sp^3-C^1-Bridged 1,3-Me_2Cp/Amido Titanium and Zirconium Complexes and Their Reactivities towards Ethylene Polymerization

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sp^3-C^1-Bridged Cp/amido titanium and zirconium complexes are synthesized by using novel fulvenes that have substituents in the 1-, 4-, and 6-positions only. Thus, the nucleophilic attack of lithium *tert*-butylamide on 1,4-dimethyl-6-phenylfulvene, 6-(2-furyl)-1,4-dimethylfulvene and 6-cyclohexyl-1,4-dimethylfulvene, and subsequent aqueous workup, yields *t*BuN(H)–CHR–$C_5H_3Me_2$ (R = phenyl, **6**; R = 2-furyl, **7**; R = cyclohexyl, **8**) in 80, 88, and 60% yields, respectively. The reactions of the ligands with $M(NMe_2)_4$ (M = Ti or Zr) afford the desired bis(dimethylamido) complexes, which can be transformed by treatment with Me_2SiCl_2 to the dichloride complexes, (1,3-$Me_2C_5H_2$–CHR–N*t*Bu–κ*N*)MCl_2 (M = Ti, R = phenyl, **10**; M = Zr, R = phenyl, **11**; M = Ti, R = 2-furyl, **13**; M = Zr, R = 2-furyl, **14**; M = Zr, R = cyclohexyl, **15**). Complex **10** is very sensitive towards water, such that an oxo-bridged dimer, (1,3-$Me_2C_5H_2$–CHPh–NH*t*Bu)$ZrCl_2$–μO–$ZrCl_2$(1,3-$Me_2C_5H_2$–CHPh–NH*t*Bu) (**12**), is easily formed by the abstraction of water from the solvents. The solid structures of (1,3-$Me_2C_5H_2$–CHPh–N*t*Bu–κ*N*)$Zr(NMe_2)_2$, **10**, **11**, and **12** have been determined by X-ray crystallography. The complexes are active towards the polymerization of ethylene when activated with MAO. The activities are rather low and the molecular weight distributions are broad (M_w/M_n = 10–36).

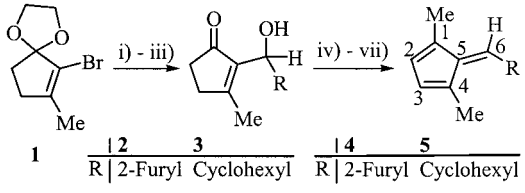
Introduction

Various group 4 *ansa*-metallocene complexes, which have drawn attention as homogeneous Ziegler catalysts, can be synthesized from fulvenes. The C^1-bridged Cp/fluorenyl and C^1-bridged Cp/indenyl complexes are typical examples.[1] Some C^1-bridged Cp/Cp,[2] C^2-bridged Cp/Cp,[3] and C^3-bridged Cp/Cp complexes[4] are also obtained from fulvenes. Recently, Erker et al. reported on the syntheses of sp^3-C^1-bridged Cp/amido titanium and zirconium complexes using 6-*tert*-butylfulvene and 1,2,3,4-tetramethylfulvene.[5] Fulvenes are conventionally synthesized by the base-mediated coupling of cyclopentadiene with aldehydes or ketones.[6] If mono-substituted or 1,3-disubstituted cyclopentadienes are used, the substituents are located mainly in the 2-position or the 1,3-positions in the resulting fulvenes due to steric reasons. Recently, we reported on a synthetic route for the preparation of 1,4-dimethyl-6-phenylfulvene, which is a novel product as it has substituents in the 1-, 4-, and 6-positions only, and we demonstrated the synthesis of a C^1-bridged 1,3-Me_2Cp/fluorenyl zirconium complex using the fulvene.[7] Herein, we report on the syntheses and characterizations of C^1-bridged 1,3-Me_2Cp/amido zirconium and titanium complexes using fulvenes that have substituents in the 1-, 4- and 6-positions only. The complexes are characteristic since the methyl substituents on the cyclopentadienyl ligand are located next to the bridge.[8] In these complexes, the steric congestion at the reaction site is minimized, while an electronic effect is imposed by the substituents.[9]

Results and Discussion

Syntheses and Characterizations

6-(2-Furyl)-1,4-dimethylfulvene (**4**) and 6-cyclohexyl-1,4-dimethylfulvene (**5**) were synthesized by a similar method using the same conditions as that developed for the syn-



Scheme 1. i) *n*BuLi; ii) RC(O)H; iii) HCl; iv) dihydropyran, *p*-TsOH; v) MeLi; vi) HCl; vii) NaOMe

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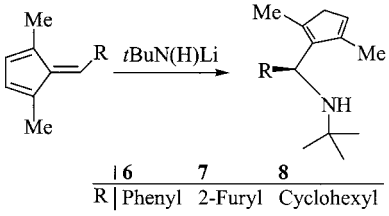
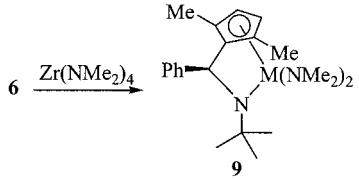
thesis of 1,4-dimethy-6-phenylfulvene (Scheme 1). The overall yields from the starting material **1** were 31% and 42% for **4** and **5**, respectively. The ^{1}H NMR spectra, ^{13}C NMR spectra, and the elemental analyses are in agreement with the fulvene structures of **4** and **5**.

The nucleophilic attack of lithium *tert*-butylamide on the fulvenes in THF, followed by aqueous workup, afforded the desired ligands **6**, **7**, and **8** in 80, 88, and 60% yields, respectively (Scheme 2). Substituted cyclopentadienes are frequently obtained as a set of isomers due to the rapid 1,5-sigmatropic rearrangement.[10] However, compounds **6**, **7**, and **8** were obtained as single isomers, as a result of the symmetry of the substituents, and were characterized unambiguously by ^{1}H and ^{13}C NMR spectroscopy. Comparison of the ^{13}C NMR spectra of the three compounds assists in the assignment of the signals. The signal at 125 ppm is assigned to Cp−*C*H and the signals for Cp−*C*(CH$_3$) are observed at 140−144 ppm. The signals assigned to Cp−*C*(bridgehead) and Cp−*C*H$_2$ are observed at 136−138 ppm and 44 ppm, respectively.



Scheme 2

The reaction of **6** with Zr(NMe$_2$)$_4$ at 100 °C for 2 days afforded the desired C^1-bridged 1,3-Me$_2$Cp/amido zirconium complex **9** (Scheme 3).[11] The dimethylamine formed was removed by a stream of nitrogen gas. When the reaction was carried out by heating without the stream of nitrogen, the reaction stops with the formation of unbridged tris(dimethylamido)Cp complex. The ^{1}H and ^{13}C NMR spectra support the structure shown in Scheme 3. Signals for the Cp protons are observed as a pair of doublets (J = 2.8 ppm) at 5.88 ppm and 5.48 ppm in the ^{1}H NMR spectrum (C$_6$D$_6$), and the methyl signals of the dimethylamido group are observed as a pair of singlets at 3.09 and 2.89 ppm. The signal for the bridgehead carbon on the Cp moiety is observed at 105.76 ppm in the ^{13}C NMR spectrum. Complex **9** is a solid, and single crystals suitable for X-ray crystallography were obtained by recrystallization in pentane at −30 °C. The X-ray crystallographic studies confirm the structure shown in Scheme 3. The thermal ellipsoid plot is shown in Figure 1.



Scheme 3

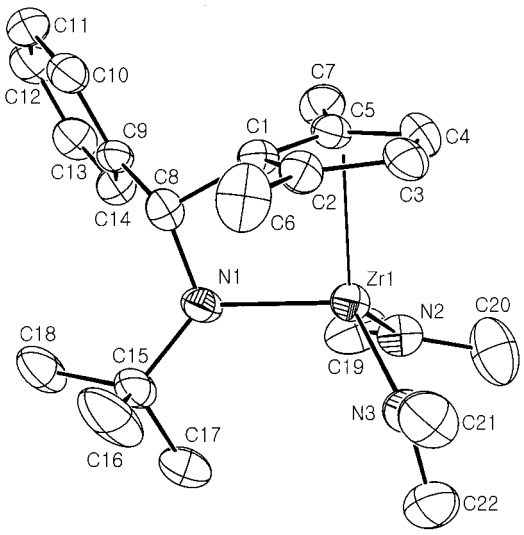
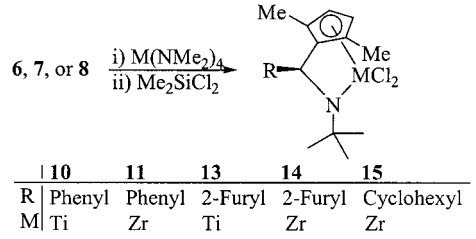


Figure 1. Thermal ellipsoid plot (30% probability level) of the structure of **9**

Similar reactions of **7** and **8** with Zr(NMe$_2$)$_4$, and reactions of **6** and **7** with Ti(NMe$_2$)$_4$, afforded the corresponding bis(dimethylamido) complexes. The reaction of **8** with Ti(NM$_2$)$_4$ was sluggish under identical conditions. The bis(dimethylamido) complexes are oily and therefore could not be purified by recrystallization; however, the ^{1}H and ^{13}C NMR spectra strongly support their formation. The crude products have been used for the proceeding chlorination reactions without further purification. The synthetic method described here is complementary to that developed by Erker, who obtained the Cp and tetramethylcyclopentadienyl analogues by treating the corresponding dilithium salts with TiCl$_2$(NMe$_2$) or ZrCl$_2$(NEt$_2$)$_2$(THF)$_2$.[5]

Erker attempted to convert (Me$_4$Cp−CH$_2$−N*t*Bu)Zr(NEt$_2$)$_2$ to (Me$_4$Cp−CH$_2$−N*t*Bu)ZrCl$_2$ by treatment with excess unpurified Me$_3$SiCl.[5] He unexpectedly obtained an μ-oxo complex, (Me$_4$Cp−CH$_2$−N*t*Bu)ZrCl$_2$−μO−ZrCl$_2$(Me$_4$Cp−CH$_2$−N*t*Bu). The yield of the μ-oxo complex was relatively low (40%), and a complicated mixture of unidentified products was observed in the ^{1}H NMR spectrum. When the reaction of two equivalents of carefully dried Me$_3$SiCl with the bis(dimethylamido) titanium complex of **6** in C$_6$D$_6$ was followed by ^{1}H NMR spectroscopy, it was seen that only one dimethylamido ligand was replaced by the chloride ligand giving (1,3-Me$_2$C$_5$H$_2$−CHPh−N*t*Bu−κ*N*)TiCl(NMe$_2$). Complete chlorination is achieved using Me$_2$SiCl$_2$.[12] Addition of four equivalents of Me$_2$SiCl$_2$ in C$_6$D$_6$ resulted in the formation of the desired dichloride complex **10** (Scheme 4). The ^{1}H and ^{13}C NMR spectra are in agreement with the structure of the dichloride complex. Single crystals of **10** suitable for X-ray crystallography were obtained in toluene at −30 °C and X-ray crystallographic studies confirm the dichloride structure (Figure 2).

Addition of two equivalents of Me$_2$SiCl$_2$ to the bis(dimethylamido)zirconium complex **9** in benzene and overnight stirring, resulted in the precipitation of a white solid. The ^{1}H and ^{13}C NMR spectra of the precipitate strongly sup-



Scheme 4

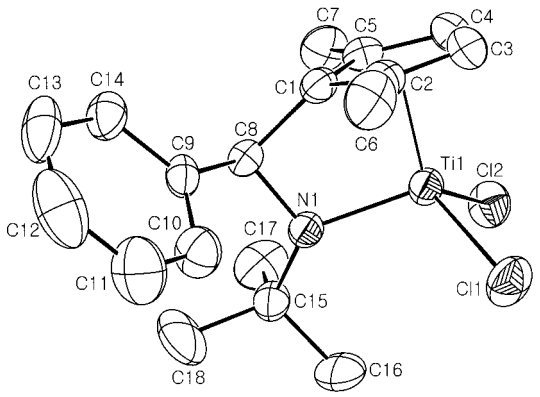
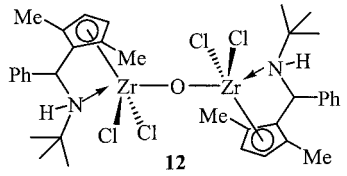


Figure 2. Thermal ellipsoid plot (30% probability level) of the structure of **10**

port the formation of the desired dichloride complex **11** (Scheme 4). The main features of the NMR spectra are almost identical to those observed for titanium complex **10**. However, X-ray crystallographic studies of a single crystal, which was obtained by dissolving the precipitate in benzene and by the slow addition of pentane vapor at room temperature, reveal the structure of an unexpected dinuclear μ-oxo complex, **12** (Figure 3). A similar dinuclear μ-oxo complex was observed by Erker when (Me_4Cp-CH_2-NtBu)$Zr(NEt_2)_2$ was treated with excess unpurified Me_3SiCl.[5]



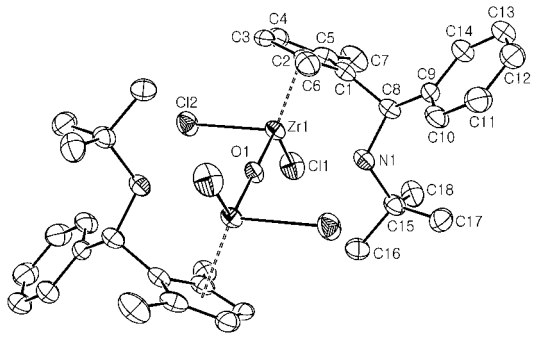


Figure 3. Thermal ellipsoid plot (30% probability level) of the structure of **12**

Since the ^1H and ^{13}C NMR spectra of the precipitate strongly support the structure of the desired mononuclear complex **11**, the formation of **12** may be attributed to the presence of water as an impurity in the recrystallization solvents. Single crystals suitable for X-ray crystallography were directly deposited when **9** and Me_2SiCl_2 were mixed in benzene and reacted without stirring for several days at room temperature. X-ray crystallographic studies of a single crystal obtained by this procedure reveal the desired structure of the mononuclear complex **11** (Figure 4). Complexes **13**–**15** were synthesized in a similar manner, by the reactions of two or three equivalents of Me_2SiCl_2 with the crude bis(dimethylamido) complexes, which are obtained by the reaction of **7** with $Ti(NMe_2)_4$ and reactions of **7** and **8** with $Zr(NMe_2)_4$ (Scheme 4).

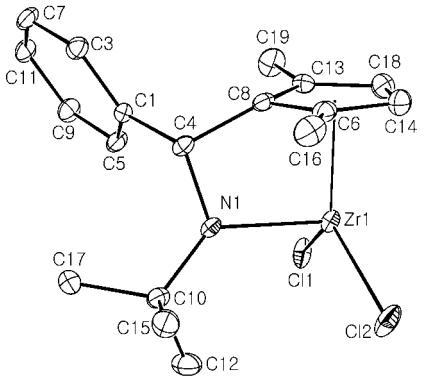


Figure 4. Thermal ellipsoid plot (30% probability level) of the structure of **11**

Crystal Structures of 9, 10, 11, and 12

The thermal ellipsoid plots of **9**, **10**, and **11** are shown in Figures 1, 2, and 4, respectively, and the selected bond lengths and angles are tabulated in Table 1. The crystal structures show the tetrahedral coordination geometry of the central zirconium or titanium atoms. The cyclopentadienyl ligands are η^5-coordinated, with a systematic increase in the Zr–C bond lengths on moving from the bridgehead carbon atom to the peripheral carbon atoms. The M–C distances observed for the titanium complex **10** are shorter than the corresponding distances observed for the zirconium complexes **9** and **11**, and the M–C distances observed for the bis(dimethylamido) complex **9** are longer than those observed for the dichloride complex **11**. A similar trend is observed for the M–N*t*Bu distances of **9**, **10**, and **11**. The Cl–M–Cl angle observed for the zirconium complex **11** [123.27(5)°] is greater than that observed for the titanium complex **10** [104.11(7)°], as well as for the N–Zr–N angle observed for **9** [104.56(16)°]. The bridge carbon atoms are out of the Cp planes, and consequently the $Cp^{centroid}-C^{bridgehead}-C^{bridge}$ bond angles deviate from the ideal value of 180°. The $Cp^{centroid}-C^{bridgehead}-C^{bridge}$ angle observed for the titanium complex **10** (152.1°) is smaller than those observed for the zirconium complexes **9** and **11** (156.2 and 155.8°, respectively), indicating that the bridge carbon atom is further out of the Cp plane in the

Table 1. Selected bond lengths (Å) and angles (°)

	9	**10**	**11**	**12**
M−Cl(or N)[a]	2.033(4)	2.2801(15)	2.5292(18)	2.4688(13)
M−Cl(or N)	2.061(4)	2.2653(16)	2.4310(15)	2.4265(14)
M−NC^{bridge}	2.106(3)	1.924(4)	2.076(3)	2.536(4)[b]
M−$C^{bridgehead}$	2.420(4)	2.256(4)	2.390(4)	2.444(4)
M−$C^{cp}(CH_3)$[a]	2.466(4)	2.338(5)	2.484(4)	2.521(5)
M−$C^{cp}(CH_3)$	2.557(4)	2.315(5)	2.462(4)	2.483(4)
M-$C^{cp}H^a$	2.525(4)	2.360(5)	2.508(4)	2.549(5)
M−$C^{cp}H$	2.587(4)	2.373(5)	2.503(4)	2.514(4)
M−$Cp^{centroid}$	2.206	1.992	2.156	2.199
$C^{bridgehead}$−C^{bridge}	1.543(5)	1.543(6)	1.529(5)	1.513(6)
C^{bridge}−N	1.470(5)	1.469(5)	1.469(4)	1.485(5)
$Cp^{centroid}$−M−NC^{bridge}	90.7	97.1	91.0	
$Cp^{centroid}$-$C^{bridgehead}$-C^{bridge}	156.2	152.1	155.8	164.8
Cl(or N)−M−Cl (or N)	104.56(16)	104.11(7)	123.27(5)	87.04(5)
$C^{bridgehead}$−C^{bridge}−N	100.9(3)	97.3(3)	99.3(3)	103.3(3)
C^{bridge}−*N*−M	106.7(2)	107.1(3)	107.5(2)	98.1(3)
C^{bridge}−*N*−CMe_3	118.2(3)	120.4(3)	119.4(3)	117.9(4)
M−*N*−CMe_3	127.9(3)	129.5(3)	131.0(2)	129.8(3)

[a] Bond length with respect to the side to which the phenyl group is located. [b] Zr−O distance, 1.9526(5) Å.

titanium complex **10**. The $C^{bridgehead}$−C^{bridge}−N angles (100.9(3), 97(3) and 99.3(3) ° for **9**, **10**, and **11**, respectively) deviate from the ideal sp^3-tetrahedral angle (109.5°). The $Cp^{centroid}$−M−NC^{bridge} angles observed for **9**, **10**, and **11** are smaller than that observed for the related complex $(Me_4CpSiN)Zr(NR_2)_2$ (100.2°).[13] The $Cp^{centroid}$−M−NC^{bridge} angles observed for the zirconium complexes **9** and **11** (90.7 and 91.0°, respectively) are smaller than that observed for the titanium complex **10** (97.1°), reflecting that the constraint imposed by the Cp−C^{bridge}−N−M frame is larger in the zirconium complexes than in the titanium complex. The nitrogen atoms on the dimethylamido ligand in **10** form a perfect trigonal planar structure (sum of the bond angles are 359.1° and 359.9°). The nitrogen atoms bonded to the *tert*-butyl group in the dichloride complexes **10** and **11** also almost form a trigonal planar structure (sum of bonding angles, 357.0° and 357.9°, respectively), however, the corresponding nitrogen atoms in the bis(dimethylamido) complex **9** deviate from the trigonal planar structure (sum of the bond angles is 352.8°).

The thermal ellipsoid plot of **12** is shown in Figure 3 and the selected bond lengths and angles are tabulated in Table 1. The metrical parameters observed for **12** are very similar to those observed for $[Me_4Cp-CH_2-N(H)tBu]ZrCl_2-O-ZrCl_2[Me_4Cp-CH_2-N(H)tBu]$, with the exception of the Zr−O−Zr angle. A strictly linear Zr−O−Zr arrangement (180°) is observed for complex **12**, while a somewhat bent structure is observed for $[Me_4Cp-CH_2-N(H)tBu]ZrCl_2-O-ZrCl_2[Me_4Cp-CH_2-N(H)tBu]$ (the Zr−O−Zr angle is 168.2°).

Ethylene Polymerization Studies

The dichloride complexes **10**, **11**, and **13**−**15** are active towards the polymerization of ethylene when activated with MAO (Table 2). The activities are low compared with that of Cp_2ZrCl_2, but are similar to those of the cyclopentadienyl or tetramethylcyclopentadienyl analogues previously prepared by Erker.[5] The titanium complexes show higher activities relative to the zirconium complexes (entry 1 and 3 versus entry 2 and 4). The activity depends strongly on the substituent attached to the bridge carbon atom. The complexes that have the 2-furyl group show the highest activity (entry 3 and 4), and the activity of the zirconium complex that has the 2-furyl substituent is 10 times higher than the complex that has a phenyl substituent (entry 2 and 4). The complex *rac*-(EBI)$Zr(NMe_2)_2$ was reported to be less active than the corresponding dichloride complex when activated with MAO.[14] However, in this case, the bis(dimethylamido) complex **9** shows a higher activity than the corresponding dichloride complex **11** (entry 2 and 6). The titanium complex **13**, which shows the highest activity, produces a polymer with the highest molecular weight (M_w, 610,000). The molecular weight distributions are very broad (M_w/M_n = 10−36), indicating that there are several types of active species in the polymerization solution.

Table 2. Ethylene polymerization results

Entry	Compound[a]	Time (min)	Activity (kg/mol·h)	M_w[c]	M_w/M_n[c]
1	**10**[b]	30	92	34000	14
2	**11**	30	16	361000	36
3	**13**	10	318	610000	32
4	**14**	20	150	198000	29
5	**15**	30	71	348000	10
6	**9**	30	122	150000	24

[a] Polymerization conditions: 30 mL toluene, 60 °C, 10 μmol catalyst, Al/Zr or Ti = 500, 100 psig ethylene. [b] 5.0 μmol catalyst, Al/Zr or Ti = 1000. [c] Determined by GPC in 1,2,4-trichlorobenzene at 140 °C against polystyrene standards.

Conclusion

sp^3-C^1−bridged Cp/amido CGC complexes (1,3-$Me_2C_5H_2$−CHR−N*t*Bu−κ*N*)MCl_2 (M = Ti, Zr; R = phenyl, 2-furyl, cyclohexyl) have been synthesized using novel fulvenes that have substituents in the 1-, 4-, and 6-positions only. The bis(dimethylamido) complexes, which have been prepared by the reaction of $M(NMe_2)_4$ with *t*BuN(H)−CHR−$C_5H_3Me_2$, can be transformed to the dichloride complexes by treatment with Me_2SiCl_2. The complexes are active towards the polymerization of ethylene when activated with MAO. The titanium complexes show higher activities relative to the zirconium complexes, and the titanium complex that has a 2-furyl group on the bridge carbon atom shows the highest activity. The molecular weight distributions are broad (M_w/M_n, 10−36).

Experimental Section

General Remarks: All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Toluene, pentane, THF, diethyl ether, and benzene were distilled from benzophenone ketyl. Toluene used for the polymerization reaction was purchased from Aldrich (anhydrous grade) and purified further over Na/K alloy. Dichlorodimethylsilane was dried over CaH_2. Ethylene was purchased from Conley Gas (99.9%) and purified by contactwith molecular sieves and copper overnight under a pressure of 150 psig. Methylaluminoxane (MAO) was purchased as a solution in toluene from Akzo (7.6 weight% of Al, MMAO type 4). The NMR spectra were recorded on a Varian Mercury plus 400 spectrometer. Elemental analyses were carried out at the Inter-University Center Natural Science Facilities, Seoul National University. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using a Waters Model 150-C+ GPC, and the data were analyzed using a polystyrene analyzing curve.

Compound 2: *n*BuLi (3.82 g, 2.5 M in hexane, 13.8 mmol) at −78 °C was added dropwise to a Schlenk flask containing **1** (3.00 g, 13.8 mmol) in THF (5 mL), and the solution was stirred for 1 hour at −78 °C. Furfural (1.32 g, 13.8 mmol) was added and the solution was stirred for 2 hours at −78 °C. The solution was poured into a separating funnel containing water (20 mL), and the product was extracted with ethyl acetate (10 mL × 5). The combined organic layer was shaken with aqueous HCl (1 N, 20 mL) for about 30 seconds, in which step the ketal group was deprotected to give a carbonyl compound. The organic layer was washed with concentrated aqueous $NaHCO_3$ solution (20 mL). The organic layer was collected and dried over anhydrous $MgSO_4$. The solvent was removed to give a residue, which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 2:1) (white solid, 1.44 g, 54%). M.p. 74 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.10 (s, 3 H, CH_3), 2.44−2.48 (m, 2 H, CH_2), 2.58−2.63 (m, 2 H, CH_2), 4.64 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, OH), 5.60 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, OCH), 6.22 [dd, $^3J_{H,H}$ = 3.2, $^3J_{H,H}$ = 0.8 Hz, 1 H, furyl-C(4)−H], 6.31 [dd, $^3J_{H,H}$ = 3.2, $^4J_{H,H}$ = 2.0 Hz, 1 H, furyl-C(5)−H], 7.34 [dd, $^4J_{H,H}$ = 2.0, $^3J_{H,H}$ = 0.8 Hz, 1 H, furyl-C(3)−H] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 17.41 (CH_3), 32.18 (CH_2), 34.65 (CH_2), 64.28 (COH), 106.26 [furyl-C(3 or 4)], 110.23 [furyl-C(3 or 4)], 137.27 (C=C), 142.04 [furyl-C(5)], 154.57 [furyl-C(2)], 173.18 (C=C), 210.05 (carbonyl) ppm. IR (neat): ṽ = 1635 and 1673 (C=C−C=O), 3315 (br., OH) cm^{-1}. $C_{11}H_{12}O_3$ (192.21): calcd. C 68.7, H 6.31; found C 68.8, H 6.50.

Compound 3: This compound was synthesized according to a procedure similar to that of **2**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 2:1) (oil, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.19 (td, $J_{H,H}$ = 12.0, $J_{H,H}$ = 3.2 Hz, 1 H, Cy-H), 1.00 (td, $J_{H,H}$ = 12.0, $J_{H,H}$ = 3.2 Hz, 1 H, Cy-H), 1.08−1.84 (m, 9 H, Cy-H), 2.05 (s, 3 H, CH_3), 2.38−2.43 (m, 2 H, CH_2), 2.52−2.62 (m, 2 H, CH_2), 3.66 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, OH), 4.10 (dd, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 8.4 Hz, 1 H, OCH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 17.72 (CH_3), 25.93 (Cy-CH_2), 26.10 (Cy-CH_2), 26.46 (Cy-CH_2), 29.30 (Cy-CH_2), 29.46 (Cy-CH_2), 31.94 (CH_2), 34.64 (CH_2), 43.79 (Cy-CH), 73.14 (COH), 139.49 (C=C), 171.91 (C=C), 210.88 (carbonyl) ppm. IR (neat): ṽ = 2850 and 2923 (C=C−C=O), 3446 (br., OH) cm^{-1}. $C_{13}H_{20}O_2$ (208.30): calcd. C 75.0, H 9.70; found C 75.3, H 9.52.

6-(2-Furyl)-1,4-dimethylfulvene (4): Compound **2** (1.44 g, 7.50 mmol) was dissolved in CH_2Cl_2 (10 mL). Dihydropyran (0.95 g, 11 mmol) and pyridinium *p*-toluenesulfonate (PPTS) (0.19 g, 0.75 mmol) were then added at room temperature. The solution was stirred for 4 hours and then diluted with diethyl ether (50 mL). The solution was washed with saturated aqueous NaCl solution. The organic phase was collected and dried over anhydrous $MgSO_4$. Removal of the solvent using a rotary evaporator gave a residue that was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 2:1). Signals of two diastereomers are observed in the ^{1}H NMR spectrum. The yield was 1.77 g (yield, 85%). The compound was dissolved in diethyl ether (5 mL), and MeLi (6.4 mL, 1.5 M in diethyl ether, 9.6 mmol) was added dropwise at −78 °C. The solution was allowed to warm to room temperature and stirred overnight. Water (10 mL) was then added. The diethyl ether was removed using a rotary evaporator. Ethyl acetate (30 mL) was added to the residue and the mixture was poured into a separating funnel. The aqueous layer was removed and aqueous HCl (2 N, 30 mL) was added. The mixture was shaken vigorously for 2.5 minutes. The aqueous layer was removed and the organic layer was washed with saturated aqueous $NaHCO_3$ solution (30 mL). The organic layer was collected and dried over anhydrous $MgSO_4$. The solvent was removed using a rotary evaporator, thus giving a residue. NaH (0.23 g, 9.6 mmol) and anhydrous THF (10 mL) was added to the residue under a nitrogen atmosphere. Methanol (1.0 mL) was added using a syringe, upon which hydrogen gas was evolved and the solution became red. The solution was stirred for 20 minutes at room temperature under nitrogen. The solution was poured into a separating funnel containing water (20 mL), and the red compound was extracted with ethyl acetate (50 mL). The organic layer was dried over anhydrous $MgSO_4$. Removal of the solvent gave a red residue that was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). The yield was 0.750 g (overall yield from **2**, 58%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.09 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 5.97 [s, 1 H, fulvene-C(2 or 3)-H], 6.11 [quadruplet, $^4J_{H,H}$ = 1.2 Hz, 1 H, fulvene-C(2 or 3)−H)], 6.51 [dd, $^3J_{H,H}$ = 3.2, $^3J_{H,H}$ = 1.6 Hz, 1 H, furyl-C(4)−H], 6.73 [d, $^3J_{H,H}$ = 3.2 Hz, 1 H, furyl-C(3)−H], 6.80 [(s, 1 H, fulvene-C(6)−H)], 7.56 [dd, $^3J_{H,H}$ = 1.6, $^4J_{H,H}$ = 0.4 Hz, 1 H, furyl-C(5)−H)] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.09 (CH_3), 17.42 (CH_3), 112.22 (furyl-CH), 116.84 (furyl-CH), 119.38 (furyl-CH), 126.29 [fulvene-C(2 or 3)], 129.38 [fulvene-C(1 or 4)], 131.68 [fulvene-C(2 or 3)], 134.05 [fulvene-C(1 or 4)], 141.77 [fulvene-C(5)], 144.49 [fulvene-C(6)], 151.28 [furyl-C(2)] ppm. $C_{12}H_{12}O_1$ (172.22): calcd. C 83.7, H 7.04; found C 83.6, H 7.00.

6-Cyclohexyl-1,4-dimethylfulvene (5): This compound was synthesized according to a procedure similar to that for **4**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). A yellow oily compound was obtained in a 51% overall yield from **3**. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.12−1.44 (m, 5 H, Cy-CH_2), 1.68−1.90 (m, 5 H, Cy-CH_2), 2.01 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 2.93 (qt, $^3J_{H,H}$ = 10.4, $^3J_{H,H}$ = 3.2 Hz, 1 H, Cy-CH), 5.92 [s, 1 H, fulvene-C(2 or 3)−H], 6.03 [quadruplet, $^4J_{H,H}$ = 1.2 Hz, 1 H, fulvene-C(2 or 3)−H], 6.11 [d, $^3J_{H,H}$ = 10.4 Hz, 1 H, fulvene-C(6)−H] ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 12.68 (CH_3), 16.95 (CH_3), 25.79 (Cy-CH_2), 25.98 (Cy-CH_2), 33.12 (Cy-CH_2), 37.55 (Cy-CH), 125.34 [fulvene-C(2 or 3)], 130.03 [fulvene-C(1 or 4)], 130.28 [fulvene-C(2 or 3)], 133.43 [fulvene-C(1 or 4)], 142.65 [fulvene-C(5)], 144.10 [fulvene-C(6)] ppm. $C_{14}H_{20}$ (188.31): calcd. C 89.3, H 10.7; found C 89.0, H 10.5.

Substituted Cyclopentadiene (6): 1,4-Dimethyl-6-phenylfulvene (0.95 g, 5.21 mmol) was dissolved in cold THF (−30 °C, 40 mL) and lithium *tert*-butylamide (0.41 g, 5.21 mmol) was added. The solution was stirred overnight at room temperature. Water (20 mL) was added and the product was extracted with hexane (50 mL). It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 10:1). The yield was 80% (1.06 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.13 (s, 9 H, *t*Bu-H), 1.82 (quadruplet, $J_{H,H}$ = 2.0 Hz, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.80 (quintet, $J_{H,H}$ = 2.0 Hz, 2 H, CH_2), 4.98 (s, 1 H, bridge-CH), 5.78 (d, $J_{H,H}$ = 2.0 Hz, 1 H, Cp-CH), 7.14 [t, $^3J_{H,H}$ = 8 Hz, 1 H, Ph-C(*para*)−H], 7.25 [t, $^3J_{H,H}$ = 8 Hz, 2 H, Ph-C(*meta*)−H], 7.46 [d, $^3J_{H,H}$ = 8 Hz, 2 H, Ph-C(*ortho*)−H] ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.65 (CH_3), 15.92 (CH_3), 30.12 [C(*C*H_3)$_3$], 44.12 (CH_2), 51.41 [N*C*(CH_3)$_3$], 52.98 (NCH), 125.09 (Cp-CH), 125.69 [Ph-C(*para*)], 127.07 [Ph-C(*ortho* or *meta*)], 127.63 [Ph-C(*ortho* or *meta*)], 137.05 [Cp-C(bridgehead)], 143.02 [Cp-C(CH_3)], 143.11 [Cp-C(CH_3)], 145.66 [Ph-C(*ipso*)] ppm. $C_{18}H_{25}N_1$ (255.40): calcd. C 84.7, H 9.89, N 5.48; found C 84.6, H 10.1, N 5.15.

Substituted Cyclopentadiene 7: This compound was synthesized according to a procedure similar to that for **6**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). The yield was 88%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.14 (s, 9 H, *t*Bu-H), 1.99 (quadruplet, $J_{H,H}$ = 2.0 Hz, 3 H, CH_3), 2.10 (s, 3 H, CH_3), 2.82 (quintet, $J_{H,H}$ = 2.0 Hz, 2 H, CH_2), 4.99 (s, 1 H, NCH), 5.83 (d, $J_{H,H}$ = 1.6 Hz, 1 H, Cp-CH), 6.10 [d, $^3J_{H,H}$ = 3.2 Hz, 1 H, furyl-C(3)−H], 6.28 [dd, $^3J_{H,H}$ = 3.2, $^3J_{H,H}$ = 2.0 Hz, 1 H, furyl-C(4)−H], 7.32 [d, $^3J_{H,H}$ = 2.0 Hz, 1 H, furyl-C(5)−H] ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.32 (CH_3), 15.56 (CH_3), 29.87 [C(*C*H_3)$_3$], 44.15 (CH_2), 48.48 (NCH), 51.30 [N*C*(CH_3)$_3$], 105.49 [furyl-C(3 or 4)], 109.95 [furyl-C(3 or 4)], 124.79 (Cp-*C*H), 138.36 [Cp-C(bridgehead)], 140.49 [Cp-C(CH_3)], 140.75 [furyl-C(5)], 143.03 [Cp-C(CH_3)], 157.78 [furyl-C(2)] ppm. $C_{16}H_{23}O_1N_1$ (245.36): calcd. C 78.3, H 9.47, N 5.71; found C 78.2, H 9.50, N 5.83.

Substituted Cyclopentadiene 8: This compound was synthesized according to a procedure similar to that for **6**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The yield was 60%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.7−2.2 (m, 11 H, Cy-H), 1.00 (s, 9 H, *t*Bu-H), 1.94 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3), 2.65−2.82 (m, 2 H, Cp-CH_2), 3.34 (d, $J_{H,H}$ = 9.6 Hz, 1 H, NCH), 5.78 (s, 1 H, Cp-CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.33 (CH_3), 16.71 (CH_3), 26.66, 26.71, 26.83, 30.21 [C(*C*H_3)$_3$], 30.40, 32.11, 42.80, 43.62, 50.78, 55.89, 124.79 (Cp-CH), 136.70 [Cp-C(bridgehead)], 142.73 [Cp-C(CH_3)], 143.73 [Cp-C(CH_3)] ppm. $C_{18}H_{31}N_1$ (261.45): calcd. C 82.7, H 12.0, N 5.35; found C 82.9, H 12.1, N 5.40.

(1,3-$Me_2C_5H_2$-CHPh−N*t*Bu−κ*N*)Zr(NMe_2)$_2$ (9): Compound **6** (0.511 g, 2.00 mmol) and Zr(NMe_2)$_4$ (0.535 g, 2.00 mmol) were weighed in a flask and toluene (30 mL) was added. The solution was stirred for 2 days at 100 °C under a weak stream of nitrogen gas. The volatiles were removed to give a white oil, which was quite pure (analyzed by ^{1}H and ^{13}C NMR spectroscopy) (crude yield, 97%). Analytically pure single crystals suitable for X-ray crystallography were obtained in pentane at −30 °C. M.p. 135 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.24 (s, 9 H, *t*Bu-H), 1.54 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.89 (s, 6 H, NCH_3), 3.09 (s, 6 H, NCH_3), 5.48 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H), 5.85 (s, 1 H, bridge-CH), 5.88 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H), 7.13 [t, $^3J_{H,H}$ = 7.6 Hz, 1 H, Ph-C(*para*)−H], 7.25 [t, $^3J_{H,H}$ = 7.6 Hz, 2 H, Ph-C(*meta*)−H], 7.61 [d, $^3J_{H,H}$ = 7.6 Hz, 2 H, Ph-C(*ortho*)−H] ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 13.52 (CH_3), 14.79 (CH_3), 32.24 [C(*C*H_3)$_3$], 43.58 [N(CH_3)$_2$], 47.37 [N(CH_3)$_2$], 56.20 [N*C*(CH_3)$_3$], 59.33 (bridge-CH), 105.76 [Cp-C(bridgehead)], 107.74 (Cp-CH), 112.60 (Cp-CH), 123.77 [Cp-C(CH_3)], 125.43 [Cp-C(CH_3)], 126.45 (Ph-C), 127.64 (Ph-C), 128.45 (Ph-C), 147.10 [Ph-C(*ipso*)] ppm. $C_{22}H_{35}N_3Zr$ (432.76): calcd. C 61.1, H 8.15, N 9.71; found C 61.3, H 8.23, N 9.65.

(1,3-$Me_2C_5H_2$−CHPh−N*t*Bu−κ*N*)$TiCl_2$ (10): The bis(dimethylamido) complex was synthesized according to a procedure similar to that of **9**, however, **6** (0.511 g, 2.00 mmol) and Ti(NMe_2)$_4$ (0.450 g, 2.00 mmol) were used. A deep red oil was obtained, which was quite pure (analyzed by ^{1}H and ^{13}C NMR spectroscopy). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.28 (s, 9 H, *t*Bu-H), 1.44 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 3.01 (s, 6 H, NCH_3), 3.27 (s, 6 H, NCH_3), 5.44 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H), 5.80 (s, 1 H, bridge-CH), 5.94 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H), 7.12 [t, $^3J_{H,H}$ = 7.6 Hz, 1 H, Ph-C(*para*)−H], 7.24 [t, $^3J_{H,H}$ = 7.6 Hz, 2 H, Ph-C(*meta*)−H], 7.55 [d, $^3J_{H,H}$ = 7.6 Hz, 2 H, Ph-C(*ortho*)−H] ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 13.76 (CH_3), 14.59 (CH_3), 32.11 [C(*C*H_3)$_3$], 48.42 [N(CH_3)$_2$], 52.65 [N(CH_3)$_2$], 59.95 [N*C*(CH_3)$_3$], 60.98 (bridge-CH), 103.29 [Cp-C(bridgehead)], 109.85 (Cp-CH), 115.62 (Cp-CH), 123.25 [Cp-C(CH_3)], 126.37 (Ph-C), 128.35 (Ph-C), 146.95 [Ph-C(*ipso*)] ppm. The crude residue was dissolved in toluene (12 mL) and dichlorodimethylsilane (1.03 g, 8.00 mmol) was added. The solution was stirred overnight. The volatiles were removed under a vacuum. The complex was dissolved in toluene and stored in a freezer (−30 °C) overnight to give red crystals which were suitable for X-ray crystallography (0.234 g, 37%). The major constituent of the mother liquor was the desired complex, but further isolation of the clean complex from the mother liquor was not achieved. M.p. 163 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.37 (s, 9 H, *t*Bu-H), 1.52 (s, 3 H, CH_3), 1.88 (s, 3 H, CH_3), 6.06 (d, $^3J_{H,H}$ = 3.6 Hz, 1 H, Cp-H), 6.08 (s, 1 H, bridge-CH), 6.20 (d, $^3J_{H,H}$ = 3.6 Hz, 1 H, Cp-H), 7.00−7.15 (m, 5 H, Ph-H) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 15.12 (CH_3), 17.88 (CH_3), 30.83 [C(*C*H_3)$_3$], 62.45 (bridge-CH), 63.76 [N*C*(CH_3)$_3$], 102.13 [Cp-C(bridgehead)], 122.14 (Cp-CH), 122.78 (Cp-CH), 127.76 (Ph-C), 127.92 (Ph-C), 128.44 (Ph-C), 138.47 [Cp-C(CH_3)], 138.79 [Cp-C(CH_3)], 141.43 [Ph-C(*ipso*)] ppm. $C_{18}H_{23}Cl_2NTi$ (372.15): calcd. C 58.1, H 6.24, N 3.76; found C 57.8, H 6.25, N 3.93.

(1,3-$Me_2C_5H_2$−CHPh−N*t*Bu−κ*N*)$ZrCl_2$ (11): Compound **9** (0.530 g, 1.22 mmol) was dissolved in toluene (20 mL) and dichlorodimethylsilane (0.315 g, 2.44 mmol) was added. The solution was stirred overnight, upon which a white solid precipitated. The solid was filtered and dried under vacuum. The yield was 44% (0.222 g).

The major constituent of the filtrate was the desired complex. The reaction for 4 days without stirring gave single crystals suitable for X-ray crystallography. M.p. 194 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.27 (s, 9 H, *t*Bu-H), 1.60 (s, 3 H, CH_3), 1.99 (s, 3 H, CH_3), 5.77 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H, Cp-H), 5.91 (s, 1 H, bridge-CH), 5.95 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H, Cp-H), 7.00−7.10 [m, 3 H, Ph-C(*meta* or *para*)−H], 7.10−7.22 [m, 2 H, Ph-C(*ortho*)−H] ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 14.00 (CH_3), 16.58 (CH_3), 30.70 [C(*C*H$_3$)$_3$], 57.84 [N*C*(CH$_3$)$_3$], 59.65 (bridge-CH), 104.27 [Cp-C(bridgehead)], 116.17 (Cp-CH), 116.40 (Cp-CH), 127.56 (Ph-C), 128.29 (Ph-C), 128.49 (Ph-C), 132.17 [Cp-C(CH_3)], 132.25 [Cp-C(CH_3)], 142.21 [Ph-C(*ipso*)] ppm. $C_{18}H_{23}Cl_2NZr$ (415.51): calcd. C 52.0, H 5.59, N 3.37; found C 51.7, H 6.00, N 3.34.

[1,3-Me$_2$C$_5$H$_2$−CH(C$_4$H$_3$O)−N*t*Bu−κ*N*]TiCl$_2$ (13): The bis(dimethylamido) complex was synthesized according to a procedure similar to that for **9**. The reaction time was 4 days. A deep red oil was obtained. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.26 (s, 9 H, *t*Bu-H), 1.75 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 3.04 (s, 6 H, NCH_3), 3.22 (s, 6 H, NCH_3), 5.50 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H), 5.91 (s, 1 H, bridge-CH), 5.94 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H), 6.15−6.20 [m, 2 H, furyl-C(3 and 4)−H], 7.17 [dd, $^3J_{H,H}$ = 1.6, $^4J_{H,H}$ = 0.8 Hz, 1 H, furyl-C(5)−H] ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 13.50 (CH_3), 14.49 (CH_3), 31.27 [C(*C*H$_3$)$_3$], 48.35 [N(CH_3)$_2$], 52.40 [N(CH_3)$_2$], 54.94 (bridge-CH), 59.62 [N*C*(CH$_3$)$_3$], 102.26 [Cp-C(bridgehead)], 106.94 [furyl-C(3 or 4)], 109.31 (Cp-CH), 110.75 [furyl-C(3 or 4)], 115.68 (Cp-CH), 123.23 [Cp-C(CH_3)], 126.06 [Cp-C(CH_3)], 139.91 [furyl-C(5)], 158.57 [furyl-C(2)] ppm. Chlorination was accomplished using the method and conditions developed for **10**. A crude red oil, which is quite pure (analyzed by NMR spectroscopy), was obtained by evaporation of all the volatiles, in a 86% yield. An analytically pure compound was obtained by recrystallization in pentane at −30 °C. M.p. 117 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.33 (s, 9 H, *t*Bu-H), 1.82 (s, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 5.97 [d, $^3J_{H,H}$ = 3.6 Hz, 1 H, furyl-C(3)−H], 6.00 [dd, $^3J_{H,H}$ = 3.6, $^3J_{H,H}$ = 1.6 Hz, 1 H, furyl-C(4)−H], 6.14 (s, 1 H, bridge-CH), 6.16 (d, $^3J_{H,H}$ = 3.6 Hz, 1 H, Cp-H), 6.17 (d, $^3J_{H,H}$ = 3.6 Hz, 1 H, Cp-H), 6.92 [dd, $^3J_{H,H}$ = 1.6, $^4J_{H,H}$ = 0.8 Hz, 1 H, furyl-C(5)−H] ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 15.08 (CH_3), 18.12 (CH_3), 29.29 [C(*C*H$_3$)$_3$], 55.88 (bridge-*C*H), 63.09 [N*C*(CH$_3$)$_3$], 102.95 [Cp-C(bridgehead)], 109.36 [furyl-C(3 or 4), 110.95 [furyl-C(3 or 4)], 121.52 (Cp-CH), 122.68 (Cp-CH), 137.46 [Cp-C(CH_3)], 138.83 [Cp-C(CH_3)], 141.31 [furyl-C(5)], 152.64 [furyl-C(2)] ppm. $C_{16}H_{21}Cl_2NOTi$ (362.12): calcd. C 53.1, H 5.85, N 3.86; found C 52.8 (52.6), H 6.32 (6.30), N 3.80 (3.75).

[1,3-Me$_2$C$_5$H$_2$−CH(C$_4$H$_3$O)−N*t*Bu−κ*N*]ZrCl$_2$ (14): The bis(dimethylamido) complex was synthesized according to a procedure similar to that for **9**. The reaction time was 4 days. A white oil was obtained. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.21 (s, 9 H, *t*Bu-H), 1.92 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 2.91 (s, 6 H, NCH_3), 3.04 (s, 6 H, NCH_3), 5.56 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H), 5.87 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H), 5.93 (s, 1 H, bridge-CH), 6.18−6.22 [m, 2 H, furyl-C(3 and 4)−H], 7.18 [dd, $^3J_{H,H}$ = 2.8, $^4J_{H,H}$ = 0.8 Hz, 1 H, furyl-C(5)−H] ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 13.22 (CH_3), 14.01 (CH_3), 31.21 [C(*C*H$_3$)$_3$], 43.52 [N(CH_3)$_2$], 47.14 [N(CH_3)$_2$], 53.45 (bridge-CH), 55.86 [N*C*(CH$_3$)$_3$], 105.55 [Cp-C(bridgehead)], 107.12 (Cp-CH), 107.71 [furyl-C(3 or 4)], 110.72 [furyl-C(3 or 4)], 112.55 (Cp-CH), 123.91 [Cp-C(CH_3)], 125.29 [Cp-C(CH_3)], 140.00 [furyl-C(5)], 158.71 [furyl-C(2)] ppm. Chlorination was accomplished by stirring the crude bis(dimethylamido) complex with 3.0 equivalents of dichlorodimethylsilane in pentane overnight. The precipitated white solid was filtered and dried under vacuum. The yield was 47%. M.p. 128 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.23 (s, 9 H, *t*Bu-H), 1.96 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 5.92 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H), 5.94 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H), 5.98 (s, 1 H, bridge-CH), 6.01 [d, $^3J_{H,H}$ = 3.2 Hz, 1 H, furyl-C(3)−H], 6.04 [dd, $^3J_{H,H}$ = 3.2, $^3J_{H,H}$ = 1.6 Hz, 1 H, furyl-C(4)−H], 6.99 [d, $^3J_{H,H}$ = 1.6 Hz, 1 H, furyl-C(5)−H] ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 14.08 (CH_3), 16.77 (CH_3), 29.11 [C(*C*H$_3$)$_3$], 53.30 (bridge-CH), 57.53 [N*C*(CH$_3$)$_3$], 105.13 [Cp-C(bridgehead)], 108.93 [furyl-C(3 or 4)], 110.88 [furyl-C(3 or 4)], 115.55 (Cp-CH), 116.43 (Cp-CH), 131.91 [Cp-C(CH_3)], 132.27 [Cp-C(CH_3)], 141.17 [furyl-C(5)], 153.82 [furyl-C(2)] ppm. $C_{16}H_{21}Cl_2NOZr$ (405.47): calcd. C 47.4, H 5.23, N 3.46; found C 47.1, H 5.68, N 3.54.

[1,3-Me$_2$C$_5$H$_2$−CH(C$_6$H$_{11}$)−N*t*Bu−κ*N*]ZrCl$_2$ (15): The bis(dimethylamido) complex was synthesized according to a procedure similar to that for **9**. The reaction time was 4 days. A white oil was obtained. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.9−2.5 (m, 11 H, Cy-H), 1.38 (s, 9 H, *t*Bu-H), 2.04 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 2.87 (s, 6 H, NCH_3), 3.01 (s, 6 H, NCH_3), 4.55 (d, $J_{H,H}$ = 8.0 Hz, 1 H, bridge-CH), 5.65 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H), 5.92 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, Cp-H) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 13.31 (CH_3), 16.64 (CH_3), 27.23, 27.48, 27.83, 31.35 [C(*C*H$_3$)$_3$], 35.45, 44.00 [N(CH_3)$_2$], 44.31, 45.48, 46.94, 55.39, 62.80 (bridge-CH), 108.08 (Cp-CH), 109.03 [Cp-C(bridgehead)], 111.57 (Cp-CH), 123.54 [Cp-C(CH_3)], 124.03 [Cp-C(CH_3)] ppm. Chlorination was accomplished by stirring the crude bis(dimethylamido) complex with 3.0 equivalent dichlorodimethylsilane in pentane overnight. The precipitated white solid was filtered and dried under vacuum. The yield was 83%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.7−2.2 (m, 11 H, Cy-H), 1.39 (s, 9 H, *t*Bu-H), 1.87 (s, 3 H, CH_3), 1.94 (s, 3 H, CH_3), 4.89 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, bridge-C*H*), 5.96 (s, 2 H, Cp-H) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 13.82 (CH_3), 16.93 (CH_3), 26.32, 26.82, 27.04, 29.02 [C(*C*H$_3$)$_3$], 30.00, 35.68, 41.97, 56.69 [N*C*(CH$_3$)$_3$], 63.20 (bridge-CH), 107.54 [Cp-C(bridgehead)], 114.97 (Cp-CH), 116.39 (Cp-CH), 130.26 [Cp-C(CH_3)], 130.84 [Cp-C(CH_3)] ppm. $C_{18}H_{29}Cl_2NZr$ (421.56): calcd. C 51.3, H 6.95, N 3.32; found C 51.6, H 7.32, N 3.25.

Ethylene Polymerization: In a dry box, toluene (30 mL) was added to a dried 70 mL glass reactor. The activated complex, prepared by mixing the complex (10 μmol) and MAO (Al/Zr or Ti = 500), was added to the reactor. The reactor was assembled and removed from the dry box. The reactor was immersed in an oil bath whose temperature had been set to 60 °C, and stirred for 15 minutes, at which time the solution temperature reached that of the bath. Ethylene was fed under the pressure of 100 psig. After the polymerization reaction was performed for the given time, it was quenched by venting ethylene gas and pouring the mixture into acetone. The white precipitates were collected by filtration and dried under vacuum. Table 2 summarizes the polymerization results.

X-ray Crystallographic Study: Crystals of **9**, **10**, and **12** were coated with grease (Apiezon N) and mounted inside a thin glass tube with epoxy glue and placed on an Enraf−Nonius CCD single-crystal X-ray diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystal of **11** was mounted onto a thin glass fiber with paratone and immediately placed in a cold nitrogen stream at 150 K on a MXC3 diffractometer (Mac Science) The structures were solved by direct methods (SHELXS-97)[15] and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and

Table 3. Crystallographic parameters of **9**, **10**, **11**, and **12**

	9	**10**	**11**	**12**
Empirical formula	$C_{22}H_{35}N_3Zr$	$C_{18}H_{23}Cl_2NTi$	$C_{18}H_{23}Cl_2NZr$	$C_{21}H_{27}Cl_2NO_{0.50}Zr$
Formula mass	432.75	372.17	415.49	463.56
Temperature [K]	293	293	150	293
a (Å)	11.5090(10)	19.7430(10)	8.982(5)	10.6331(6)
b (Å)	13.3210(10)	14.5910(10)	9.246(4)	12.3576(7)
c (Å)	15.3180(10)	16.3030(10)	11.639(7)	16.3256(10)
α [°]	90	90	83.84(4)	90
β [°]	101.808(2)	126.436(2)	70.32(4)	103.888(3)
γ [°]	90	90	84.76(4)	90
Volume [Å^3]	2298.7(3)	3778.4(4)	903.2(8)	2082.5(2)
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $C2/c$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
d (calcd.) [g/cm^3]	1.250	1.309	1.528	1.479
Z	4	8	2	4
Absorption coefficient [mm^{-1}]	0.488	0.732	0.901	0.791
F(000)	912	1552	424	952
Crystal size [mm]	0.2 × 0.15 × 0.15	0.3 × 0.2 × 0.15	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2
θ range [°]	3.12 to 27.45	2.79 to 25.72	1.86 to 25.00	2.84 to 27.07
Limiting indices	$-14 \le h \le 14$	$-23 \le h \le 24$	$-10 \le h \le 10$	$-13 \le h \le 13$
	$-15 \le k \le 16$	$-15 \le k \le 17$	$0 \le k \le 10$	$-14 \le k \le 15$
	$-18 \le l \le 18$	$-19 \le l \le 19$	$-13 \le l \le 13$	$-20 \le l \le 20$
Reflections collected/unique	7542/4567 [R(int) = 0.0921]	6099/3501 [R(int) = 0.0655]	3237/3032 [R(int) = 0.0308]	8034/4536 [R(int) = 0.0726]
Data/restraints/parameters	4567/0/244	3501/0/205	3032/0/204	4536/0/241
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0443, ω$R2$ = 0.0674	$R1$ = 0.0523, ω$R2$ = 0.1320	$R1$ = 0.0342, ω$R2$ = 0.0858	$R1$ = 0.0493, ω$R2$ = 0.0984
R indices (all data)	$R1$ = 0.1830, ω$R2$ = 0.0811	$R1$ = 0.1408, ω$R2$ = 0.1506	$R1$ = 0.0411, ω$R2$ = 0.0887	$R1$ = 0.1413, ω$R2$ = 0.1152
Largest diff. peak and hole [e·Å^3]	0.326 and −0.283	0.428 and −0.479	0.435 and −0.592	0.468 and −0.371
Goodness-of-fit on F^2	0.759	0.815	1.066	0.882

refinement results are summarized in Table 3. Selected bond lengths and angles are listed in Table 1.

CCDC-221028 (for **9**), -221029 (for **10**), -221030 (for **11**), and -221031 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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