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Synthesis and characterization of η^5-tetramethylcyclopentadienyl-hydrido- and -chloro-silyl-η^1-amido zirconium complexes

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Abstract

The silylated tetramethylcyclopentadienes $C_5Me_4(SiMeCl_2)(SiMe_3)$ (**1**) and $C_5Me_4H(SiMeHCl)$ (**3**) were isolated by reaction of their corresponding trimethylsilyltetramethylcyclopentadienyl and tetramethylcyclopentadienyl lithium salts with $SiMeCl_3$ and $SiMeHCl_2$, respectively. Reaction of a toluene suspension of $ZrCl_4$ with one equivalent of **1** afforded the monocyclopentadienyl zirconium complex $[Zr(\eta^5\text{-}C_5Me_4SiMeCl_2)Cl_3]$ (**2**). Reaction of **3** with NH_2^tBu gave $C_5Me_4H[SiMeH(NH^tBu)]$ (**4**) which was further metallated to give $Li_2[C_5Me_4SiMeH(N^tBu)]$ (**5**), used to prepare the silyl-η^1-amido zirconium derivative $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)Cl_2]$ (**6**) by reaction with $ZrCl_4(THF)_2$. Chlorination of **6** with BCl_3 afforded $[Zr(\eta^5\text{-}C_5Me_4SiMeCl\text{-}\eta^1\text{-}N^tBu)Cl_2]$ (**12**). Alkylation and amidation of **6** and **12** provided the corresponding disubstituted $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)R_2]$ ($R = Me$ **7**, CH_2Ph **8**, NMe_2 **9**) and $[Zr(\eta^5\text{-}C_5Me_4SiMeCl\text{-}\eta^1\text{-}N^tBu)Me_2]$ (**13**) and monosubstituted $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)ClR]$ ($R = C_6F_5$ **10**, $N(SiMe_3)_2$ **11**) and $[Zr(\eta^5\text{-}C_5Me_4SiMeCl\text{-}\eta^1\text{-}N^tBu)Cl\{N(SiMe_3)_2\}]$ (**14**). All of the new compounds reported were characterized by elemental analyses and NMR spectroscopy.

Keywords: Zirconium; Linked amido-cyclopentadienyl ligand; Synthesis

1. Introduction

Bidentate ligands in which the η^5-cyclopentadienyl group is tethered by one additional anionic or neutral N- or O-donor group form interesting types of metal chelate complexes, reviewed recently [1]. In particular, Group 4 metal (η^5-cyclopentadienyl)silyl-η^1-amido complexes provide 'constrained geometry' catalysts of increasing interest in the production of high-molecular weight copolymers as a result of their well known lower steric requirements and enhanced acidity [2].

We were interested in isolating cyclopentadienyl(chlorosilyl)-η^1-amido Group 4 and 5 metal derivatives, by exploring new, more convenient synthetic strategies. Double deprotonation of $C_5R_4H[SiMeCl(NHR')]$ ($R = H$, Me) using basic tetra-amides $M(NR_2)_4$ [3], tetra-benzyls $M(CH_2Ph)_4$ [4] and di-butyl-chlorides MCl_2Bu_2 [5], with the elimination of amine, toluene and butane, respectively, is not a convenient method as further transformation into the corresponding metal chlorides is required. Metathetical reactions of metal halides with the doubly lithiated precursor [6] are not available as the formation of $Li_2[C_5R_4SiMeCl(NR')]$ is accompanied by rapid elimination of lithium chloride affording silylene decomposition products. Intramolecular aminolysis [7] by reaction of $[M(C_5R_4SiMeCl_2)Cl_3]$ with excess primary amines or with the corresponding lithium amides has proved to be an efficient synthetic method when selective reactions at Si–Cl and M–Cl bonds can be made and has been used to isolate various Group 4 metal [8–12] and Nb complexes [13]. An alternative method could be based on the chlorination of Si–H bonds [14] in the more easily accessible $[M(C_5R_4SiMeH\text{-}\eta^1\text{-}NR')Cl_2]$ derivatives.

We report here the application of convenient methods to synthesize the new zirconium complexes $[Zr(\eta^5\text{-}C_5Me_4SiMeCl_2)Cl_3]$, $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)Cl_2]$ and $[Zr(\eta^5\text{-}C_5Me_4SiMeCl\text{-}\eta^1\text{-}N^tBu)Cl_2]$ and some

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of their alkyl and amido derivatives which were characterized by elemental analysis and ^{1}H-, ^{13}C- and ^{29}Si-NMR spectroscopy.

2. Results and discussion

The disilylated precursor [1-(dichloromethylsilyl)-1-trimethylsilyl]tetramethyl cyclopentadiene (**1**) was isolated as a pale yellow solid in 94% yield by reaction of the corresponding (trimethylsilyl)cyclopentadienyl lithium salt with trichloromethylsilane in THF. Compound **1** was characterized by elemental analysis and NMR spectroscopy (see Section 3). As shown in Scheme 1, a slow reaction of one equivalent of **1** with a toluene suspension of $ZrCl_4$ took place on heating the mixture for 3 h at 100 °C affording the monocyclopentadienyl derivative $[Zr(\eta^5\text{-}C_5Me_4SiMeCl_2)Cl_3]$ (**2**), isolated in 67% yield as a pale brown solid. Compound **2** which could not be obtained free of toluene (ca. 2%, see Section 3) was characterized by elemental analysis and NMR spectroscopy. The ^{1}H- and ^{13}C-NMR spectra of complex **2** show the behaviour expected for AA′BB′ ring spin systems.

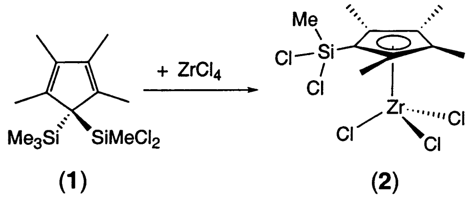
Various reactions were investigated to determine the comparative reactivity of the Si–Cl and Zr–Cl bonds of compound **2**. All the reactions using different molar ratios of *tert*-butylamine and its lithium salt resulted in inseparable mixtures of various substituted products. This unselective reactivity of both Si–Cl and Zr–Cl bonds, is an important limitation when the objective is to isolate (η^5-cyclopentadienyl-chlorosilyl)-η^1-amido complexes. For this reason, we decided to use a different approach based on the known capacity of BCl_3 to chlorinate Si–H bonds [14], and because the dilithium salt of the aminosilyl cyclopentadiene $Li_2[C_5Me_4SiMeH(N^tBu)]$ can be easily isolated.

Reaction of $Li(C_5Me_4H)$ with $SiMeHCl_2$ in THF gave the silylated cyclopentadiene $C_5Me_4H(SiMeHCl)$ (**3**), isolated as a yellow oil in 89% yield and characterized by elemental analysis and NMR spectroscopy. Reaction of **3** with two equivalents of NH_2^tBu in THF afforded the aminosilylcyclopentadiene derivative $C_5Me_4H[SiMeH(NH^tBu)]$ (**4**) isolated as a yellow oil in 93% yield and characterized by elemental analysis and NMR spectroscopy. Metallation of **4** with two equivalents of Li^nBu afforded the dilithium salt $Li_2[C_5Me_4SiMeH(N^tBu)]$ (**5**) as a white solid in 96% yield which was characterized by elemental analysis. An equimolar mixture of **5** and $ZrCl_4(THF)_2$ was stirred for 2 days at room temperature to give the silyl-η^1-amido complex $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)Cl_2]$ (**6**) as a yellow solid in 72% yield (see Scheme 2).

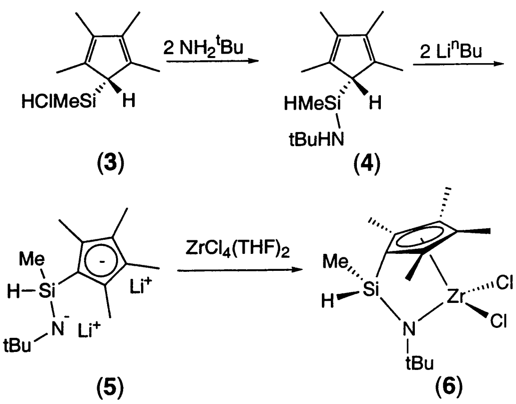
As shown in Scheme 3, alkylation of compound **6** with two equivalents of MgClR (R = Me, CH_2Ph) afforded the dialkyl complexes $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)R_2]$ (R = Me **7**, CH_2Ph **8**) and a similar reaction with two equivalents of $LiNMe_2$ gave the diamido complex $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)(NMe_2)_2]$ (**9**). However, only monosubstituted compounds resulted when bulkier substituents were used. So, the same reaction with $MgCl(C_6F_5)$ gave only the monoalkylated derivative $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)Cl(C_6F_5)]$ (**10**) even when excess alkylating agent was used. The same behaviour was observed for the reaction with $Li[N(SiMe_3)_2]$ which afforded the monoamido complex $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)Cl\{N(SiMe_3)_2\}]$ (**11**).

The chloro **6**, alkyl **7**, **8**, **10** and amido **9** and **11** complexes are air sensitive and thermally stable compounds which can be stored for long periods under an inert atmosphere. All were soluble in hexane and isolated as yellow solids (**6**, **8**–**11**) or an analytically pure waxy orange product **7** by concentration and cooling their hexane solutions at −30 °C. Their formulations are consistent with the analytical and NMR spectroscopic data.

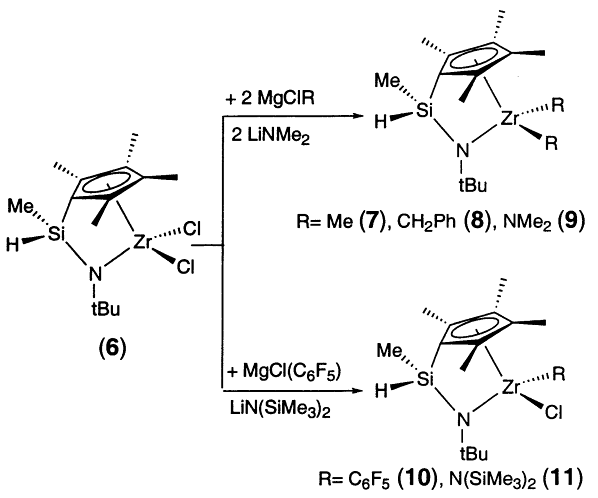
All of the complexes **6**–**9** have two identical zirconium bound substituents and are asymmetric molecules with a chiral centre at silicon. Their ^{1}H-NMR spectra showed the expected four resonances for the ring methyl groups of a ABCD spin system, along with one singlet due to the *t*-butylamido ligand and one doublet and one quadruplet corresponding to the Me and H groups bound to silicon, respectively. Accordingly, the ^{13}C-NMR spectra showed four resonances for the ring methyl groups and five resonances for the ring carbon atoms, along with two resonances for the *t*-butylamido



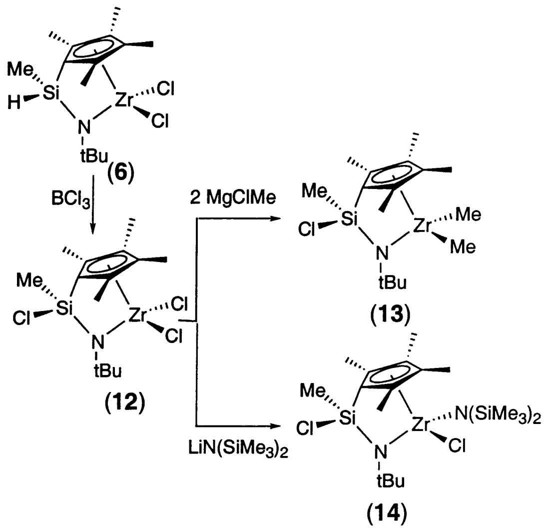
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

ligand and one resonance corresponding to the silicon bound methyl group. The two non-equivalent methyl groups in **7** give rise to two resonances (^1H and ^{13}C) whereas the benzyl groups in **8** contain diastereotopic methylene protons giving rise to four doublets (^1H) and two ^{13}C resonances. Each of the non-equivalent dimethylamido groups in **9** show equivalent methyl groups observed as two singlets (^1H and ^{13}C) indicating that amido substituents rotate freely.

The monosubstituted pentafluorophenyl **10** and amido **11** complexes contain two chiral centres at zirconium and silicon and comprise 1.8/1 (**10**) and 1.6/1 (**11**) molar ratio mixtures of two enantiomeric pairs of diastereomers which could not be separated. The pairs can be clearly distinguished by the two identical sets of resonances observed in their ^1H- and ^{13}C-NMR spectra (see Section 3), although some of the resonances appear as overlapped signals.

Conversion of the hydrido- into the chloro-silyl derivative $[Zr(\eta^5\text{-}C_5Me_4SiMeCl\text{-}\eta^1\text{-}N^tBu)Cl_2]$ (**12**) was carried out by reaction of a dichloromethane solution of **6** with one equivalent of a 1 M heptane solution of BCl_3 (see Scheme 4). Complex **12** was isolated as a pale yellow solid in 72% yield and was characterized by elemental analysis and NMR spectroscopy, its ^1H and ^{13}C spectral pattern being similar to those described for **6** (see Section 3). When complex **12** was treated with two equivalents of MgClMe selective alkylation of the Zr–Cl bonds took place to give the dimethyl complex $[Zr(\eta^5\text{-}C_5Me_4SiMeCl\text{-}\eta^1\text{-}N^tBu)Me_2]$ (**13**), isolated as a pale yellow solid in 65% yield and characterized by elemental analysis and NMR spectroscopy. Formulation of **13** is consistent with its ^1H- and ^{13}C-NMR spectra which are similar to those described above for the related dimethyl complex **7**, demonstrating the presence of only one chiral centre at silicon. The presence of the unaltered Si–Cl bond is also consistent with the downfield signal observed at δ 0.75, analogous to that observed for **12** and the two highfield signals observed at δ −0.04 and 0.04 for the two Zr–Me bonds analogous to those observed for **7**.

A similar reaction of **12** with $LiN(SiMe_3)_2$ afforded the monoamido complex $[Zr(\eta^5\text{-}C_5Me_4SiMeCl\text{-}\eta^1\text{-}N^tBu)Cl\{N(SiMe_3)_2\}]$ (**14**), isolated as a pale yellow solid in 97% yield and characterized by elemental analysis and NMR spectroscopy. Complex **14** contains two chiral centres at silicon and zirconium and consists of a mixture of two enantiomeric pairs of diastereomers in a 1/1 molar ratio, which could not be separated. As described above for the related monosubstituted compounds **10** and **11**, the ^1H- and ^{13}C-NMR spectra of **14** show two identical sets of resonances, each one corresponding to one of the two diastereomers (see Section 3).

The π-bonding contribution of the bridging *t*-butylamido ligand in complexes **6**–**14** measured by the $\Delta\delta = (\delta C_{tert} - \delta C_{Me})$ values [15] is in the range known for this type of cyclopentadienylsilyl-η^1-amido complexes going from 20.8 ppm for the more donating **7** to 25.8 ppm for the less donating **10** substituents.

3. Experimental

3.1. General considerations

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox MBraun model 150B-G. Solvents were purified by distillation under argon before use by employing the appropriate drying agent (sodium for toluene, sodium–potassium alloy for hexane and pentane, phosphorus pentoxide for CH_2Cl_2 and sodium-benzophenone for diethyl ether and THF). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. NH_2^tBu (Aldrich) was distilled before use and stored over activated 4 Å molecular sieves. $C_5Me_4H_2$ (Aldrich), Li^nBu (Aldrich), $SiMeCl_3$ (Aldrich), $SiMeHCl_2$ (ABCR), BCl_3 (Aldrich), MgClMe (Aldrich), MgClBz (Aldrich), $ZrCl_4$ (Fluka) were purchased from commercial sources and used without further purification. $Li(C_5Me_4H)$ [16], $C_5Me_4H(SiMe_3)$ [17], $ZrCl_4(THF)_2$ [18] and $LiN(SiMe_3)_2$ [19] were prepared according to the literature procedures. C, H and N microanalyses were performed on a Perkin–Elmer 240B and/or Heraeus –CHN–O-rapid microanalyzer. NMR spectra, measured at 25 °C, were recorded on a Varian Unity FT-300 (^{1}H-NMR at 300 MHz, ^{13}C-NMR at 75 MHz, ^{29}Si-NMR at 59.6 MHz). In the ^{1}H-NMR spectra, the chemical shifts refer to the residual proton signal of the solvent ($\delta = 7.24$ ppm for $CHCl_3$ and $\delta = 7.15$ ppm for C_6H_6), in ^{13}C-NMR spectra to the solvent signal ($\delta = 77.0$ ppm for $CHCl_3$-d_1 and $\delta = 128.0$ ppm for C_6H_6-d_6) and in ^{29}Si-NMR spectra to the resonance of external Me_4Si ($\delta = 0.0$ ppm).

3.2. Synthesis of $(C_5Me_4)(SiMeCl_2)(SiMe_3)$ (**1**)

A 1.6 M solution of Li^nBu in hexane (17 ml, 27 mmol) was added dropwise, at 0 °C, to a solution of $C_5Me_4H(SiMe_3)$ (5.25 g, 27 mmol) in THF. The reaction mixture was slowly warmed to room temperature (r.t.) and stirred for 16 h. After THF removal, the residue was washed with pentane (2 × 50 ml) to give $Li[C_5Me_4(SiMe_3)]$ as a white solid. Methyltrichlorosilane (6.30 ml, 54 mmol) was added at once to a solution of $Li[C_5Me_4(SiMe_3)]$ (5.41 g, 27 mmol) in THF (175 ml) at −78 °C. The reaction mixture was slowly warmed to r.t. and was stirred for 48 h to ensure complete reaction. After THF removal, the residue was extracted into hexane (2 × 75 ml). The hexane solvent was removed under vacuum to give **1** as a pale yellow solid (7.8 g, 25.4 mmol, 94% yield). Anal. Calc. for $C_{13}H_{24}Cl_2Si_2$: C, 50.79; H, 7.87. Found: C, 50.60; H, 7.92%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ 0.10 (s, 9H, Si*Me*$_3$), 0.20 (s, 3H, Si*Me*Cl$_2$), 1.69 (s, 6H, C$_5$*Me*$_4$), 2.07 (s, 6H, C$_5$*Me*$_4$). ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.04 (s, 9H, Si*Me*$_3$), 0.26 (s, 3H, Si*Me*Cl$_2$), 1.83 (s, 6H, C$_5$*Me*$_4$), 2.08 (s, 6H, C$_5$*Me*$_4$). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 25 °C): δ −0.5 (Si*Me*$_3$), 3.3 (Si*Me*Cl$_2$), 11.6, 15.0 (C$_5$*Me*$_4$), 58.3 (C$_{ipso}$, C$_5$Me$_4$), 131.0, 140.8 (*C*$_5$Me$_4$).

3.3. Synthesis of $[Zr(\eta^5\text{-}C_5Me_4SiMeCl_2)Cl_3]$ (**2**)

A solution of **1** (3.00 g, 9.75 mmol) in toluene (10 ml) was added to a suspension of $ZrCl_4$ (2.27 g, 9.75 mmol) in toluene (35 ml). The Schlenk was connected to a bubbler and the reaction mixture was warmed at 100 °C for 3 h. The formation of a brown solution was observed when the $ZrCl_4$ reacted gradually. After filtration, the hot solvent was removed under vacuum to give a pale brown solid, which was washed with cold hexane and was characterized as **2** (2.83 g, 6.55 mmol, 67% yield). Anal. Calc. for $C_{10}H_{15}Cl_5SiZr(0.1C_7H_8)$: C, 29.14; H, 3.58. Found: C, 29.16; H, 3.46%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ 0.96 (s, 3H, Si*Me*Cl$_2$), 1.68 (s, 6H, C$_5$*Me*$_4$), 2.19 (s, 6H, C$_5$*Me*$_4$). ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.22 (s, 3H, Si*Me*Cl$_2$), 2.20 (s, 6H, C$_5$*Me*$_4$), 2.47 (s, 6H, C$_5$*Me*$_4$). ^{13}C{^{1}H}-NMR (75 MHz, C_6D_6, 25 °C): δ 8.6 (Si*Me*Cl$_2$), 12.3, 15.5 (C$_5$*Me*$_4$), 119.8 (C$_{ipso}$, C$_5$Me$_4$), 135.6, 136.9 (*C*$_5$Me$_4$). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 25 °C): δ 9.0 (Si*Me*Cl$_2$), 12.9, 15.8 (C$_5$*Me*$_4$), 119.8 (C$_{ipso}$, *C*$_5$Me$_4$), 135.5, 136.8 (*C*$_5$Me$_4$).

3.4. Synthesis of $C_5Me_4H(SiMeHCl)$ (**3**)

Methyldichlorosilane (4.3 ml, 41 mmol) was added at once to a suspension of $Li(C_5Me_4H)$ (5.04 g, 39 mmol) in THF (125 ml) at −78 °C. The reaction mixture was slowly warmed to r.t. and stirred for 17 h. After THF removal, the residue was extracted into hexane (2 × 75 ml). The hexane solvent was removed under vacuum to give **3** as a yellow oil (6.99 g, 35 mmol, 89% yield). Anal. Calc. for $C_{10}H_{17}ClSi$: C, 59.82; H, 8.53. Found: C, 60.23; H, 8.64%. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.05 (d, 3H, Si*Me*, $J = 3$ Hz), 1.81 (2s, 6H, C$_5$*Me*$_4$), 1.94 (s, 3H, C$_5$*Me*$_4$), 1.99 (s, 3H, C$_5$*Me*$_4$), 3.21 (br s, 1H, C$_5$Me$_4$*H*), 4.80 (m, 1H, Si*H*). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 25 °C): δ −4.2 (Si*Me*), 11.2, 11.4, 13.5, 13.9 (C$_5$*Me*$_4$), 54.6 (C$_{ipso}$, C$_5$Me$_4$), 131.9, 135.9, 137.6, 138.4 (*C*$_5$Me$_4$).

3.5. Synthesis of $C_5Me_4H[SiMeH(NH^tBu)]$ (**4**)

NH_2^tBu (12.4 ml, 118 mmol) was added to a solution of **3** (11.83 g, 58.9 mmol) in THF (250 ml) at −78 °C. After warming to r.t., the reaction mixture was stirred for 17 h. The volatiles were removed under reduced pressure and the residue was extracted into hexane (2 × 100 ml). After filtration, solvent was removed under vacuum to give **4** as a yellow oil (13 g, 54.7 mmol, 93% yield). Anal. Calc. for $C_{14}H_{27}NSi$: C, 70.81; H, 11.46; N, 5.90. Found: C, 70.43; H, 11.41; N, 5.50%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ −0.15 (d, 3H, Si*Me*, $J = 3$ Hz), 0.29 (br s, 1H, N*H*), 1.11 (s, 9H, N^t*Bu*), 1.82 (s, 3H, C$_5$*Me*$_4$), 1.85 (s, 3H, C$_5$*Me*$_4$), 2.00 (s, 3H, C$_5$*Me*$_4$), 2.05 (s, 3H, C$_5$*Me*$_4$), 2.91 (br s, 1H, C$_5$Me$_4$*H*), 4.98 (m, 1H, Si*H*). ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ −0.27 (d, 3H, Si*Me*, $J = 3$ Hz), 0.40 (br s, 1H, N*H*), 1.16 (s, 9H, N^t*Bu*), 1.80 (2s, 6H, C$_5$*Me*$_4$), 1.93 (s, 3H, C$_5$*Me*$_4$), 1.98 (s, 3H, C$_5$*Me*$_4$), 2.92 (br s, 1H, C$_5$Me$_4$*H*), 4.69 (m, 1H, Si*H*). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 25 °C): δ −5.5 (Si*Me*), 11.0, 11.1, 13.6, 13.9 (C$_5$*Me*$_4$), 33.2 (N^t*Bu*), 49.1 (C$_{ipso}$, N^t*Bu*), 55.5 (C$_{ipso}$, C$_5$Me$_4$), 131.7, 132.9, 135.3, 135.4 (*C*$_5$Me$_4$).

3.6. Synthesis of $Li_2[C_5Me_4SiMeH(N^tBu)]$ (**5**)

A 1.6 M solution of Li^nBu in hexane (78 ml, 124 mmol) was added dropwise, at −78 °C, to a solution of **4** (12.25 g, 51.6 mmol) in diethyl ether (200 ml). The reaction mixture was slowly warmed to r.t. and stirred for 18 h. A white precipitate was formed which after filtration was washed with hexane (2 × 50 ml) and dried under vacuum to give **5** as a white solid (12.34 g, 49.5 mmol, 96% yield). Anal. Calc. for $C_{14}H_{25}Li_2NSi$: C, 67.44; H, 10.11; N, 5.62. Found: C, 67.08; H, 10.15; N, 5.48%.

3.7. Synthesis of $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)Cl_2]$ (**6**)

Toluene (70 ml) at 0 °C was added to a mixture of **5** (2.69 g, 10.8 mmol) and $ZrCl_4(THF)_2$ (4.07 g, 10.8 mmol). The reaction mixture was warmed to r.t. and then stirred for 2 days. The volatiles were removed under reduced pressure and the residue was extracted into hexane (2 × 100 ml). After filtration, the solution was concentrated and cooled at −30 °C to give a yellow solid characterized as **6** (3.09 g, 7.77 mmol, 72% yield). Anal. Calc. for $C_{14}H_{25}Cl_2NSiZr$: C, 42.30; H, 6.34; N, 3.52. Found: C, 42.47; H, 6.44; N, 3.70%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ 0.45 (d, 3H, Si*Me*, $J = 3.3$ Hz), 1.32 (s, 9H, N^tBu), 1.91 (s, 3H, C_5Me_4), 1.92 (s, 3H, C_5Me_4), 1.99 (s, 3H, C_5Me_4), 2.13 (s, 3H, C_5Me_4), 5.60 (q, 1H, Si*H*, $J = 3.3$ Hz). ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.69 (d, 3H, Si*Me*, $J = 3.3$ Hz), 1.38 (s, 9H, N^tBu), 2.15 (s, 3H, C_5Me_4), 2.18 (3s, 9H, C_5Me_4), 5.52 (q, 1H, Si*H*, $J = 3.3$ Hz). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6, 25 °C): δ 2.6 (Si*Me*), 11.6, 11.9, 13.3, 14.4 (C_5Me_4), 32.5 (N^tBu), 56.3 (C_{ipso}, N^tBu), 98.1 (C_{ipso}, C_5Me_4), 131.9, 132.0, 134.5, 134.5 (C_5Me_4). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 25 °C): δ 2.6 (Si*Me*), 11.8, 12.0, 13.3, 14.4 (C_5Me_4), 32.5 (N^tBu), 56.4 (C_{ipso}, N^tBu), 98.0 (C_{ipso}, C_5Me_4), 131.8, 131.9, 134.5, 134.5 (C_5Me_4). $^{29}Si\{^1H\}$-NMR (59.6 MHz, $CDCl_3$, 25 °C): δ −40.76.

3.8. Synthesis of $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)Me_2]$ (7)

A 3 M solution of MgClMe in THF (1.6 ml, 4.6 mmol) was added to a solution of **6** (0.92 g, 2.3 mmol) in diethyl ether (40 ml) cooled at −78 °C. The reaction mixture was slowly warmed to r.t. and then stirred for 16 h. The volatiles were removed under reduced pressure and the residue was extracted into hexane (50 ml). After filtration, solvent was removed under vacuum to give **7** as an analytically pure orange waxy solid (0.79 g, 2.2 mmol, 96% yield). Anal. Calc. for $C_{16}H_{31}NSiZr$: C, 53.87; H, 8.76; N, 3.93. Found: C, 54.11; H, 8.88; N, 4.07%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ 0.01 (s, 3H, Zr*Me*), 0.02 (s, 3H, Zr*Me*), 0.51 (d, 3H, Si*Me*, $J =$ 3.3 Hz), 1.40 (s, 9H, N^tBu), 1.89 (2s, 6H, C_5Me_4), 1.95 (s, 3H, C_5Me_4), 2.09 (s, 3H, C_5Me_4), 5.62 (q, 1H, Si*H*, $J = 3.3$ Hz). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6, 25 °C): δ 3.4 (Si*Me*), 11.2, 11.4, 12.8, 14.0 (C_5Me_4), 33.7 (N^tBu), 36.0, 37.0 (Zr*Me*), 54.5 (C_{ipso}, N^tBu), 92.7 (C_{ipso}, C_5Me_4), 125.6, 125.9, 130.5, 130.6 (C_5Me_4).

3.9. Synthesis of $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)(CH_2Ph)_2]$ (**8**)

A 2 M solution of MgClBz in THF (2.9 ml, 5.8 mmol) was added to a solution of **6** (1.11 g, 2.8 mmol) in diethyl ether (80 ml) cooled at −78 °C. The reaction mixture was slowly warmed to r.t. and then stirred for 16 h. The volatiles were removed under reduced pressure and the residue was extracted into hexane (100 ml). After filtration, the solution was concentrated to 10 ml and cooled to −30 °C to give a yellow solid characterized as **8** (1.02 g, 2 mmol, 71% yield). Anal. Calc. for $C_{28}H_{39}NSiZr$: C, 66.08; H, 7.72; N, 2.75. Found: C, 66.17; H, 7.90; N, 2.67%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ 0.49 (d, 3H, Si*Me*, $J = 3$ Hz), 1.14 (s, 9H, N^tBu), 1.54 (d, 1H, $TiCH_2Ph$, $J = 10.8$ Hz), 1.71 (d, 1H, $TiCH_2Ph$, $J = 11.1$ Hz), 1.74 (2s, 6H, C_5Me_4), 1.90 (d, 1H, $TiCH_2Ph$, $J = 10.8$ Hz), 1.91 (s, 3H, C_5Me_4), 1.94 (d, 1H, $TiCH_2Ph$, $J = 11.1$ Hz), 2.05 (s, 3H, C_5Me_4), 5.56 (q, 1H, Si*H*, $J = 3$ Hz), 6.78–7.15 (m, 10H, *Ph*). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6, 25 °C): δ 3.3 (Si*Me*), 11.1, 11.4, 12.9, 14.1 (C_5Me_4), 33.1 (N^tBu), 56.2 (C_{ipso}, N^tBu), 61.8, 61.9 ($TiCH_2Ph$), 94.9 (C_{ipso}, C_5Me_4), 122.0, 122.4, 127.2, 127.3, 129.0, 129.3 (*Ph*), 126.6, 128.6, 130.4 (C_5Me_4, one not observed), 146.2, 147.3 (C_{ipso}, *Ph*).

3.10. Synthesis of $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)(NMe_2)_2]$ (**9**)

Toluene (40 ml) at −78 °C was added to a mixture of **6** (0.24 g, 0.61 mmol) and $LiNMe_2$ (0.062 g, 1.22 mmol). The reaction mixture was warmed to r.t. and stirred for 21 h. The solvent was removed under vacuum and the residue was extracted into hexane (40 ml). After filtration, the solvent was evaporated under vacuum to give **9** as a yellow solid (0.24 g, 0.58 mmol, 95% yield). Anal. Calc. for $C_{18}H_{37}N_3SiZr$: C, 52.12; H, 8.99; N, 10.13. Found: C, 51.24; H, 8.88; N, 9.20%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ 0.71 (d, 3H, Si*Me*, $J = 3$ Hz), 1.34 (s, 9H, N^tBu), 1.86 (s, 3H, C_5Me_4), 1.89 (s, 3H, C_5Me_4), 2.11 (s, 3H, C_5Me_4), 2.27 (s, 3H, C_5Me_4), 2.80 (s, 6H, $ZrNMe_2$), 2.86 (s, 6H, $ZrNMe_2$), 5.88 (q, 1H, Si*H*, $J = 3$ Hz). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6, 25 °C): δ 4.4 (Si*Me*), 10.9, 11.1, 12.7, 13.5 (C_5Me_4), 33.9 (N^tBu), 44.1, 44.7 ($ZrNMe_2$), 55.6 (C_{ipso}, N^tBu), 97.7 (C_{ipso}, C_5Me_4), 124.4, 125.5, 127.1 (2) (C_5Me_4).

3.11. Synthesis of $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)Cl(C_6F_5)]$ (**10**)

A 1.02 M solution of $MgCl(C_6F_5)$ in diethyl ether (4.0 ml, 4.0 mmol) was added to a solution of **6** (0.8 g, 2 mmol) in diethyl ether (50 ml) cooled at −78 °C. The reaction mixture was slowly warmed to r.t. and then stirred for 16 h. The volatiles were removed under reduced pressure and the residue was extracted into hexane (60 ml). After filtration, the solution was concentrated to 10 ml and cooled to −30 °C to give a yellow solid characterized as the monoalkylated product **10** (0.75 g, 1.42 mmol, 71% yield). Anal. Calc. for $C_{20}H_{25}ClF_5NSiZr$: C, 45.40; H, 4.76; N, 2.65. Found: C, 44.55; H, 4.46; N, 2.77%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ 0.47 (d, 3H, Si*Me*, $J = 3.3$ Hz), 0.51 (d, 3H, Si*Me*, $J = 3.3$ Hz), 1.39 (2s, 18H, N^t*Bu*), 1.47, 1.49, 1.67, 1.83, 2.05, 2.06, 2.07, 2.21 (8s, 24H, C_5Me_4), 5.58 (q, 1H, Si*H*, $J = 3.3$ Hz), 5.62 (q, 1H, Si*H*, $J = 3.3$ Hz). ^{13}C{^{1}H}-NMR (75 MHz, C_6D_6, 25 °C): δ 2.5, 3.1 (Si*Me*), 11.6, 11.7, 12.6, 12.9, 13.7, 14.6, 14.7, 15.8 (C_5Me_4), 32.5, 32.8 (N^t*Bu*), 58.3, 58.4 (C_{ipso}, N^t*Bu*), 96.9, 97.2 (C_{ipso}, C_5Me$_4$), 131.4, 131.5, 132.1, 132.4, 135.3, 135.6, 135.7 (C_5Me$_4$, one not observed).

3.12. Synthesis of $[Zr(\eta^5\text{-}C_5Me_4SiMeH\text{-}\eta^1\text{-}N^tBu)Cl\{N(SiMe_3)_2\}]$ (**11**)

A mixture of **6** (0.62 g, 1.56 mmol) and $LiN(SiMe_3)_2$ (0.26 g, 1.56 mmol) in toluene (35 ml) was stirred at 100 °C for 18 h. The volatiles were removed under reduced pressure and the residue was extracted into hexane (60 ml). After filtration, solvent was removed under vacuum to give **11** as a yellow solid (0.74 g, 1.42 mmol, 91% yield). Anal. Calc. for $C_{20}H_{43}ClN_2Si_3Zr$: C, 45.97; H, 8.29; N, 5.36. Found: C, 46.05; H, 8.32; N, 5.10%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ 0.28 (s, 9H, N(SiMe_3)), 0.30 (s, 9H, N(SiMe_3)), 0.38 (2s, 18H, N(SiMe_3)$_2$), 0.61 (2d, 6H, Si*Me*H, $J = 3.3$ Hz), 1.40 (2s, 18H, N^t*Bu*), 1.89, 1.91, 2.02, 2.03, 2.13, 2.13, 2.26, 2.26 (8s, 24H, C_5Me_4), 5.64 (q, 1H, Si*H*, $J = 3.3$ Hz), 5.75 (q, 1H, Si*H*, $J = 3.3$ Hz). ^{13}C{^{1}H}-NMR (75 MHz, C_6D_6, 25 °C): δ 3.4, 3.8 (Si*Me*H), 5.9 (2), 7.1, 7.3 (N(SiMe_3)$_2$), 12.5, 12.6, 12.8, 14.4, 14.5, 15.2, 15.6, 15.9 (C_5Me_4), 32.3, 32.3 (N^t*Bu*), 56.9, 57.0 (C_{ipso}, N^t*Bu*), 98.0, 99.2 (C_{ipso}, C_5Me$_4$), 126.1, 126.5, 127.1, 131.3, 131.8, 131.9, 133.4, 133.8 (C_5Me$_4$).

3.13. Synthesis of $[Zr(\eta^5\text{-}C_5Me_4SiMeCl\text{-}\eta^1\text{-}N^tBu)Cl_2]$ (**12**)

A 1 M solution of BCl_3 in heptane (4.4 ml, 4.33 mmol) was added to a solution of **6** (1.72 g, 4.33 mmol) in CH_2Cl_2 (45 ml) cooled at −78 °C. The reaction mixture was slowly warmed to r.t. and then stirred for 16 h. The solvent was removed and the residue was extracted into pentane (100 ml). The pentane solution was concentrated to 10 ml and cooled to −30 °C to give a pale yellow solid characterized as **12** (1.35 g, 3.1 mmol, 72% yield). Anal. Calc. for $C_{14}H_{24}Cl_3NSiZr$: C, 38.92; H, 5.60; N, 3.24. Found: C, 39.02; H, 5.64; N, 3.03%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ 0.71 (s, 3H, Si*Me*Cl), 1.38 (s, 9H, N^t*Bu*), 1.85 (s, 3H, C_5Me_4), 1.86 (s, 3H, C_5Me_4), 1.87 (s, 3H, C_5Me_4), 2.27 (s, 3H, C_5Me_4). ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.96 (s, 3H, Si*Me*Cl), 1.46 (s, 9H, N^t*Bu*), 2.13 (s, 3H, C_5Me_4), 2.20 (s, 3H, C_5Me_4), 2.21 (s, 3H, C_5Me_4), 2.26 (s, 3H, C_5Me_4). ^{13}C{^{1}H}-NMR (75 MHz, C_6D_6, 25 °C): δ 9.3 (Si*Me*Cl), 11.7, 11.9, 14.5, 14.6 (C_5Me_4), 32.9 (N^t*Bu*), 57.1 (C_{ipso}, N^t*Bu*), 101.8 (C_{ipso}, C_5Me$_4$), 130.5, 132.6, 132.8, 135.7 (C_5Me$_4$). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 25 °C): δ 9.3 (Si*Me*Cl), 11.9, 12.1 14.5 14.6 (C_5Me_4), 32.9 (N^t*Bu*), 57.2 (C_{ipso}, N^t*Bu*), 101.6 (C_{ipso}, C_5Me$_4$), 130.5, 132.5, 132.8 135.7 (C_5Me$_4$). ^{29}Si{^{1}H}-NMR (59.6 MHz, $CDCl_3$, 25 °C): δ −23.15.

3.14. Synthesis of $[Zr(\eta^5\text{-}C_5Me_4SiMeCl\text{-}\eta^1\text{-}N^tBu)Me_2]$ (**13**)

A 3 M solution of MgClMe in THF (0.76 ml, 2.28 mmol) was added to a solution of **12** (0.49 g, 1.14 mmol) in diethyl ether (40 ml) cooled at −78 °C. The reaction mixture was slowly warmed to r.t. and then stirred for 15 h. The volatiles were removed under reduced pressure and the residue was extracted into pentane (40 ml). After filtration, solvent was removed under vacuum to give **13** as a pale yellow solid (0.29 g, 0.74 mmol, 65% yield). Anal. Calc. for $C_{16}H_{30}ClNSiZr$: C, 49.13; H, 7.73; N, 3.58. Found: C, 48.77; H, 7.67; N, 3.85%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ −0.04 (s, 3H, Zr*Me*), 0.04 (s, 3H, Zr*Me*), 0.75 (s, 3H, Si*Me*Cl), 1.45 (s, 9H, N^t*Bu*), 1.80 (2s, 6H, C_5Me_4), 1.81 (s, 3H, C_5Me_4), 2.23 (s, 3H, C_5Me_4). ^{13}C{^{1}H}-NMR (75 MHz, C_6D_6, 25 °C): δ 9.9 (Si*Me*Cl), 11.2, 11.3, 14.0, 14.1 (C_5Me_4), 34.0 (N^t*Bu*), 37.7, 38.7 (Zr*Me*), 55.3 (C_{ipso}, N^t*Bu*), 95.9 (C_{ipso}, C_5Me$_4$), 124.7, 125.9, 128.5, 131.7 (C_5Me$_4$).

3.15. Synthesis of $[Zr(\eta^5\text{-}C_5Me_4SiMeCl\text{-}\eta^1\text{-}N^tBu)Cl\{N(SiMe_3)_2\}]$ (**14**)

A mixture of **12** (0.44 g, 1.02 mmol) and $LiN(SiMe_3)_2$ (0.17 g, 1.02 mmol) in toluene (30 ml) was stirred at 105 °C for 20 h. The volatiles were removed under reduced pressure and the residue was extracted into hexane (40 ml). After filtration, solvent was removed under vacuum to give **14** as a pale yellow solid (0.55 g, 0.99 mmol, 97% yield). Anal. Calc. for $C_{20}H_{42}Cl_2N_2Si_3Zr$: C, 43.13; H, 7.60; N, 5.03. Found: C, 43.48; H, 7.71; N, 4.76%. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ 0.20 (s, 9H, N(SiMe_3)), 0.33 (s, 9H, N(SiMe_3)), 0.36 (2s, 18H, N(SiMe_3)$_2$), 0.86 (s, 3H, Si*Me*Cl), 0.91 (s, 3H, Si*Me*Cl), 1.44 (s, 9H, N^t*Bu*), 1.50 (s, 9H, N^t*Bu*), 1.83, 1.85, 1.96, 1.96, 1.98, 2.00, 2.40, 2.46 (8s, 24H, C_5Me_4). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6, 25 °C): δ 5.4, 5.5, 6.6, 6.7 ($N(SiMe_3)_2$), 9.9, 10.3 (SiMeCl), 12.1, 12.2, 12.3, 12.3, 14.3, 15.2, 15.3, 15.6 (C_5Me_4), 32.2, 32.4 (N^tBu), 57.1, 57.4 (C_{ipso}, N^tBu), 101.1, 102.4 (C_{ipso}, C_5Me_4), 124.7, 126.8, 130.2, 130.9, 131.8, 132.4, 132.7, 134.9 (C_5Me_4).

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