1-Methylimidazol-2-yl-functionalized cyclopentadienyl titanium and zirconium complexes. Crystal structure of [η^5:η^1-$C_5H_4CPh_2CH_2$-(1-$MeC_3H_2N_2$)]$TiCl_3$

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The new side-chain functionalized cyclopentadienyl ligand $LiC_5H_4CPh_2CH_2R$ (R is 1-methylimidazol-2-yl) as lithium salt **2**, the trimethylsilyl derivative $Me_3SiC_5H_4CPh_2CH_2R$ (**3**), and the ligand in the CH form (**4**) were prepared starting from 6,6-diphenylfulvene and 1,2-dimethylimidazole lithiated at the 2-Me group (**1**) and then characterized. The half-sandwich complexes (η^5:η^1-$C_5H_4CPh_2CH_2R$)$TiCl_3$ (**5**) and (η^5:η^1-$C_5H_4CPh_2CH_2R$)$ZrCl_3$ (**6**) were synthesized. The molecular structure of complex **5** was established by X-ray diffraction. Complexes **5** and **6** exhibit dynamic behavior in solution associated with degenerate interconversion of the pseudo-six-membered metallacycle. For titanium complex **5** in a solvating solvent, a dynamic process due to intramolecular dissociation—coordination of the imidazole fragment was observed.

Key words: zirconium, titanium, cyclopentadienyl ligands, imidazole, intramolecular coordination, NMR spectroscopy, X-ray diffraction analysis.

Group IV transition metal complexes with cyclopentadienyl ligands bearing a nitrogen-containing *n*-donor moiety in the side chain have been extensively studied (see the reviews[1—4]) and still attract considerable attention.[5—14] In most known complexes of this type, the nitrogen atom is bound to aliphatic substituents and is either in the sp^3-hybridized state (N→M coordination bond, type **I**, Scheme 1) or is transformed into the sp^2-hybridized state through additional donation of the lone electron pair to the metal atom (so-called geometry constrained complexes, type **II**, see Scheme 1). Complexes in which the coordination interaction with the metal atom occurs through the sp^2-hybridized nitrogen atom (type **III**, see Scheme 1) are few in number and these are primarily pyridine or quinoline systems.[9,15—24]

Taking into account all mentioned above, it was of interest to synthesize and study half-sandwich Ti^{IV} and Zr^{IV} complexes in which the imidazole fragment serves as a side nitrogen-containing group (type **IV**, see Scheme 1). As opposed to related compounds of type **III**, the presence of the second, "external," nitrogen atom, which is involved in the conjugation system with the first nitrogen atom, provides additional possibilities for control of the nitrogen—metal coordination (for example, interconversions of complexes **IV** and **V**) and "fine tuning" of the π-donor-acceptor and σ-donor properties of the coordinating nitrogen atom.

The imidazole ligands seldom occur in organometallic chemistry of Group IV metals, and publications on such complexes are few.[25—28] The aim of the present study was to synthesize new half-sandwich titanium(IV) and zirconium(IV) complexes with the 2-(1-methylimidazol-2-yl)-1,1-diphenylethylcyclopentadienyl ligand and investigate their structures in the crystalline state and in solution.

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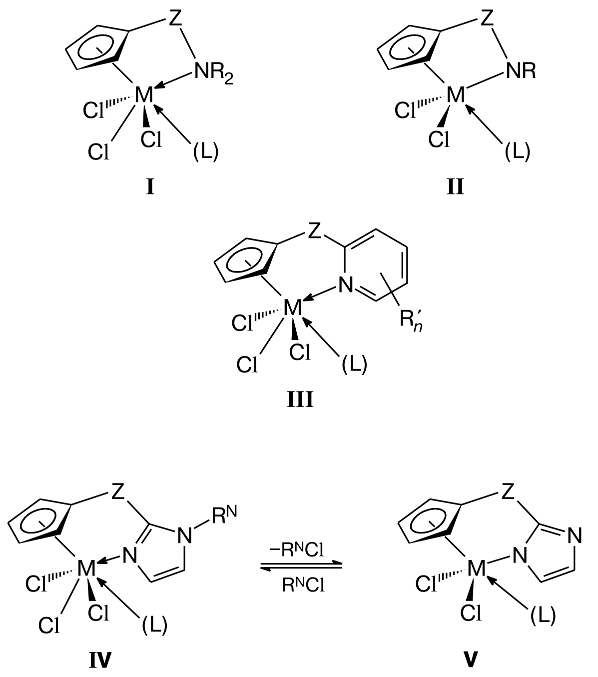
Scheme 1



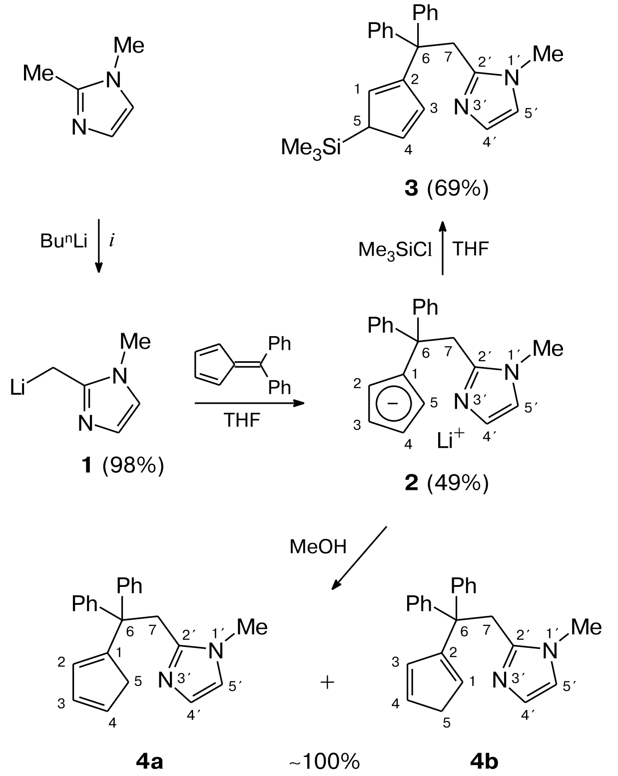
Results and Discussion

Synthesis of ligands and their trimethylsilyl derivatives

The lithium salt of the [2-(1-methylimidazol-2-yl)-1,1-diphenylethyl]cyclopentadienyl ligand (**2**) was synthesized starting from metallated 1,2-dimethylimidazole (**1**) and 6,6-diphenylfulvene (Scheme 2). Imidazole **1** lithiated at the 2-methyl group was isolated in pure state and characterized by ^{1}H and ^{13}C NMR spectroscopy. Attempts to use fulvenes containing hydrogen atoms at position 7 (for example, 6,6-dimethylfulvene) as the starting compounds did not give good results because the reaction was accompanied by deprotonation at this position and efforts to separate the resulting mixtures of lithium isopropenylcyclopentadienide and the target product of type **2** failed.

Silylation and protonation reactions of cyclopentadienide **2** occur readily under treatment with trimethylchlorosilane or methanol, respectively, to give silane **3** (major isomer) or cyclopentadiene **4** (two isomers, **4a** and **4b**). The resulting products are crystallizable oils that decompose on heating. 6,6-Diphenylfulvene is one of decomposition products. The structures of these compounds were established by ^{1}H (including NOE difference spectra) and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.

Scheme 2

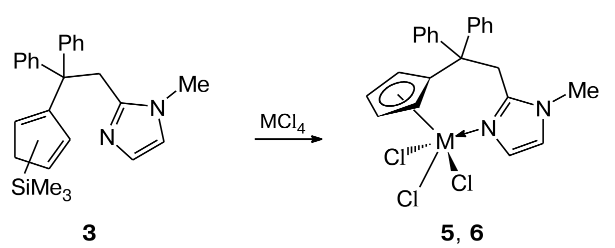


i. Hexane—diethyl ether.

Cyclopentadienyl zirconium and titanium complexes

Half-sandwich titanium and zirconium complexes (**5** and **6**, respectively) were synthesized from silane **3** and the corresponding transition metal tetrachloride (Scheme 3). Both compounds were isolated in good yields and characterized by ^{1}H and ^{13}C NMR spectroscopy (including low-temperature spectroscopy) and elemental analysis. The molecular structure of titanium complex **5** was established by X-ray diffraction.

Scheme 3



M = Ti (**5**), Zr (**6**)

Reaction conditions and yields: toluene; the yields were 64% (**5**) and 71% (**6**).

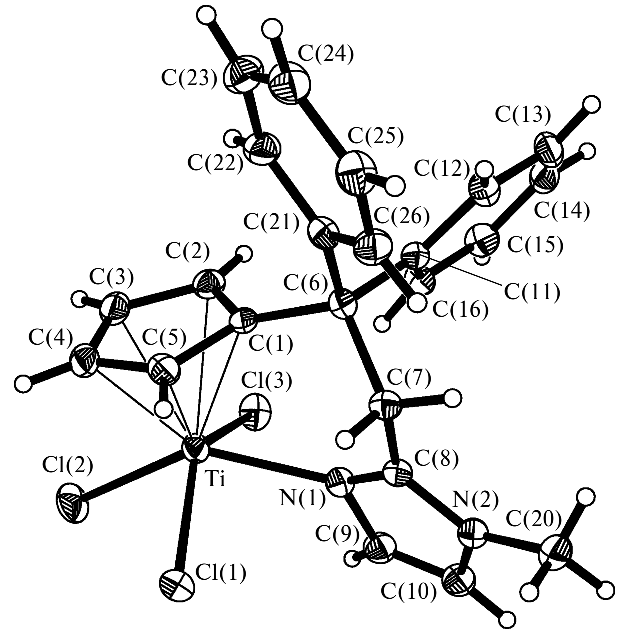


Fig. 1. Molecular structure of complex **5**.

Crystal structure of titanium complex 5

The coordination polyhedron of complex **5** is a tetragonal pyramid (a four-legged piano stool) with the Cp ring occupying the apex position (Fig. 1). Selected bond lengths and bond angles are given in Table 1. In general, the geometric parameters of **5** are similar to those determined earlier for other titanium complexes with functionalized chelating cyclopentadienyl ligands.[29,30] The Ti—N(1) bond length (2.163(2) Å) is in the range of bond lengths characteristic of imidazole titanium complexes (2.131—2.246 Å, Cambridge Structural Database,[31] January 2006 release). The imidazole ring is planar within 0.004(2) Å.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the structure of **5**

Bond	*d*/Å	Angle	ω/deg
Ti—N(1)	2.163(2)	N(1)—Ti—Cl(2)	140.05(6)
Ti—Cl(3)	2.3340(8)	N(1)—Ti—Cl(3)	81.19(6)
Ti—Cl(2)	2.3486(8)	Cl(3)—Ti—Cl(2)	86.01(3)
Ti—Cl(1)	2.3513(8)	N(1)—Ti—Cl(1)	79.24(6)
Ti—Pl*	2.034(1)	Cl(2)—Ti—Cl(1)	86.06(3)
N(1)—C(8)	1.329(3)	Cl(3)—Ti—Cl(1)	138.52(3)
N(1)—C(9)	1.388(3)	C(8)—N(1)—C(9)	106.2(2)
N(2)—C(8)	1.351(3)	C(8)—N(1)—Ti	131.1(2)
N(2)—C(10)	1.380(3)	C(9)—N(1)—Ti	119.4(2)
N(2)—C(20)	1.472(4)	C(8)—N(2)—C(10)	107.8(2)
C(9)—C(10)	1.338(4)	C(8)—N(2)—C(20)	126.7(2)
		C(10)—N(2)—C(20)	125.3(2)
		N(1)—C(8)—N(2)	110.0(2)
		N(1)—C(8)—C(7)	127.3(2)
		N(2)—C(8)—C(7)	122.7(2)
		C(10)—C(9)—N(1)	109.6(2)
		C(9)—C(10)—N(2)	106.5(2)

* Pl is the mean plane of the cyclopentadienyl ring.

NMR spectroscopy studies on the dynamic behavior of complexes 5 and 6 in solution

Dynamic processes in solutions of half-sandwich complexes **5** and **6** were studied by low-temperature NMR spectroscopy. The temperature dependence of the ^{1}H NMR spectra of a solution of complex **6** in THF-d_8 is shown in Fig. 2.

At 55 °C, complex **6** has the pseudosymmetry C_s, which disappears as the temperature is lowered due to a decrease in the rate of inversion of the six-membered metallacycle —Zr—Cp—CPh$_2$—CH$_2$—C—N—. Earlier, we have observed analogous processes for the (C$_5$Me$_4$CH$_2$CH$_2$SMe)ZrCl$_3$ (see Ref. 32) and (C$_5$Me$_4$CH$_2$CH$_2$NMe$_2$)ZrCl$_3$ complexes.[12] At –60 °C, (the slow exchange limit), pairs of the signals for the protons of the cyclopentadienyl ring are nonequivalent, as well as the signals of the both Ph groups and the H atoms of the methylene fragment. At this temperature, the ^{13}C NMR spectrum shows the nonequivalence of the C(2), C(5) and C(3), C(4) atoms and two Ph substituents. The inversion barrier of the metallacycle $\Delta G^{\neq}$ estimated from the coalescence temperatures of the methylene protons and the *o*-protons of the Ph rings is 52.6±0.9 kJ mol^{-1} for the protons of CH$_2$ (T_{coal} = –20 °C) and 52.7±0.9 kJ mol^{-1} for the *o*-protons (T_{coal} = 0 °C). These values are approximately 8 kJ mol^{-1} higher than those in the half-sandwich complexes (C$_5$Me$_4$CH$_2$CH$_2$SMe)ZrCl$_3$ (see Ref. 32) and (C$_5$Me$_4$CH$_2$CH$_2$NMe$_2$)ZrCl$_3$ (see Ref. 12), which is apparently associated with higher steric hindrance in complex **6**.

The assignment of the signals of the cyclopentadienyl ring was based on the fact that, in the case of slow exchange (–60 °C), the difference in the ^{1}H and ^{13}C chemical shifts in the pairs H(2), H(5) and H(3), H(4) and in the pairs C(2)H, C(5)H and C(3)H, C(4)H should be the smaller the larger the distance between these atoms and the substituent.[12,32,33]

A change in the chemical shifts in the ^{13}C NMR spectra of a solution of complex **6** in THF as the temperature decreases from +55 °C to –60 °C is at most 0.5 ppm for all signals (at –60 °C, it is necessary to calculate the average values for the corresponding pairs of the signals: *ipso*-C, C(2)H, C(5)H and C(3)H, C(4)H). This is unambiguous evidence that the coordination of the imidazole ligand to the Zr atom is retained throughout the temperature range under study even in a solvating solvent.

The dynamic behavior of titanium complex **5** in a THF-d_8 solution differs cardinally from that of the zirconium analog. A decrease in the temperature down to

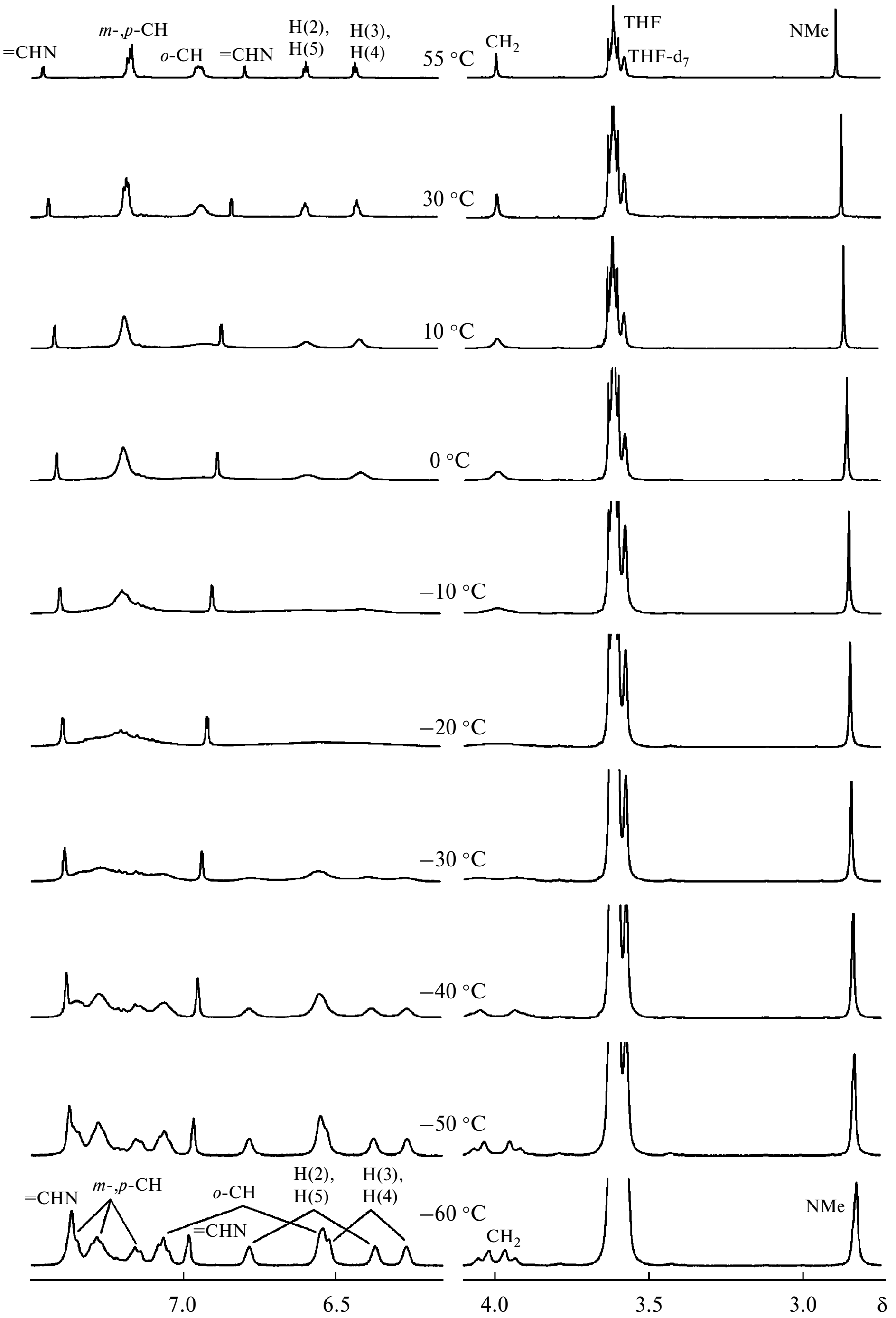


Fig. 2. Temperature dependence of the ^{1}H NMR spectra of a solution of complex **6** in THF-d_8.

−85 °C leads to a strong broadening of all signals in the ^{1}H NMR spectrum, including the signals of the Me group and the imidazole protons. The lower the temperature, the larger the broadening. This fact can be attributed only to a decrease in the rate of reversible coordination—dissociation of the imidazole moiety toward the titanium atom.

To the contrary, the dynamic behavior of half-sandwich titanium complex **5** in the nonsolvating solvent CD_2Cl_2 is analogous to that of zirconium complex **6** in THF-d_8. However, even at −85 °C the slow exchange limit is not achieved for all signals, which is accounted for by two factors. First, this is a decrease in the difference between the chemical shifts for the corresponding pairs of nonequivalent protons as the rate of inversion of the metallacycle decreases. For example, this difference for the methylene group (an AB system) is no larger than 10 Hz (in complex **6**, the corresponding parameter is

32 Hz). Second, the inversion barrier ($\Delta G^{\neq}$ = 45.2±1.3 kJ mol^{-1}) estimated from the coalescence temperatures of the H(2) and H(5) protons of the Cp ring and the *o*-protons of the Ph rings is almost 8 kJ mol^{-1} lower than that in complex **6**.

Therefore, the results of the present study suggest that coordination of the imidazole group to the Zr atom in complex **6** even in a solvating solvent is retained throughout the temperature range under investigation. For half-sandwich titanium complex **5**, this coordination is observed in the nonsolvating solvent CD_2Cl_2. In a THF solution, reversible coordination—dissociation of the nitrogen-containing moiety with the metal atom accompanied by the replacement of the imidazole fragment by the solvent molecule occurs. Both half-sandwich complexes are characterized by a decrease in the rate of inversion of the six-membered metallacycle —M—Cp—CPh_2—CH_2—C—N—, the inversion barrier for M = Ti being almost 8 kJ mol^{-1} lower than that for Zr.

Experimental

All reactions were carried out and samples for NMR spectroscopy were prepared in all-sealed evacuated Schlenk vessels. The solvents and their deuterated analogs were purified according to known procedures (THF and diethyl ether were purified with sodium benzophenone ketyl; toluene and hexane, with a Na/K alloy; CH_2Cl_2, with calcium hydride), degassed *in vacuo* (residual pressure of noncondensable gases was 10^{-3} Torr), and introduced into reaction vessels by vacuum recondensation. Operations with volatile reagents (MeI (over CaH_2), Me_3SiCl (over an Al powder), and methanol (over MgOMe) were carried out analogously. The starting reagent 1,2-dimethylimidazole (Merck) was purified under reduced pressure, and the fraction that crystallized at room temperature was collected. 6,6-Diphenylfulvene was prepared according to a known procedure;[34] $TiCl_4$ was heated with a freshly reduced finely dispersed copper and recondensed *in vacuo*; $ZrCl_4$ was purified by sublimation under a stream of dry hydrogen.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400 and 100 MHz, respectively, with the chemical shifts of Me_4Si or residual protons of the corresponding deuterated solvents (5.32 and 53.8 ppm for CD_2Cl_2, 7.15 and 128.0 ppm for C_6D_6, 1.73 and 25.3 ppm for THF-d_8) as the internal standard. The detector temperature was calibrated with a standard methanol sample.

The mass spectra were recorded on a Finnigan MAT SSQ 7000 GLC-mass-spectrometer.

Elemental analysis was performed on an automated Carlo Erba analyzer.

(1-Methylimidazol-2-yl)methyllithium (1). A 2.45 *M* Bu^{n}Li solution in hexane (13.5 mL, 33.1 mmol) was slowly added under cooling (−30—−10 °C) and vigorous stirring to a suspension of 1,2-dimethylimidazole (3.13 g, 32.56 mmol) in diethyl ether (70 mL). The voluminous white precipitate that formed was filtered off from the yellow solution, washed on a filter with diethyl ether (3×20 mL), and dried *in vacuo*. Compound **1** was obtained as a fine white crystalline powder in a yield of 3.28 g (98%). ^{1}H NMR (30 °C, THF-d_8), δ: 1.53 (s, 2 H, CH_2); 2.96 (s, 3 H, Me); 5.98 and 6.14 (both d, 1 H each, NCH=CHN, $^3J_{H,H}$ = 1.2 Hz). ^{13}C—{^{1}H} NMR, δ: 23.42 (CH_2); 32.17 (Me); 111.32, 123.81 (=CH); 166.15 (=NCN).

Lithium [2-(1-methylimidazol-2-yl)-1,1-diphenylethyl]cyclopentadienide (2). Compound **1** (0.55 g, 5.38 mmol) was added with cooling and stirring to a red solution of 6,6-diphenylfulvene (1.23 g, 5.33 mmol) in THF (20 mL). The reaction mixture immediately turned dark-green. Then the solution was heated at 35—45 °C for 2 days. The course of the reaction was monitored by ^{1}H NMR spectroscopy (a reference sample in THF-d_8). The solution was concentrated to dryness to obtain a residue as a green foam that solidified and is soluble in diethyl ether and toluene. To completely remove THF, the dry residue was dissolved in toluene (20 mL) and the solvent was again removed. The product was washed with hexane (3×20 mL) and dried *in vacuo*. The adduct **2**·1.5THF was obtained as a pale-green solid compound in a yield of 1.15 g (49%). ^{1}H NMR (THF-d_8, 30 °C), δ: 3.02 (s, 3 H, NMe); 3.68 (s, 2 H, CH_2); 5.62 and 5.72 (both virt. t, 2 H, C_5H_4, $^{3+4}J_{H,H}$ = 5.4 Hz); 6.60 and 6.74 (both d, 1 H, NCH=CHN, $^3J_{H,H}$ = 1.2 Hz); 7.00—7.30 (set of m, 10 H, Ph). ^{13}C NMR, δ: 32.38 (q, NMe, $^1J_{C,H}$ = 140 Hz); 39.56 (t, CH_2, $^1J_{C,H}$ = 129 Hz); 55.35 (s, $\underline{C}Ph_2$); 103.33 and 105.02 (both d, CH in C_5H_4, $^1J_{C,H}$ = 159 Hz); 120.68 (ddq, =C(5´)H, $^1J_{C,H}$ = 189 Hz, $^2J_{C,H}$ = 15.3 Hz, $^3J_{C,H}$ = 3.0 Hz); 123.22 (s, C_5H_4); 125.65 (d, *p*-CH, $^1J_{C,H}$ = 159 Hz); 126.56 (dd, =C(4´)H, $^1J_{C,H}$ = 188 Hz, $^2J_{C,H}$ = 9.7 Hz); 127.50 (d, *m*-CH, $^1J_{C,H}$ = 158 Hz); 129.87 (d, *o*-CH, $^1J_{C,H}$ = 157 Hz); 149.13 (s, =NCN); 151.63 (s, *ipso*-C). The atomic numbering scheme is shown in Scheme 2.

Trimethylsilyl[2-(1-methylimidazol-2-yl)-1,1-diphenylethyl]cyclopentadiene (3). Solutions of compound **2** (1.13 g, 2.57 mmol) and Me_3SiCl (0.35 mL, 0.30 g, 2.76 mmol) in THF (the total volume was 20 mL) were mixed under cooling. The mixture was allowed to warm up to room temperature and then kept for 16 h. The solvent was removed, the yellow residue (an oil that solidified) was dissolved in hexane (15 mL) and filtered off from LiCl that precipitated, hexane was removed, and the residue was dried *in vacuo* (10^{-3} Torr). Compound **3** was obtained as a red oil that solidified in a yield of 0.77 g (69%). Found (%): C, 78.20; H, 7.59; N, 6.88. $C_{26}H_{30}N_2Si$. Calculated (%): C, 78.34; H, 7.59; N, 7.03. ^{1}H NMR (C_6D_6, 30 °C), δ: −0.10 (s, 9 H, $SiMe_3$); 2.04 (s, 3 H, NMe); 3.20 (s, 1 H, C(5)H); 3.58 (A part of the AB system, 1 H, $C\underline{H}H$, $^2J_{H,H}$ = 14.5 Hz); 3.90 (B part of the AB system, 1 H, $CH\underline{H}$, $^2J_{H,H}$ = 14.5 Hz); 6.15 (d, 1 H, =C(5´)H, $^3J_{H,H}$ = 1.1 Hz); 6.36 (br.s, 1 H, =CH(4)); 6.56 (s, 1 H, =CH(1)); 6.57 (d, 1 H, =C(3)H, $^3J_{H,H}$ = 3.8 Hz); 6.98—7.47 (set of m, 10 H, Ph); 7.00 (d, 1 H, =C(4´)H, $^3J_{H,H}$ = 1.1 Hz). Nuclear Overhauser effects (%): η_{NMe}(=C(5´)H) = 1.6; $\eta_{=C(4')H}$(=C(5´)H) = 6.6; η_{CH_2}(NMe) = 2.2; $\eta_{=C(5')H}$(NMe) = 2.4. ^{13}C—{^{1}H} NMR, δ: −1.80 ($SiMe_3$); 31.00 (NMe); 36.46 (CH_2); 50.66 (C(5)H in C_5H_4); 55.94 ($\underline{C}Ph_2$); 119.69 (=C(5´)H); 126.14, 126.27 (*p*-CH in Ph); 127.65, 127.69 (*m*-CH in Ph); 127.91 (=C(4´)H); 129.52, 133.07, 133.21 (=CH in C_5H_4); 130.00, 130.04 (*o*-CH in Ph); 144.84 (=NCN); 146.68, 146.76 (*ipso*-C in Ph); 151.30 (=C(2) in C_5H_4). The atomic numbering scheme for the major isomer is shown in Scheme 2. MS (GC/MS, EI, 70 eV), *m/z* (I_{rel} (%)): 326 $[M - Me_2SiCH_2]^+$ (13.6), 303 $[M - C_3N_2H_2MeCH_2]^+$ (20.7), 302 $[M - C_3N_2H_2Me_2]^+$ (95.0), 231 $[C_5H_5CPh_2]^+$ (30.6), 230 $[C_5H_4CPh_2]^+$ (12.7), 153 $[C_5H_4CPh]^+$ (10.6), 96

$[C_3N_2H_2Me_2]^+$ (100), 95 $[C_3N_2H_2MeCH_2]^+$ (19.8), 73 $[Me_3Si]^+$ (65.3), 59 $[Me_2SiH]^+$ (14.6).

[2-(1-Methylimidazol-2-yl)-1,1-diphenylethyl]cyclopentadiene (4). A weighed sample of salt **2** (0.56 g, 1.28 mmol) was dissolved in methanol (5 mL). Then methanol was evaporated, and the residue was extracted with hexane (3×5 mL). The hexane solution was concentrated and yellow crystals of compound **4** were obtained. The product was dried *in vacuo* (10^{-3} Torr). The yield was ~100%. Found (%): C, 84.53; H, 6.98; N, 8.38. $C_{23}H_{22}N_2$. Calculated (%): C, 84.63; H, 6.79; N, 8.58. ^1H NMR (C_6D_6, 30 °C), δ: for **4a**: 1.91 (s, NMe); 3.34 (q, $C(5)H_2$, $^3J_{H,H} = {}^4J_{H,H}$ = 1.3 Hz); 3.52 (s, $CH_2(7)$); 6.12 (d, =C(5′)H, $^3J_{H,H}$ = 1.0 Hz); 6.30 (m, =C(4)H); 6.39 (m, =C(3)H); 6.42 (m, =C(2)H); 6.99—7.37 (set of m, Ph); 7.02 (d, =C(4′)H, $^3J_{H,H}$ = 1.2 Hz); for **4b**: 2.04 (s, NMe); 2.75 (q, $C(5)H_2$, $^3J_{H,H} = {}^4J_{H,H}$ = 1.5 Hz); 3.68 (s, $C(7)H_2$); 6.13 (d, =C(5′)H, $^3J_{H,H}$ = 1.2 Hz); 6.17 (m, =C(4)H); 6.27 (m, =C(1)H); 6.39 (m, =C(3)H); 6.99—7.37 (set of m, Ph); 7.02 (d, =C(4′)H, $^3J_{H,H}$ = 1.2 Hz). Nuclear Overhauser effects (%) for **4a**: η_{NMe}(=C(5′)H) = 0.2; $\eta_{=C(4')H}$(=C(5′)H) = 0.8; $\eta_{=C(4)H}(CH_2(5))$ = 0.5; $\eta_{C(7)H_2}$(NMe) = 1.0; $\eta_{=C(5')H}$(NMe) = 2.1; for **4b**: η_{NMe}(=C(5′)H) = 0.2; $\eta_{=C(4')H}$(=C(5′)H) = 0.8; $\eta_{=C(4)H}(CH_2(5))$ = 1.8; $\eta_{=C(1)H}(CH_2(5))$ = 2.0; $\eta_{C(7)H_2}$(NMe) = 1.4; $\eta_{=C(5')H}$(NMe) = 1.3. ^{13}C—{^1H} NMR, δ: 30.77, 30.97 (NMe); 36.11, 36.78 ($C(7)H_2$); 41.00, 43.02 ($C(5)H_2$); 55.73, 56.77 ($\underline{C}Ph_2$); 119.56, 119.62 (=C(5′)H); 126.38 (*p*-CH); 127.76 (*m*-CH); 127.92, 129.76, 131.60, 132.66, 133.16, 135.25 (=CH in C_5H_5); 128.07, 128.08 (=C(4′)H); 129.60, 129.98 (*o*-CH); 144.71, 144.76 (=NCN); 145.70, 146.93 (*ipso*-C); 152.88, 154.71 (=C in C_5H_5). The atomic numbering scheme is shown in Scheme 2 (**4b** : **4a** = 1.15). MS (GC/MS, EI, 70 eV), *m/z* (I_{rel} (%)): 326 $[M]^+$ (69.9), 231 $[C_5H_5CPh_2]^+$ (40.2), 153 $[C_5H_4CPh]^+$ (20.8), 96 $[C_3N_2H_2Me_2]^+$ (100), 95 $[C_3N_2H_2MeCH_2]^+$ (9.2), 91 $[C_7H_7]^+$ (5.5), 81 $[C_3N_2H_2Me]^+$ (7.1).

{η^5:η^1-*N*-[2-(1-Methylimidazol-2-yl)-1,1-diphenylethyl]cyclopentadienyl}trichlorotitanium, [η^5:η^1-$C_5H_4CPh_2CH_2$-(1-$MeC_3H_2N_2$)]$TiCl_3$ (5). Solutions of silylated cyclopentadiene **3** (1.02 g, 2.56 mmol) and $TiCl_4$ (0.28 mL, 0.48 g, 2.55 mmol) in toluene (the total amount was 10 mL) were mixed under cooling (–78 °C) with vigorous stirring. The mixture was allowed to gradually warm up to room temperature and stirred for 4 days, after which a red oil poorly soluble in toluene was obtained. After removal of volatile components and drying *in vacuo*, a new portion of toluene (15 mL) was added, which caused crystallization of the oil. The red mother liquor was decanted, and the yellow-orange crystalline precipitate was washed with toluene (3×10 mL) and dried *in vacuo*. The yield of complex **5** was 0.79 g (64%). Found (%): C, 57.57; H, 4.32; N, 5.70. $C_{23}H_{21}Cl_3N_2Ti$. Calculated (%): C, 57.59; H, 4.41; N, 5.84. ^1H NMR (THF-d_8, 30 °C), δ: 3.36 (s, 3 H, NMe); 3.96 (s, 2 H, CH_2); 6.92 (m, 4 H, C_5H_4); 6.95 and 7.58 (both d, 1 H, NCH=CHN, $^3J_{H,H}$ = 1.6 Hz); 7.05 (m, 4 H, *o*-CH); 7.20 (m, 6 H, *m*-, *p*-CH). ^{13}C—{^1H} NMR (THF-d_8) δ: 33.73 (NMe); 38.10 (CH_2); 53.00 ($\underline{C}Ph_2$); 120.27 (=C(5′)H); 124.13, 125.59 (CH in C_5H_4); 127.80 (*p*-CH); 129.03, 129.22 (*m*-, *o*-CH); 129.60 (=C(4′)H); 144.73, 145.28, 146.30 (C in C_5H_4, =NCN, *ipso*-C). ^1H NMR (CD_2Cl_2, 30 °C), δ: 3.37 (s, 3 H, NMe); 3.88 (s, 2 H, CH_2); 6.84 and 7.60 (both d, 1 H, NCH=CHN, $^3J_{H,H}$ = 1.6 Hz); 6.95 and 7.01 (both virt. t, 2 H, C_5H_4, $^{3+4}J_{H,H}$ = 5.4 Hz); 6.97 (m, 4 H, *o*-CH); 7.26 (m, 6 H, *m*-, *p*-CH). ^{13}C—{^1H} NMR (CD_2Cl_2), δ: 34.45 (NMe); 37.95 (CH_2); 52.50 ($\underline{C}Ph_2$); 120.07 (=C(5′)H); 124.89, 125.57 (CH in C_5H_4); 127.82 (*p*-CH); 128.39, 128.95 (*m*-, *o*-CH); 129.22 (=C(4′)H); 144.61, 145.03, 145.05 (C in C_5H_4, =NCN, *ipso*-C).

Single crystals of **5** suitable for X-ray diffraction were prepared by slow recrystallization from dichloromethane.

{η^5:η^1-*N*-[2-(1-Methylimidazol-2-yl)-1,1-diphenylethyl]cyclopentadienyl}trichlorozirconium, [η^5:η^1-$C_5H_4CPh_2CH_2$-(1-$MeC_3H_2N_2$)]$ZrCl_3$ (6). A solution of silylated cyclopentadiene **3** (0.90 g, 2.25 mmol) in toluene (5 mL) was added to a suspension of $ZrCl_4$ (0.52 g, 2.23 mmol) in the same solvent (15 mL) under cooling (–20 °C) with vigorous stirring. After stirring at –20 °C for 15 min, $ZrCl_4$ was partially dissolved. The mixture was allowed to gradually warm up to room temperature, stirred for 2 h and then at 50 °C for 7 h, and kept for 16 h. The precipitate was separated from the mother liquor by decantation, washed with toluene (3×10 mL), and dried on a vacuum line. Complex **6** was obtained in a yield of 0.83 g (71%). Found (%): C, 52.57; H, 4.15; N, 5.06. $C_{23}H_{21}Cl_3N_2Zr$. Calculated (%): C, 52.82; H, 4.05; N, 5.36. ^1H NMR (THF-d_8, 55 °C), δ: 2.89 (s, 3 H, NMe); 4.01 (s, 2 H, CH_2); 6.43 (virt. t, 2 H, H(3), H(4), $^{3+4}J_{H,H}$ = 5.7 Hz); 6.59 (virt. t, 2 H, H(2), H(5), $^{3+4}J_{H,H}$ = 5.7 Hz); 6.79 and 7.46 (both d, 1 H, NCH=CHN, $^3J_{H,H}$ = 1.7 Hz); 6.95 (m, 4 H, *o*-CH); 7.17 (m, 6 H, *m*-, *p*-CH). ^{13}C—{^1H} NMR (THF-d_8, 55 °C), δ: 33.05 (NMe); 38.50 (CH_2); 54.12 ($\underline{C}Ph_2$); 116.88, 125.12 (CH in C_5H_4); 120.27 (=C(5′)H); 127.43 (*p*-CH); 128.78, 129.30 (*m*-, *o*-CH); 130.69 (=C(4′)H); 133.64 (C in C_5H_4); 147.33 (*ipso*-C); 148.90 (=NCN). ^1H NMR (THF-d_8, –60 °C), δ: 2.83 (s, 3 H, NMe); 3.96 (A part of the AB system, 1 H, $C\underline{H}H$, $^2J_{H,H}$ = 13.5 Hz); 4.04 (B part of the AB system, 1 H, $CH\underline{H}$, $^2J_{H,H}$ = 13.5 Hz); 6.27 and 6.52 (both br.s, 1 H, H(3), H(4)); 6.37 and 6.79 (both br.s, 1 H, H(2), H(5)); 6.54 and 7.07 (both m, 2 H, *o*-CH); 6.98 and 7.37 (both s, 1 H, NCH=CHN); 7.16 and 7.29 (both m, 1 H, *p*-CH); 7.29 and 7.35 (both m, 2 H, *m*-CH). ^{13}C—{^1H} NMR (THF-d_8, –60 °C), δ: 32.95 (NMe); 38.20 (CH_2); 53.63 ($\underline{C}Ph_2$); 113.39, 119.59 (C(2)H, C(5)H); 120.76 (=C(5′)H); 122.58, 127.66 (C(3)H, C(4)H); 127.51, 128.60, 129.01, 129.24, 129.44 (*o*-, *m*-, *p*-CH); 130.29 (=C(4′)H); 133.86 (C(1)); 144.93, 149.26 (*ipso*-C); 148.59 (=NCN). ^1H NMR (CD_2Cl_2, 30 °C), δ: 2.94 (s, 3 H, NMe); 3.88 (s, 2 H, CH_2); 6.62 and 6.73 (both virt. t, 2 H, C_5H_4, $^{3+4}J_{H,H}$ = 5.5 Hz); 6.70 and 7.58 (both d, 1 H, NCH=CHN, $^3J_{H,H}$ = 1.5 Hz); 6.93 (m, 4 H, *o*-CH); 7.24 (m, 6 H, *m*-, *p*-CH).

X-ray diffraction study of compound 5 was carried out on an automated Bruker SMART 6K diffractometer at 120 K (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator). Crystals of **5** ($C_{23}H_{21}Cl_3N_2Ti$, M = 479.67) are monoclinic, space group $P2_1/c$, a = 8.5730(7), b = 13.4748(13), c = 18.4369(17) Å, β = 99.790(3)°, V = 2098.8(3) $Å^3$, Z = 4, d_{calc} = 1.518 g cm^{-3}, μ(Mo-Kα) = 0.803 mm^{-1}, $F(000)$ = 984. The intensities of 13919 reflections (5068 independent reflections, R_{int} = 0.0521) were measured using the ω scanning technique in the angle range 2.24 < θ < 28.00° ($-11 \le h \le 6$, $-17 \le k \le 17$, $-24 \le l \le 24$). The absorption correction was applied based on the measured intensities of equivalent reflections.[35] The structure was solved by direct methods (SHELXS-97).[36] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method against F^2 (SHELXL-97).[37] The positions of all hydrogen atoms were located in difference electron density maps and refined isotropically. The final R factors were

$R_1 = 0.0474$ and $wR_2 = 0.1150$ for 3510 reflections with $I > 2\sigma(I)$; 658 parameters were refined; GOOF = 0.969, $\Delta\rho$ (min/max) = $-0.522/0.816$ e $\cdot$ Å^{-3}.

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