C, THF-d_8): $\delta = 2.29$, 2.39 [each s, 6H, $C_5(CH_3)_4$], 4.35 (s, 2H, CH$_2$), 7.31 (t, 1H, $^3J_{HH} = 6.7$ Hz, H^5), 7.51 (d, 1H, $^3J_{HH} = 7.8$ Hz, H^3), 7.85 (t, 1H, $^3J_{HH} = 7.8$ Hz, H^4), 8.65 (d, 1H, $^3J_{HH} = 5.6$ Hz, H^6). ^{1}H NMR (30 °C, CDCl$_3$): $\delta = 2.36$, 2.47 [each s, 6H, $C_5(CH_3)_4$], 4.30 (s, 2H, CH$_2$), 7.29 (t, 1H, $^3J_{HH} = 6.7$ Hz, H^5), 7.43 (d, 1H, $^3J_{HH} = 7.8$ Hz, H^3), 7.80 (t, 1H, $^3J_{HH} = 7.8$ Hz, H^4), 8.71 (d, 1H, $^3J_{HH} = 5.6$ Hz, H^6). ^{13}C{^{1}H} NMR (30 °C, CDCl$_3$): $\delta = 14.89$, 15.06 [$C_5(\mathit{C}H_3)_4$], 33.61 (CH$_2$), 122.15 (CH^5), 123.32 (CH^3), 138.77 (CH^4), 150.46 (CH^6). Calc. for $C_{15}H_{18}Cl_3NTi$: C, 49.15; H, 4.75; N, 3.82. Found: C, 48.88; H, 4.77; N, 3.95%. The signals of quaternary carbons were not observed because of low solubility.

3.5. *[η^5:η^1-κN-$C_5Me_4CH_2$-(2-C_5H_4N)]$ZrCl_3$ (**5**) and its adduct with pyridine (**5-py**)*

To a suspension of $ZrCl_4$ (0.816 g, 3.5 mmol) in CH_2Cl_2 a solution of silane **3** in the same solvent was added (totally 50 mL CH_2Cl_2). The mixture was heated under stirring at 60 °C for 12 h. The slurry was concentrated down to one third of the initial volume, the precipitate was filtered off and washed on a filter with cold dichloromethane (3 × 3 mL). White crystalline powder (0.71 g). The mother liquor was concentrated till nearly dryness and recrystallized from a THF–hexane mixture (1:1) that gave additionally 100 mg of the product **5**. Total yield 810 mg (56%). ^{1}H NMR (30 °C, THF-d_8): $\delta = 2.00$, 2.12 [each s, 6H, $C_5(CH_3)_4$], 4.17 (s, 2H, CH_2), 7.34 (t, 1H, $^3J_{HH} = 6.7$ Hz, H^5), 7.52 (d, 1H, $^3J_{HH} = 7.8$ Hz, H^3), 7.88 (td, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.8$ Hz, H^4), 8.67 (d, 1H, $^3J_{HH} = 5.6$ Hz, H^6). ^{13}C{^{1}H} NMR (30 °C, THF-d_8): $\delta = 12.78$, 14.30 [$C_5(CH_3)_4$], 33.92 (CH_2), 122.69 (CH^5), 123.82 [CCH_2 in $C_5(CH_3)_4$], 124.67 (CH^3), 127.78, 129.15 (CCH_3), 140.15 (CH^4), 150.18 (CH^6), 168.19 (C^2). EI MS (70 eV) *m/z* (%): 374 (58.4) $[M - Cl]^+$, 287 (42.1) $[M - 3Cl - CH_3]^+$, 286 (86.2) $[M - 2Cl - HCl - CH_3]$, 212 (100) $[C_5(CH_3)_4CH_2C_5H_4N]^+$. Calc. for $C_{15}H_{18}Cl_3NZr$: C, 43.95; H, 4.43; N, 3.42. Found: C, 43.56; H, 4.28; N, 3.26%.

Recrystallization of **5** (0.71 g) from pyridine afforded 0.77 g of its 1:1 adduct with pyridine **5-py** (yield 91%). ^{1}H NMR (30 °C, py-d_5): $\delta = 2.15$, 2.31 [each s, 6H, $C_5(CH_3)_4$], 4.21 (s, 2H, CH_2), 7.01 (t, 1H, $^3J_{HH} = 6.5$ Hz, H^5), 7.39 (d, 1H, $^3J_{HH} = 7.8$ Hz, H^3), 7.66 (td, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.7$ Hz, H^4), 8.93 (d, 1H, $^3J_{HH} = 5.2$ Hz, H^6). ^{13}C{^{1}H} NMR (30 °C, py-d_5): $\delta = 12.65$, 14.02 [$C_5(CH_3)_4$], 33.70 (CH_2), 122.41 (CH^5), 123.34 [CCH_2 in $C_5(CH_3)_4$], 124.35 (CH^3), 128.00, 128.30 (CCH_3), 139.59 (CH^4), 150.25 (CH^6), 167.45 (C^2).

3.6. *[η^5-$C_5Me_4CH_2$-(2-C_5H_4N)][η^5-C_5Me_5]$ZrCl_2$ (**6**)*

Solutions of [η^5-C_5Me_5]$ZrCl_3$ (1.27 g, 3.8 mmol) and lithium salt **1-Li** (0.86 g, 3.9 mmol) in THF (total amount 70 mL) were mixed at room temperature and the mixture was heated at 100 °C for 38 h. The solvent was removed, toluene (30 mL) was added, the precipitated LiCl was filtered off, washed with toluene (2 × 5 mL) and the combined toluene extracts were concentrated under high vacuum. The residue was recrystallized from ether–hexane mixture (1:4) that gave the **6** as pale yellow solid. Yield 67%. ^{1}H NMR (30 °C, THF-d_8): $\delta = 1.99$ [s, 6H, $C_5(CH_3)_4$], 2.01 [s, 21H, $C_5(CH_3)_5$, $C_5(CH_3)_4$], 3.95 (s, 2H, CH_2), 6.90 (d, 1H, $^3J_{HH} = 7.7$ Hz, H^3), 7.03 (dd, 1H, $^3J_{HH} = 7.7$ Hz, $^3J_{HH} = 5.0$ Hz, H^5), 7.52 (td, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.8$ Hz, H^4), 8.40 (d, 1H, $^3J_{HH} = 5.0$ Hz, H^6). ^{13}C{^{1}H} NMR (30 °C, THF-d_8): $\delta = 12.13$, 12.69 [$C_5(CH_3)_4$], 12.24 [$C_5(CH_3)_5$], 36.55 (CH_2), 121.70 (CH^5), 122.80 (CH^3), 124.28, 124.83 [CCH_3 in $C_5(CH_3)_4$], 124.30 [$C_5(CH_3)_5$], 125.51 [CCH_2 in $C_5(CH_3)_4$], 136.79 (CH^4), 150.05 (CH^6), 161.62 (C^2). ^{1}H NMR (30 °C, C_6D_6): $\delta = 1.81$, 2.04 [each s, 6H, $C_5(CH_3)_4$], 1.88 [s, 15H, $C_5(CH_3)_5$], 4.14 (s, 2H, CH_2), 6.52 (dd, 1H, $^3J_{HH} = 7.7$ Hz, $^3J_{HH} = 4.9$ Hz, H^5), 6.61 (d, 1H, $^3J_{HH} = 7.7$ Hz, H^3), 6.94 (td, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.9$ Hz, H^4), 8.37 (d, 1H, $^3J_{HH} = 4.9$ Hz, H^6). ^{13}C NMR (30 °C, C_6D_6): $\delta = 11.98$, 12.65 [each q, $^1J_{CH} = 127$ Hz, $C_5(CH_3)_4$], 12.12 [q, $^1J_{CH} = 127$ Hz, $C_5(CH_3)_5$], 36.15 (t, $^1J_{CH} = 128$ Hz, CH_2), 121.02 (d, $^1J_{CH} = 163$ Hz, CH^5), 122.34 (d, $^1J_{CH} = 166$ Hz, CH^3), 123.67, 124.33 [each s, CCH_3 in $C_5(CH_3)_4$], 123.74 [s, $C_5(CH_3)_5$] 124.84 [s, CCH_2 in $C_5(CH_3)_4$], 136.07 (d, $^1J_{CH} = 161$ Hz, CH^4), 149.56 (d, $^1J_{CH} = 178$ Hz, CH^6), 161.01 (s, C^2). EI MS (70 eV) *m/z* (%): 472 (100) $[M - Cl]^+$, 437 (7.0) $[M - 2Cl]^+$, 374 (5.5) $[M - C_5(CH_3)_5]$, 212 (15.2) $[C_5(CH_3)_4CH_2C_5H_4N]^+$. Calculated for $C_{25}H_{33}NCl_2Zr$: C, 59.92; H, 6.53; N, 2.75. Found: C, 59.79; H, 6.62; N, 2.49%.

4. X-ray crystallographic study of 5-py

Crystal data: $C_{20}H_{23}Cl_3N_2Zr$, M = 488.97, monoclinic, $a = 8.2453(4)$, $b = 15.0415(7)$, $c = 16.2732(8)$ Å, $\beta = 91.632(1)°$, $V = 2017.4(2)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.610$ g/cm^3, $F(000) = 992$, μ(Mo-Kα) = 0.949 mm^{-1}. Total of 14,297 reflections (5290 unique, $R_{int} = 0.0244$) were measured on a Bruker SMART CCD diffractometer (graphite monochromatized Mo-Kα radiation, $\lambda = 0.71073$ Å) at 120 K. Data were collected in the range $1.84 < \theta < 29.00$ ($-11 \leqslant h \leqslant 10$, $-20 \leqslant k \leqslant 14$, $-22 \leqslant 1 \leqslant 19$) using ω scan mode. Semi-empirical absorption correction based on measurements of equivalent reflections was applied. The structure was solved by direct methods [36] and refined by full matrix least-squares on F^2 [37] with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were found from diff. Fourier synthesis and refined isotropically. The final residuals were: $R_1 = 0.0249$, $wR_2 = 0.0592$ for 4673 reflections with $I > 2\sigma(I)$ and 0.0306, 0.0610 for all data and 328 parameters. Gof = 1.052, maximum $\Delta\rho = 0.424$ e × Å^{-3}.

5. Supplementary material

CCDC 614186 contains the supplementary crystallographic data for the compound reported in this paper. These data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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