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Synthesis and reactivity of asymmetrically substituted *ansa*-bridged zirconocene complexes: X-ray crystal structures of $[Zr\{R(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ ($R = Bu^n$, Bu^t) and $[Zr\{Bu^n(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}(CH_2Ph)_2]$

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Abstract

The dialkyl complexes, $[Zr\{R(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}R'_2]$ ($R = Pr^i$, $R' = Me$ (**2a**), CH_2Ph (**3a**); $R = Bu^n$, $R' = Me$ (**2b**), CH_2Ph (**3b**); $R = Bu^t$, $R' = Me$ (**2c**), CH_2Ph (**3c**); $R = Ph$, $R' = Me$ (**2d**), CH_2Ph (**3d**)), have been synthesized by the reaction of the *ansa*-metallocene dichloride complex, $[Zr\{R(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ ($R = Pr^i$ (**1a**), Bu^n (**1b**), Bu^t (**1c**), Ph (**1d**)), and two molar equivalents of the alkyl Gringard reagent. The insertion reaction of the isocyanide reagent, $CNC_6H_3Me_2$-2,6, into the zirconium–carbon σ-bond of **2** gave the corresponding η^2-iminoacyl derivatives, $[Zr\{R(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}\{\eta^2\text{-}MeC{=}NC_6H_3Me_2\text{-}2,6\}Me]$ ($R = Pr^i$ (**4a**), Bu^n (**4b**), Bu^t (**4c**), Ph (**4d**)). The molecular structures of **1b**, **1c** and **3b** have been determined by single-crystal X-ray diffraction studies.

Keywords: Metallocenes; Zirconium; Insertion reactions; Isocyanides

1. Introduction

Zirconocene complexes owe their place of importance in organometallic chemistry to their catalytic activity in the polymerization of olefins [1]. It is now well established that the structural make up of the catalyst not only plays a part in its activity in polymerization but also in determining the microstructure of the polymer [2]. It is therefore evident the necessity of rational ligand design in order to fulfil differing polymerization goals [3].

Alkyl zirconocene cations are currently of interest due to their role as single-site Ziegler–Natta polymerization catalysts [4]. Common precursors to these cationic catalysts include dimethyl- and dibenzyl zirconocene complexes which are stable species [5].

As part of our ongoing studies in the design of olefin polymerization catalysts [6], we present in this paper the synthesis, characterization and reactivity of chiral *ansa*-zirconocene complexes. Part of this work has been previously communicated [7].

2. Results and discussion

We have previously communicated the synthesis of $[Zr\{R(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ ($R = Bu^n$ (**1b**), Bu^t (**1c**), Ph (**1d**)) [7] and in a similar manner $[Zr\{Pr^i(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**1a**) was prepared (Eq. (1)).

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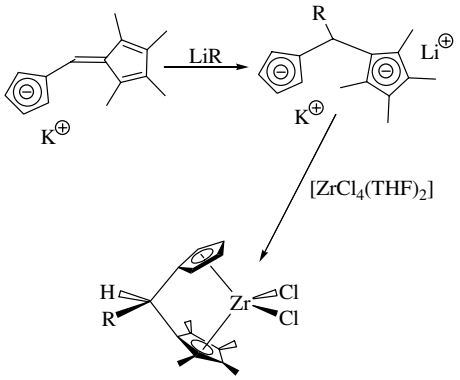


(1)

R = Pr^i (**1a**), Bu^n (**1b**), Bu^t (**1c**), Ph (**1d**)

Compound **1a** was isolated as a white crystalline solid and characterized spectroscopically. In the ^1H NMR spectrum of the C_1 symmetric complex **1a** four singlets, between 1.49 and 1.87 ppm, assigned to the four methyl groups of the tetramethylcyclopentadienyl fragment were observed. Four multiplets, between 5.06 and 6.48 ppm, were recorded for the protons of the unsubstituted cyclopentadienyl moiety. The proton at the *ansa* bridge gave a doublet at 3.42 ppm. For the isopropyl group the chirality of the complex makes the two methyl units diastereotopic and two doublets were observed at 0.87 and 0.91 ppm. The isopropyl proton gave a multiplet (2.30 ppm) with coupling to both the isopropyl methyl protons and the *ansa* bridge proton. The ^{13}C NMR spectrum gave the expected signals, namely four signals for the methyl substituents of the C_5 ring (between 11.7 and 14.5 ppm), 10 signals for the carbon atoms of the C_5 rings (between 104.1 and 130.0 ppm), three signals for the isopropyl group (20.4, 21.5 and 29.0 ppm) and one signal for the carbon atom *ansa* bridge at 48.5 ppm.

The molecular structures of **1b** and **1c** were established by single-crystal X-ray diffraction studies. The molecular structures and atomic numbering schemes are shown in Figs. 1 and 2. Selected bond lengths and angles for **1b** and **1c** are given in Table 1.

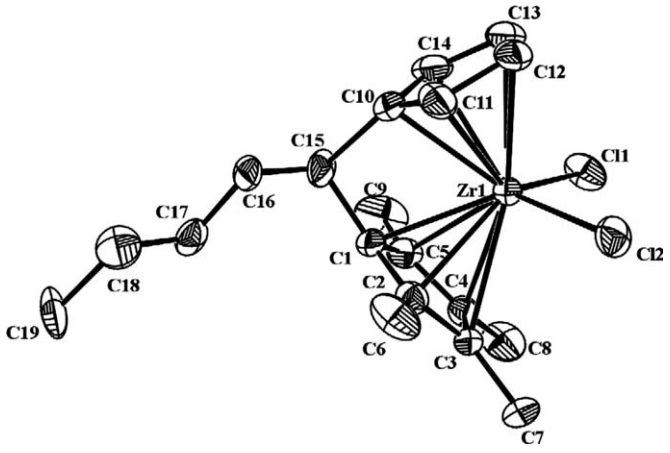


Fig. 1. Molecular structure and atom labelling scheme for [Zr{Bu^n(H)C(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**1b**) with thermal ellipsoids at 30% probability.

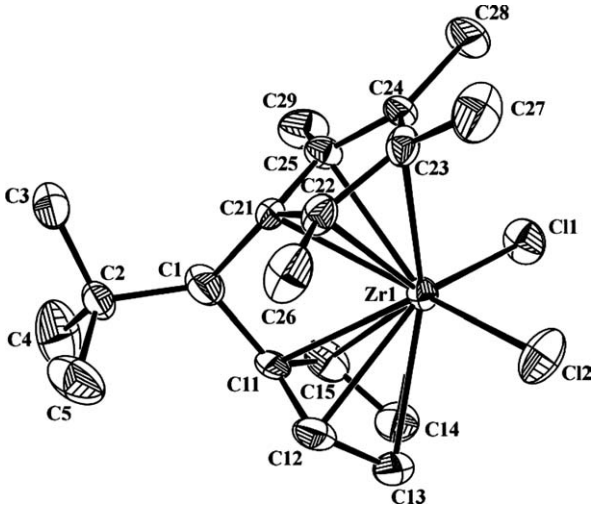


Fig. 2. Molecular structure and atom-labeling scheme for [Zr{Bu^t(H)C(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**1c**) with thermal ellipsoids at 30% probability.

Table 1
Selected bond lengths (Å) and angles (°) for **1b** and **1c**

Compound	**1b**	**1c**
Bond lengths (Å)		
Zr(1)–Cent(1)	2.193	2.186
Zr(1)–Cent(2)	2.190	2.186
av. Zr(1)–C(C(1)–C(5))*	2.500(6)	2.491(6)
av. Zr(1)–C(C(10)–C(14))*	2.493(8)	2.486(7)
Zr(1)–Cl(1)	2.415(2)	2.429(2)
Zr(1)–Cl(2)	2.437(2)	2.419(2)
C(1)–C(15)	1.64(3)	1.559(9)
C(10)–C(15)	1.48(4)	1.53(1)
C(15)–C(16)	1.47(6)	1.534(9)
Bond angles (°)		
Cent(1)–Zr(1)–Cent(2)	117.5	118.3
C(15)–C(1)–Cent(1)	162.23	161.45
C(15)–C(10)–Cent(2)	166.67	163.38
C(1)–C(15)–C(10)	98(2)	101.0(5)
C(1)–C(15)–C(16)	111(3)	121.3(7)
C(10)–C(15)–C(16)	122(4)	123.3(6)
Cl(1)–Zr(1)–Cent(1)	109.01	108.95
Cl(1)–Zr(1)–Cent(2)	109.05	109.77
Cl(2)–Zr(1)–Cent(1)	108.91	108.26
Cl(2)–Zr(1)–Cent(2)	108.93	108.89
Cl(1)–Zr(1)–Cl(2)	102.37(9)	101.56(8)

Cent(1) and Cent(2) are the centroids of C(1)–C(5) and C(10)–C(14), respectively; * refers to the average bond distance between Zr(1) and the carbon atoms of the C_5 ring of the corresponding cyclopentadienyl moiety.

The structures of **1b** and **1c** exhibit the typical bent metallocene conformation observed in zirconocene dichloride complexes with the geometry around the zirconium atom being pseudo-tetrahedral. The *ansa* ligand chelates the zirconium atom and both C_5 rings are bound to the metal in an η^5 mode. The centroids of the cyclopentadienyl rings form an angle with the zirconium atom of 117.5° **1b**, and 118.3° **1c**, typical for carbon atom bridged *ansa*-zirconocene complexes (for example, [Zr{$Me_2C(\eta^5$-$C_5H_4)_2$}Cl_2], Ct–Zr–Ct 116.7°) [8]. Selected structural data of **1b** and

1c can be compared with similar carbon atom bridged *ansa*-zirconocene complexes using Table 2.

The dialkyl derivatives, [Zr{R(H)C(η^5-C_5Me_4)-(η^5-C_5H_4)}R'_2] (R = Pr^i, R′ = Me (**2a**), CH_2Ph (**3a**); R = Bu^n, R′ = Me (**2b**), CH_2Ph (**3b**); R = Bu^t, R′ = Me (**2c**), CH_2Ph (**3c**); R = Ph, R′ = Me (**2d**), CH_2Ph (**3d**)), were prepared via the reaction of two equivalents of the corresponding Grignard reagent and the *ansa*-zirconocene dichloride complex **1a–d** (Eq. (2)). Compounds **2** and **3** were characterized by spectroscopic methods (see Section 4). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** gave two unique signals for the metal bonded methyl groups (in **2a** these signals overlap), thus confirming the dialkylation of the *ansa*-metallocene complex. The chiral nature of **3**, means that the methylene protons of the non-equivalent benzyl ligands are diastereoscopic and thus four doublets were observed in the ^1H NMR spectra.

(2)

R = Pr^i, R' = Me (**2a**), CH_2Ph (**3a**);
R = Bu^n, R' = Me (**2b**), CH_2Ph (**3b**);
R = Bu^t, R' = Me (**2c**), CH_2Ph (**3c**);
R = Ph, R' = Me (**2d**), CH_2Ph (**3d**)

We have previously shown that the alkylation process of silicon bridged *ansa*-zirconocene complexes is controlled by steric factors and that this may be due to the alkyl ligand or the substituents in the β-position of the cyclopentadienyl ring [6e]. The benzyl group was shown to give only monoalkylation in the complexes with β substituents in one of the C_5 rings. However, when no substituent was present, e.g., [Zr{Me_2Si(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2], dialkylation took place. One might think that the reduction of the "bite angle" from the silicon atom to carbon atom *ansa* bridge should increase the steric hindrance around the metal atom and may disfavour dialkylation. This, nevertheless, is not the case for **1** which behaves in the alkylation reactions in an identical manner to the silicon *ansa*-bridged complex.

The molecular structure of **3b** was established by single-crystal X-ray diffraction studies. The molecular structure and atomic numbering scheme are shown in Fig. 3. Selected bond lengths and angles for **3b** are given in Table 3.

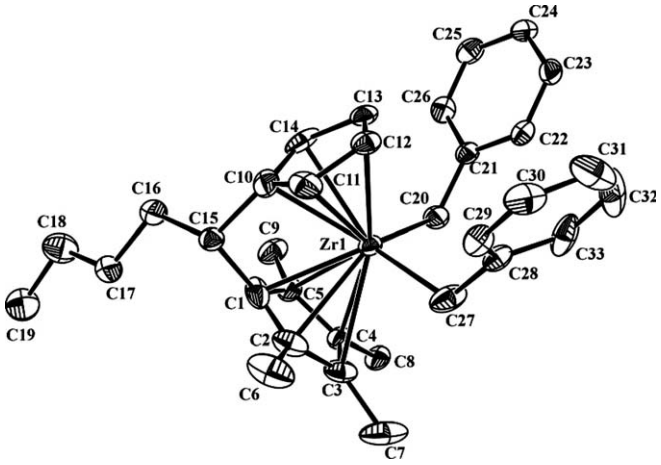


Fig. 3. Molecular structure and atom-labeling scheme for [Zr{Bu^n(H)C(η^5-C_5Me_4)(η^5-C_5H_4)}$(CH_2Ph)_2$] (**3b**) with thermal ellipsoids at 30% probability.

Table 2
Selected structural data of single carbon atom *ansa* bridge zirconocene complexes

Complex	Zr–Cp (Å)[a]	Zr–Cl (Å)	Cp–Zr–Cp (°)	Cl–Zr–Cl (°)	$C_{(cp)}$–C–$C_{(cp)}$ (°)	Reference
[Zr{$H_2C(\eta^5$-$C_5H_4)_2$}Cl_2]			116.4			[9]
[Zr{$Me_2C(\eta^5$-$C_5H_4)_2$}Cl_2]	2.213	2.4364	116.7	100.25(3)	99.5(2)	[8]
[Zr{$(CH_2)_4C(\eta^5$-$C_5H_4)_2$}Cl_2]	2.191	2.433	116.6	100.51(7)	99.8(5)	[10]
[Zr{$(CH_2)_5C(\eta^5$-$C_5H_4)_2$}Cl_2]	2.192	2.445	116.4	99.48(7)	99.7(5)	[10]
[Zr{$(CH_2)_6C(\eta^5$-$C_5H_4)_2$}Cl_2]	2.178	2.437	116.3	100.0(1)	99.1(2)	[10]
[Zr{$CH_2CH_2(Me)NCH_2CH_2C(\eta^5$-$C_5H_4)_2$}$Cl_2$]		2.432		100.6(3)	99.7	[11]
[Zr{$C_{12}H_8C(\eta^5$-$C_5H_4)_2$}Cl_2]		2.427		100.92(8)	99.2(4)	[12]
rac-[Zr{$Me_2C(\eta^5$-$C_5H_3Bu^t)_2$}Cl_2]		2.427		99.17(9)	99.2(6)	[13]
meso-[Zr{$Me_2C(\eta^5$-$C_5H_3Bu^t)_2$}Cl_2]		2.432		98.5(2)	99(1)	[13]
[Zr{$H_2C(\eta^5$-$C_5H_2Me_2$-2,5)$_2$}Cl_2][b]	2.202	2.4386	117.13	102.46(4)	102.7(2)	[14]
	2.198	2.4379	117.60	102.98(4)	102.9(2)	
[Zr{$Me(H)C(\eta^5$-$C_5H_2Me_2$-2,5)$_2$}Cl_2][b]	2.198	2.4404	117.64	100.69(4)	102.2(3)	[14]
	2.205	2.4357	117.59	101.73(5)	101.7(3)	
[Zr{$Bu^n(H)C(\eta^5$-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**1b**)	2.190 Cp	2.426	117.5	102.37(9)	98(2)	This work
	2.193 Cp*					
[Zr{$Bu^t(H)C(\eta^5$-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**1c**)	2.186 Cp	2.424	118.3	101.56(8)	101.0(5)	This work
	2.186 Cp*					
[Zr{$Ph(H)C(\eta^5$-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**1d**)	2.187 Cp	2.434	117.1(1)	99.40(2)	100.9(2)	[7]
	2.192 Cp*					
[Zr{$Me(H)C(\eta^5$-C_5H_4)(η^5-$C_5H_2Me_2$-2,5)}Cl_2]	2.188 Cp	2.4353(10)	117.00	102.11(7)	100.7(4)	[15]
	2.186 Cp^R					

[a] Cp* refers to the C_5Me_4 moiety; Cp^R refers to the C_5H_3R moiety.
[b] There are two independent molecules in the asymmetric cell.

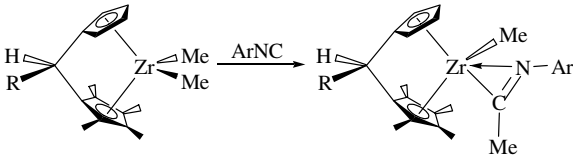
Table 3
Selected bond lengths (Å) and angles (°) for **3b**

Compound	**3b**
Bond lengths (Å)	
Zr(1)–Cent(1)	2.210
Zr(1)–Cent(2)	2.196
av. Zr(1)–C(C(1)–C(5)) *	2.516(4)
av. Zr(1)–C(C(10)–C(14))*	2.498(4)
Zr(1)–C(20)	2.294(5)
Zr(1)–C(27)	2.321(5)
C(15)–C(16)	1.494(8)
C(1)–C(15)	1.531(7)
C(10)–C(15)	1.549(7)
Bond angles (°)	
Cent(1)–Zr(1)–Cent(2)	117.4
C(15)–C(1)–Cent(1)	164.32
C(15)–C(10)–Cent(2)	163.59
C(1)–C(15)–C(10)	101.1(4)
C(1)–C(15)–C(16)	117.8(5)
C(10)–C(15)–C(16)	114.1(5)
C(20)–Zr(1)–Cent(1)	107.29
C(20)–Zr(1)–Cent(2)	111.64
C(27)–Zr(1)–Cent(1)	105.07
C(27)–Zr(1)–Cent(2)	110.77
C(20)–Zr(1)–C(27)	103.5(2)
Zr(1)–C(20)–C(21)	122.1(3)
Zr(1)–C(27)–C(28)	122.7(3)

Cent(1) and Cent(2) are the centroids of C(1)–C(5) and C(10)–C(14), respectively; * refers to the average bond distance between Zr(1) and the carbon atoms of the C_5 ring of the corresponding cyclopentadienyl moiety.

The structure of **3b** shows the typical bent metallocene conformation observed in zirconocene dichloride complexes. The *ansa* ligand chelates the zirconium atom and both C_5 rings are bound to the metal in an η^5 mode. The pseudo-tetrahedral environment of the zirconium atom is completed by the two α-carbon atoms of the benzyl groups. The structural parameters of **3b** are directly comparable with those of its parent zirconocene dichloride complex **1b**.

The reaction of the isocyanide reagent $CNC_6H_3Me_2$-2,6 with **2** has been studied (Eq. (3)). The products of the insertion reactions, $[Zr\{R(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}\{\eta^2\text{-}MeC{=}NC_6H_3Me_2\text{-}2,6\}Me]$ (R = Pr^i (**4a**), Bu^n (**4b**), Bu^t (**4c**), Ph (**4d**)) were characterized by ^1H and ^{13}C NMR spectroscopy.



(3)

R = Pr^i (**4a**), Bu^n (**4b**), Bu^t (**4c**), Ph (**4d**)

Ar = $C_6H_3Me_2$-2,6

The migratory insertion of alkyl groups towards isocyanide ligands allow the introduction of iminoacyl groups which are present in different coordination modes. In fact, for high valent oxophilic early transition metals, the iminoacyl group typically adopts an η^2-coordination mode through both the nitrogen and carbon atoms [16]. Similarly, an η^2-coordination mode is proposed for the iminoacyl ligand in **4** on the basis of the IR and ^{13}C NMR spectroscopy which show the characteristic stretching vibration ν(C=N) at ca. 1600 cm^{-1} and iminoacyl quaternary carbon atom signal at ca. 250 ppm, respectively. The ^1H NMR spectra of **4** in addition to the expected signals for the *ansa*-metallocene protons, gave signals corresponding to the iminoacyl alkyl group (see Section 4).

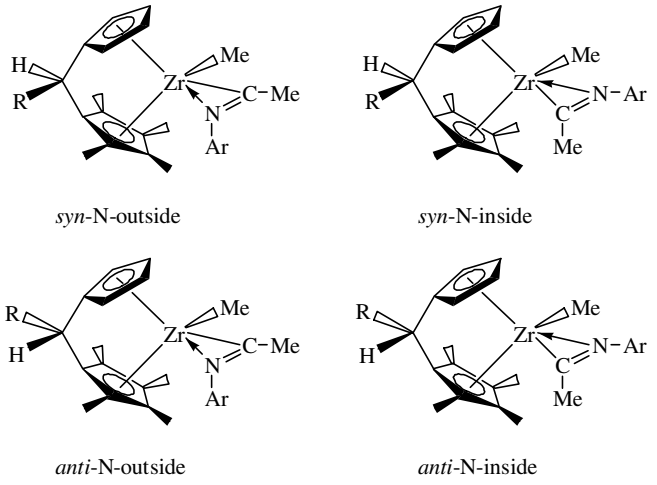


Fig. 4. Possible conformations for the iminoacyl metal complexes **4**.

The iminoacyl group can position itself in two distinct conformations, the "proximal" or "N-outside" and the "distal" or "N-inside" configurations (Fig. 4). In addition, in **4** the zirconium atom is now a chiral centre and therefore the formation of two diastereomers (*syn* and *anti*) is possible (Fig. 4). Due to the distance between the zirconium and the chiral carbon atom, the relative positioning of the substituents of the *ansa* bridge most probably will have no influence in the preferential insertion reaction at the *syn* or *anti* alkyl group. Therefore, we can expect that both the *syn* and *anti* isomers will be present in the final product. ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data indicate the presence of only two of the four possible conformations. Although it has been demonstrated that the N-outside isomer is the resulting initial kinetic iminoacyl product of the insertion reaction, most group 4 metal derivatives show the structure of the N-inside isomer which results from thermodynamic control [17]. For **4** the isolated product was observed not to evolve over time and therefore we tentatively propose that they are the products resulting from thermodynamic control and adopt the N-inside conformation. A second insertion was not observed even when stoichiometries other than 1:1 were tested.

3. Conclusions

In this paper, we report the synthesis and X-ray structures of chiral carbon atom bridged *ansa*-zirconocene complexes. The preparation and characterization of their dialkyl derivatives and their reactivity in isocyanide insertion reactions are also described.

4. Experimental

4.1. Materials and procedures

All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. [Zr{R(H)C(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (R = Bu^n, Bu^t, Ph) were prepared as described earlier [7]. MgMeCl, Mg(CH_2Ph)Cl and $CNC_6H_3Me_2$-2,6 were purchased from Aldrich and used directly. IR spectra were recorded on a Perkin–Elmer PE 883 IR spectrophotometer. ^1H and $^{13}C\{^1H\}$ spectra were recorded on a Varian Gemini FT-400 spectrometer and referenced to the residual protons in the deuteriated solvent. Microanalyses were carried out with a Perkin–Elmer 2400 microanalyzer.

4.2. Synthesis of [Zr{Pr^i(H)C(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**1a**)

[$ZrCl_4(THF)_2$] (1.81 g, 4.80 mmol) in toluene (50 ml) was added to a solution of LiK{Pr^i(H)C(η^5-C_5Me_4)(η^5-C_5H_4)} (1.37 g, 4.80 mmol) in Et_2O (100 ml). The reaction mixture was allowed to stir for 12 h. Solvent was removed under reduced pressure and hexane (100 ml) added to the resulting solid. The mixture was filtered and the filtrate concentrated (10 ml) and cooled to −30 °C to yield crystals of the title complex (1.10 g, 60%). ^1H NMR (400 MHz, C_6D_6): δ 0.87 (3H) ($^3J(^1H–^1H)$ 6.6 Hz), 0.91 (3H) ($^3J(^1H–^1H)$ 6.2 Hz) (d, HC*Me*$_2$), 1.49 (3H), 1.65 (3H), 1.86 (3H), 1.87 (3H) (s, C_5*Me*$_4$), 2.30 (m, 1H, *H*CMe$_2$), 3.42 (d, 1H, Pr^iCH) ($^3J(^1H–^1H)$ 12.1 Hz), 5.06 (1H), 5.13 (1H), 6.37 (1H), 6.48 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 11.7, 11.9, 12.7, 14.5 (C_5Me_4), 20.4, 21.5 (HC*Me*$_2$), 29.0 (H*C*Me$_2$), 48.5 (Pr^iCH), 104.1, 107.9, 119.5, 122.3, 128.9 (C_5H_4), 104.8, 114.8, 117.3, 120.9, 130.0 (C_5Me$_4$). Anal. Calc. for $C_{18}H_{24}Cl_2Zr$: C, 53.71; H, 6.01. Found: C, 53.45; H, 5.98%.

4.3. Synthesis of [Zr{Pr^i(H)C-(η^5-C_5Me_4)(η^5-C_5H_4)}$_2$$Me_2$] (**2a**)

A 3 M solution of MgMeBr in THF (0.50 ml, 1.50 mmol) was added to a stirring solution of [Zr{Pr^i(H)-C(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**1a**) (0.30 g, 0.75 mmol) in THF (25 ml) at −78 °C. The solution was allowed to warm to room temperature and stirred for 4 h. Solvent was removed in vacuo and the remaining solid extracted in hexane (30 ml). A white crystalline solid was obtained by concentrating (5 ml) and cooling (−30 °C) the solution (0.21 g, 80%). ^1H NMR (400 MHz, C_6D_6): δ −0.32 (s, 6H, Zr–*Me*), 0.93 (3H) ($^3J(^1H–^1H)$ 6.6 Hz), 0.98 (3H) ($^3J(^1H–^1H)$ 6.2 Hz) (d, HC*Me*$_2$), 1.48 (3H), 1.62 (3H), 1.85 (6H) (s, C_5*Me*$_4$), 2.21 (m, 1H, *H*CMe$_2$), 3.06 (d, 1H, Pr^iCH) ($^3J(^1H–^1H)$ 12.1 Hz), 4.99 (1H), 5.05 (1H), 6.32 (1H), 6.43 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 11.1, 11.4, 12.1, 13.9 (C_5Me_4), 20.8, 21.9 (HC*Me*$_2$), 29.0 (H*C*Me$_2$), 31.2, 31.3 (Zr–*Me*), 48.4 (Pr^iCH), 103.0, 107.1, 113.0, 115.1, 120.4 (C_5H_4), 99.3, 107.9, 114.4, 117.8, 121.2 (C_5Me$_4$). Anal. Calc. for $C_{20}H_{30}Zr$: C, 66.42; H, 8.36. Found: C, 66.09; H, 8.30%.

The preparation of **2b–d** and **3a–d** was carried out in an identical manner to **2a**.

4.4. Synthesis of [Zr{Bu^n(H)C(η^5-C_5Me_4)-(η^5-C_5H_4)}$_2$$Me_2$] (**2b**)

From 3 M solution of MgMeBr in THF (0.24 ml, 0.72 mmol) and [Zr{Bu^n(H)C(η^5-C_5Me_4)(η^5-C_5H_4)}$_2$$Cl_2$] (**1b**) (0.15 g, 0.36 mmol). Yield: 0.11 g, 80%. ^1H NMR (400 MHz, C_6D_6): δ −0.31 (3H), −0.22 (3H) (s, Zr–*Me*), 0.83 (2H), 0.86 (3H), 1.32 (4H) (m, CH_2CH_2-CH_2CH_3), 1.51 (3H), 1.68 (3H), 1.85 (3H), 1.87 (3H) (m, C_5*Me*$_4$), 3.51 (t, 1H, Bu^nCH) ($^3J(^1H–^1H)$ 8.4 Hz), 5.00 (1H), 5.15 (1H), 6.33 (1H), 6.43 (1H) (s, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 10.7, 11.1, 11.9, 13.7 (C_5Me_4), 14.3, 22.9, 30.2, 31.1 (*Bu*^{n}), 31.0, 31.1 (Zr–*Me*), 39.1 (Bu^nCH), 113.2, 114.8, 127.8, 128.1, 128.2 (C_5H_4), 99.0, 108.6, 117.4, 120.3, 121.2 (C_5Me$_4$). Anal. Calc. for $C_{21}H_{32}Zr$: C, 67.13; H, 8.58. Found: C, 66.91; H, 8.56%.

4.5. Synthesis of [Zr{Bu^t(H)C(η^5-C_5Me_4)-(η^5-C_5H_4)}$_2$$Me_2$] (**2c**)

From 3 M solution of MgMeBr in THF (0.44 ml, 1.32 mmol) and [Zr{Bu^t(H)C(η^5-C_5Me_4)(η^5-C_5H_4)}$_2$$Cl_2$] (**1c**) (0.23 g, 0.55 mmol). Yield: 0.15 g, 75%. ^1H NMR (400 MHz, C_6D_6): δ −0.34 (3H), −0.32 (3H) (s, Zr–*Me*), 1.08 (s, 9H, Bu^t), 1.51 (3H), 1.68 (3H), 1.85 (3H), 1.87 (3H) (s, C_5*Me*$_4$), 3.41 (s, 1H, Bu^tCH), 4.99 (1H), 5.09 (1H), 6.27 (1H), 6.46 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 11.5, 11.6, 12.5, 16.3 (C_5Me_4), 30.5, 33.6 (*Bu*^{t}), 31.1, 31.3 (Zr–*Me*), 51.8 (Bu^tCH), 106.1, 109.8, 111.9, 116.5, 120.3 (C_5H_4), 100.5, 107.2, 114.1, 119.9, 121.9 (C_5Me$_4$). Anal. Calc. for $C_{21}H_{32}Zr$: C, 67.13; H, 8.58. Found: C, 66.83; H, 8.50%.

4.6. Synthesis of [Zr{Ph(H)C(η^5-C_5Me_4)-(η^5-C_5H_4)}$_2$$Me_2$] (**2d**)

From 3 M solution of MgMeBr in THF (0.55 ml, 1.65 mmol) and [Zr{Ph(H)C(η^5-C_5Me_4)(η^5-C_5H_4)}$_2$$Cl_2$] (**1d**) (0.20 g, 0.46 mmol). Yield: 0.16 g, 85%. ^1H NMR (400 MHz, C_6D_6): δ −0.41 (3H), −0.32 (3H) (s, Zr–*Me*), 1.12 (3H), 1.46 (3H), 1.58 (3H), 1.74 (3H) (s, C_5*Me*$_4$), 4.80 (s, 1H, PhC*H*), 5.03 (1H), 5.10 (1H), 6.30 (1H), 6.38 (1H) (m, C_5H_4), 6.96–7.40 (m, 5H, *Ph*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 11.3, 11.5, 12.4, 14.6 (C_5Me_4), 31.9, 32.1 (Zr–*Me*), 43.3 (Ph*C*H), 105.3, 108.2, 113.1, 115.9, 121.9 (C_5H_4), 99.5, 105.7, 117.8, 120.4, 121.6 (C_5Me$_4$), 127.0, 128.0, 128.9, 141.4 (*Ph*). Anal. Calc. for $C_{23}H_{28}Zr$: C, 69.81; H, 7.13. Found: C, 69.69; H, 7.08%.

*4.7. Synthesis of [Zr{Pr^i(H)C(η^5-C$_5$Me$_4$)-(η^5-C$_5$H$_4$)}$_2$(CH$_2$Ph)$_2$] (**3a**)*

From 2 M solution of Mg(CH$_2$Ph)Br in THF (2.6 ml, 1.8 mmol) and [Zr{Pr^i(H)C(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}$_2$Cl$_2$] (**1a**) (0.30 g, 0.75 mmol). Yield: 0.33 g, 85%. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 0.84 (3H) (^3J(^{1}H–^{1}H) 7.0 Hz), 0.88 (3H) (^3J(^{1}H–^{1}H) 6.9 Hz) (d, HC*Me*$_2$), 0.96 (1H), 0.97 (1H) (^2J(^{1}H–^{1}H) 11.0 Hz), 1.77 (1H), 1.78 (1H) (^2J(^{1}H–^{1}H) 10.6 Hz) (d, C*H*$_2$Ph), 1.37 (3H), 1.51 (3H), 1.70 (3H), 1.71 (3H) (s, C$_5$*Me*$_4$), 2.05 (m, 1H, *H*CMe$_2$), 2.94 (d, 1H, Pr^{i}C*H*) (^3J(^{1}H–^{1}H) 12.1 Hz), 4.60 (1H), 4.71 (1H), 5.59 (1H), 5.73 (1H) (m, C$_5$*H*$_4$), 6.71–7.14 (m, 10H, CH$_2$*Ph*). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ 11.1, 11.4, 12.1, 13.9 (C$_5$*Me*$_4$), 20.6, 21.6 (HC*Me*$_2$), 28.8 (H*C*Me$_2$), 48.2 (Pr^i*C*H), 59.6, 59.9 (*C*H$_2$Ph), 107.8, 116.9, 119.7, 121.2, 122.7 (*C*$_5$H$_4$), 106.7, 113.6, 117.2, 121.8, 129.9 (*C*$_5$Me$_4$), 125.9, 126.1, 126.2 (4C), 128.7 (4C), 152.0 (2C) (CH$_2$*Ph*). Anal. Calc. for C$_{32}$H$_{38}$Zr: C, 74.79; H, 7.45. Found: C, 74.52; H, 7.37%.

*4.8. Synthesis of [Zr{Bu^n(H)C(η^5-C$_5$Me$_4$)-(η^5-C$_5$H$_4$)}$_2$(CH$_2$Ph)$_2$] (**3b**)*

From 2 M solution of Mg(CH$_2$Ph)Br in THF (1.40 ml, 2.80 mmol) and [Zr{Bu^n(H)C(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}$_2$Cl$_2$] (**1b**) (0.50 g, 1.20 mmol). Yield: 0.53 g, 85%. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 0.83 (2H), 0.86 (3H), 1.32 (4H) (m, C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_3$), 1.01 (1H), 1.04 (1H) (^2J(^{1}H–^{1}H) 10.1 Hz), 1.69 (1H), 1.87 (1H) (^2J(^{1}H–^{1}H) 11.6 Hz) (d, C*H*$_2$Ph), 1.46 (3H), 1.62 (3H), 1.75 (3H), 1.77 (3H) (s, C$_5$*Me*$_4$), 3.43 (d, 1H, Bu^{n}C*H*) (^3J(^{1}H–^{1}H) 8.4 Hz), 4.70 (1H), 4.90 (1H), 5.67 (1H), 5.79 (1H) (m, C$_5$*H*$_4$), 6.79–7.17 (m, 10H, CH$_2$*Ph*). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ 11.0, 11.4, 12.1, 14.0 (C$_5$*Me*$_4$), 14.5, 23.1, 30.3, 31.1 (*Bu^n*), 39.2 (Bu^n*C*H), 59.7, 60.1 (*C*H$_2$Ph), 104.5, 107.2, 117.1, 119.4, 122.7 (*C*$_5$H$_4$), 96.9, 106.9, 114.0, 116.7, 121.2 (*C*$_5$Me$_4$), 125.9, 126.0, 126.3 (2C), 126.4 (2C), 128.5 (2C), 128.6 (2C), 151.9, 152.1 (CH$_2$*Ph*). Anal. Calc. for C$_{33}$H$_{40}$Zr: C, 75.08; H, 7.64. Found: C, 74.97; H, 7.65%.

*4.9. Synthesis of [Zr{Bu^t(H)C(η^5-C$_5$Me$_4$)-(η^5-C$_5$H$_4$)}$_2$(CH$_2$Ph)$_2$] (**3c**)*

From 2 M solution of Mg(CH$_2$Ph)Br in THF (1.15 ml, 2.30 mmol) and [Zr{Bu^t(H)C(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}$_2$Cl$_2$] (**1c**) (0.40 g, 0.96 mmol). Yield: 0.35 g, 70%. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.04 (s, 9H, Bu^t), 0.97 (1H), 1.16 (1H) (^2J(^{1}H–^{1}H) 11.9 Hz), 1.86 (1H), 1.90 (1H) (^2J(^{1}H–^{1}H) 10.8 Hz) (d, C*H*$_2$Ph), 1.47 (3H), 1.66 (3H), 1.76 (3H), 1.77 (3H) (s, C$_5$*Me*$_4$), 3.33 (s, 1H, Bu^{t}C*H*), 4.64 (1H), 4.92 (1H), 5.57 (1H), 5.89 (1H) (m, C$_5$*H*$_4$), 6.75–7.18 (m, 10H, CH$_2$*Ph*). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ 11.0, 11.1, 12.2, 15.7 (C$_5$*Me*$_4$), 29.9, 30.3 (*Bu^t*), 51.3 (Bu^t*C*H), 59.0, 60.5 (*C*H$_2$Ph), 106.3, 110.6, 115.2, 120.8, 141.7 (*C*$_5$H$_4$), 98.2, 105.5, 112.9, 119.3, 123.3 (*C*$_5$Me$_4$), 125.9, 126.0, 126.1 (4C), 128.4 (2C), 128.5 (2C), 151.3, 152.5 (CH$_2$*Ph*). Anal. Calc. for C$_{33}$H$_{40}$Zr: C, 75.08; H, 7.64. Found: C, 74.76; H, 7.58%.

*4.10. Synthesis of [Zr{Ph(H)C(η^5-C$_5$Me$_4$)-(η^5-C$_5$H$_4$)}$_2$(CH$_2$Ph)$_2$] (**3d**)*

From 2 M solution of Mg(CH$_2$Ph)Br in THF (0.80 ml, 1.63 mmol) and [Zr{Ph(H)C(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}$_2$Cl$_2$] (**1d**) (0.30 g, 0.68 mmol). Yield: 0.26 g, 70%. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 0.98 (1H), 1.02 (1H) (^2J(^{1}H–^{1}H) 11.7 Hz), 1.72 (1H), 1.88 (1H) (^2J(^{1}H–^{1}H) 10.4 Hz) (d, C*H*$_2$Ph), 1.12 (3H), 1.45 (3H), 1.67 (3H), 1.78 (3H) (s, C$_5$*Me*$_4$), 4.78 (s, 1H, PhC*H*), 4.75 (1H), 4.92 (1H), 5.67 (1H), 5.78 (1H) (m, C$_5$*H*$_4$), 6.71–7.19 (m, 15H, CH$_2$*Ph* and *Ph*CH). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ 11.1, 11.3, 12.1, 14.5 (C$_5$*Me*$_4$), 45.2 (Ph*C*H), 58.8, 59.9 (*C*H$_2$Ph), 103.4, 106.2, 117.0, 119.4, 121.7 (*C*$_5$H$_4$), 99.9, 106.7, 117.8, 120.7, 121.7 (*C*$_5$Me$_4$), 125.4, 128.2, 128.8, 141.8 (*Ph*CH), 126.1, 126.6, 127.9 (4C), 128.7 (4C), 156.6 (2C) (CH$_2$*Ph*). Anal. Calc. for C$_{35}$H$_{36}$Zr: C, 76.73; H, 6.62. Found: C, 76.48; H, 6.54%.

*4.11. Synthesis of [Zr{Pr^i(H)C(η^5-C$_5$Me$_4$)-(η^5-C$_5$H$_4$)}$_2${η^2-MeC=NC$_6$H$_3$Me$_2$-2,6}Me] (**4a**)*

(2,6-Dimethylphenyl)isocyanide (0.18 g, 1.40 mmol) and [Zr{Pr^i(H)C(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}$_2$Me$_2$] (**2a**) (0.50 g, 1.40 mmol) were dissolved in THF (100 ml). The resulting solution was stirred at room temperature for 2 h. Solvent was removed in vacuo and the remaining solid extracted with hexane (30 ml). A yellow solid was obtained by concentrating (5 ml) and cooling (−30 °C) the solution (0.59 g, 85%). IR (Nujol): ν(C=N) 1590 cm^{-1}. ^{1}H NMR (400 MHz, C$_6$D$_6$; two isomers): δ −0.01 (3H), 0.00 (3H) (s, Zr–*Me*), 0.93 (3H) (^3J(^{1}H–^{1}H) 6.6 Hz), 0.98 (3H) (^3J(^{1}H–^{1}H) 6.2 Hz) (d, HC*Me*$_2$), 1.51 (3H), 1.83 (6H), 2.07 (3H), 2.08 (3H), 2.18 (3H), 2.20 (3H), 2.25 (3H) (s, C$_5$*Me*$_4$), 1.87 (6H), 1.88 (6H) (s, C$_6$H$_3$*Me*$_2$), 2.38 (s, 6H, NC*Me*), 2.61 (1H), 2.72 (1H) (m, *H*CMe$_2$), 3.38 (1H) (^3J(^{1}H–^{1}H) 12.1 Hz), 3.52 (1H) (^3J(^{1}H–^{1}H) 11.7 Hz) (d, Pr^{i}C*H*), 5.34 (1H), 5.46 (1H), 5.51 (2H), 5.65 (1H), 5.67 (1H), 5.76 (1H), 5.92 (1H) (m, C$_5$*H*$_4$), 7.01 (m, 6H, C$_6$*H*$_3$Me$_2$). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$; two isomers): δ 10.8, 11.0, 11.1, 11.5, 11.8, 12.7, 13.8, 14.5 (C$_5$*Me*$_4$), 18.7 (2C), 18.8 (2C) (C$_6$H$_3$*Me*$_2$), 21.0 (2C), 21.9 (2C) (HC*Me*$_2$), 27.3, 27.5 (Zr–*Me*), 22.9, 23.0 (NC*Me*), 28.7, 29.2 (H*C*Me$_2$), 48.2, 48.3 (Pr^i*C*H), 101.6, 105.8, 108.5, 108.8 (2C), 110.6, 111.6, 115.1, 116.9, 117.6 (*C*$_5$H$_4$), 96.8 (2C), 99.7, 106.9, 107.6, 108.6, 110.5, 111.4, 116.0, 116.6 (*C*$_5$Me$_4$), 127.6 (4C), 127.9 (2C), 128.4 (2C), 129.1 (2C), 129.3 (2C) (*C*$_6$H$_3$Me$_2$), 248.2, 248.5 (N*C*). Anal. Calc. for C$_{29}$H$_{39}$NZr: C, 70.67; H, 7.98; N, 2.84. Found: C, 70.35; H, 7.99; N, 2.89%.

The preparation of **4b–d** was carried out in an identical manner to **4a**.

4.12. Synthesis of [Zr{Bu^n(H)C(η^5-C$_5$Me$_4$)-(η^5-C$_5$H$_4$)}$_2${η^2-MeC=NC$_6$H$_3$Me$_2$-2,6}Me] (**4b**)

From 2,6-dimethylphenyl isocyanide (0.17 g, 1.33 mmol) and [Zr{Bu^n(H)C(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}$_2$Me$_2$] (**2b**) (0.50 g, 1.33 mmol). Yield: 0.57 g, 86%. IR (Nujol): ν(C=N) 1605 cm^{-1}. ^{1}H NMR (400 MHz, C$_6$D$_6$; two isomers): δ −0.13 (3H), −0.12 (3H) (s, Zr–*Me*), 0.89 (6H), 1.31–1.46 (12H) (m, C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_3$), 1.35 (3H), 1.38 (3H), 1.69 (6H), 1.90 (3H), 1.95 (3H), 2.09 (3H), 2.12 (3H) (s, C$_5$*Me*$_4$), 1.72 (6H), 1.73 (6H) (s, C$_6$H$_3$*Me*$_2$), 2.26 (s, 6H, NC*Me*), 3.66 (1H) (^3J(^{1}H–^{1}H) 8.4 Hz), 3.81 (1H) (^3J(^{1}H–^{1}H) 8.4 Hz) (t, Bu^{n}C*H*), 5.20 (1H), 5.31 (1H), 5.37 (1H), 5.47 (1H), 5.50 (1H), 5.63 (2H), 5.76 (1H) (m, C$_5$*H*$_4$), 6.86 (m, 6H, C$_6$*H*$_3$Me$_2$). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$; two isomers): δ 11.4, 11.5, 11.7, 11.8, 12.2, 13.1, 14.2, 14.9 (C$_5$*Me*$_4$), 14.7, 14.8, 19.1 23.2, 23.3, 23.4, 30.8, 30.9 (*Bu^n*), 19.4 (2C), 19.5 (2C) (C$_6$H$_3$*Me*$_2$), 31.6, 31.8 (Zr–*Me*), 30.3, 31.4 (NC*Me*), 39.4, 39.5 (Bu^n*C*H), 97.2, 107.5, 108.5, 109.0, 110.1, 110.3, 111.1, 115.3, 115.4, 115.9 (*C*$_5$H$_4$), 99.3, 102.1, 105.2, 108.2, 108.4, 109.0 (2C), 116.7, 116.9, 117.5 (*C*$_5$Me$_4$), 124.9 (2C), 128.3 (4C), 128.4 (4C), 129.3 (2C) (*C*$_6$H$_3$Me$_2$), 247.8, 248.0 (N*C*). Anal. Calc. for C$_{30}$H$_{41}$NZr: C, 71.09; H, 8.15; N, 2.76. Found: C, 70.86; H, 8.07; N, 2.74%.

4.13. Synthesis of [Zr{Bu^t(H)C(η^5-C$_5$Me$_4$)-(η^5-C$_5$H$_4$)}$_2${η^2-MeC=NC$_6$H$_3$Me$_2$-2,6}Me] (**4c**)

From 2,6-dimethylphenyl isocyanide (0.17 g, 1.33 mmol) and [Zr{Bu^n(H)C(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}$_2$Me$_2$] (**2c**) (0.50 g, 1.33 mmol). Yield: 0.53 g, 79%. IR (Nujol): ν(C=N) 1620 cm^{-1}. ^{1}H NMR (400 MHz, C$_6$D$_6$; two isomers): δ −0.11 (3H), −0.10 (3H) (s, Zr–*Me*), 1.24 (9H), 1.25 (9H) (s, *Bu^t*), 1.37 (3H), 1.38 (3H), 1.68 (3H), 1.69 (3H), 1.70 (3H), 1.71 (3H), 1.72 (3H), 1.74 (3H) (s, C$_5$*Me*$_4$), 1.90 (6H), 1.95 (6H) (s, C$_6$H$_3$*Me*$_2$), 2.30 (s, 6H, NC*Me*), 3.61 (1H), 3.77 (1H) (s, Bu^{t}C*H*), 5.09 (1H), 5.16 (1H), 5.38 (1H), 5.42 (1H), 5.46 (1H), 5.81 (1H), 6.27 (1H), 6.46 (1H) (m, C$_5$*H*$_4$), 6.86 (m, 6H, C$_6$*H*$_3$Me$_2$). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$; two isomers): δ 11.2, 11.3, 11.5, 11.6, 12.2, 12.3, 15.8, 16.0 (C$_5$*Me*$_4$), 19.9 (2C), 20.1 (2C) (C$_6$H$_3$*Me*$_2$), 33.2, 33.3, 33.5, 33.6 (*Bu^t*), 27.3, 27.5 (Zr–*Me*), 22.9, 23.0 (NC*Me*), 51.9, 52.0 (Bu^t*C*H), 106.1, 106.2, 109.9, 110.2, 115.8, 115.9, 116.6, 116.7, 120.2, 120.3 (*C*$_5$H$_4$), 101.0, 101.5, 112.7, 112.9, 114.1, 115.4, 117.2, 118.2, 123.0, 123.9 (*C*$_5$Me$_4$), 124.4 (2C), 127.6 (4C), 128.0 (4C), 129.9 (2C) (*C*$_6$H$_3$Me$_2$), 248.9, 249.0 (N*C*). Anal. Calc. for C$_{30}$H$_{41}$NZr: C, 71.09; H, 8.15; N, 2.76. Found: C, 70.72; H, 8.11; N, 2.70%.

Table 4
Crystal data and structure refinement details for **1b**, **1c** and **3b**

Compound	**1b**	**1c**	**3b**
Formula	C$_{19}$H$_{26}$Cl$_2$Zr	C$_{19}$H$_{26}$Cl$_2$Zr	C$_{33}$H$_{40}$Zr
Formula weight	416.52	416.52	527.87
T (K)	230(2)	200(2)	100(2)
λ (Å)	0.71073	0.71073	1.54178
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	8.531(3)	9.1010(8)	9.7276(1)
b (Å)	9.352(3)	16.593(1)	17.9351(1)
c (Å)	12.144(7)	12.634(3)	15.7562(1)
α (°)	86.69(2)		
β (°)	83.59(2)	97.95(1)	100.756(1)
γ (°)	79.57(3)		
V (Å^3)	946.2(5)	1889.6(5)	2700.62(4)
Z	2	4	4
D_{calc} (g cm^{-3})	1.462	1.464	1.298
μ (mm^{-1})	0.858	0.860	3.450
F(000)	428	856	1112
Crystal dimensions (mm)	0.3 × 0.2 × 0.1	0.3 × 0.2 × 0.2	0.20 × 0.15 × 0.15
θ Range (°)	2.22–28.05	2.04–27.98	3.77–70.57
hkl Ranges	$-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 16$	$-12 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 21$, $0 \leqslant l \leqslant 16$	$-10 \leqslant h \leqslant 11$, $-21 \leqslant k \leqslant 19$, $-18 \leqslant l \leqslant 19$
Data/parameters	4530/243	4519/203	4868/366
Goodness-of-fit on F^2	1.029	1.017	1.094
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0710$, $wR_2 = 0.1684$	$R_1 = 0.0646$, $wR_2 = 0.1191$	$R_1 = 0.0505$, $wR_2 = 0.1273$
R indices (all data)	$R_1 = 0.1318$, $wR_2 = 0.2115$	$R_1 = 0.1675$, $wR_2 = 0.1489$	$R_1 = 0.0543$, $wR_2 = 0.1301$
Largest difference in peak and hole (e Å^{-3})	1.099 and −0.950	1.156 and −0.518	0.807 and −0.610

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

4.14. Synthesis of [Zr{Ph(H)C(η5-C5Me4)-(η5-C5H4)}2{η2-MeC=NC6H3Me2-2,6}Me] (4d)

From 2,6-dimethylphenyl isocyanide (0.17 g, 1.33 mmol) and [Zr{Ph(H)C(η5-C5Me4)(η5-C5H4)}2Me2] (**2d**) (0.52 g, 1.33 mmol). Yield: 0.56 g, 80%. IR (Nujol): ν(C=N) 1570 cm−1. 1H NMR (400 MHz, C6D6; two isomers): δ −0.16 (3H), −0.14 (3H) (s, Zr–*Me*), 1.34 (3H), 1.35 (3H), 1.40 (3H), 1.55 (3H), 1.58 (3H), 1.64 (3H), 1.66 (3H), 1.69 (3H) (s, C5*Me*4), 1.76 (6H), 1.77 (6H) (s, C6H3*Me*2), 1.96 (3H), 1.98 (3H) (s, NC*Me*), 4.99 (1H), 5.27 (1H) (s, PhC*H*), 4.89 (1H), 5.06 (1H), 5.15 (1H), 5.19 (1H), 5.48 (1H), 5.50 (1H), 5.58 (1H), 5.69 (1H) (m, C5*H*4), 6.80–7.20 (m, 11H, C6*H*3Me2 and *Ph*). 13C{1H} NMR (100 MHz, C6D6; two isomers): δ 11.2, 11.3, 11.4, 11.6, 12.2, 12.4, 14.3, 14.6 (C5*Me*4), 19.0 (2C), 19.5 (2C) (C6H3*Me*2), 36.6, 37.2 (Zr–*Me*), 38.0, 38.4 (NC*Me*), 44.2, 44.5 (Ph*C*H), 101.1 (2C), 107.9 (2C), 111.0, 113.6, 113.8, 117.5, 119.0, 119.3 (*C*5H4), 102.0 (2C), 103.7, 108.3, 109.3 (2C), 114.1, 115.6, 115.8, 116.2 (*C*5Me4), 125.6 (2C), 126.8 (4C), 130.01 (4C), 134.8 (2C) (*C*6H3Me2), 125.2, 125.4, 128.0 (4C), 128.6 (4C), 141.8 (2C) (*Ph*CH), 247.9, 248.5 (N*C*). Anal. Calc. for C32H37NZr: C, 72.95; H, 7.08; N, 2.66. Found: C, 72.59; H, 7.02; N, 2.63%.

4.15. X-ray structure determinations of [Zr{Bun(H)C-(η5-C5Me4)(η5-C5H4)}Cl2] (1b), [Zr{But(H)C-(η5-C5Me4)(η5-C5H4)}Cl2] (1c) and [Zr{Bun(H)C-(η5-C5Me4)(η5-C5H4)}(CH2Ph)2] (3b)

For **1b** and **1c**, data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromated Mo Kα radiation source (λ = 0.71073 Å). The crystal data, data collection, structural solution, and refinement parameters for both compounds are summarized in Table 4. Intensity data were collected using an ω/2θ scan-technique. Examination of two standard reflections, monitored after 60 min, showed no sign of crystal deterioration. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction (ψ-scans) was made [18]. The structures were solved by direct methods using the SIR-92 program [19] and refined by full-matrix least-squares methods (SHELXL-97) [20] on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

For **3b**, data were collected on a Bruker SMART CCD-based diffractometer (Cu Kα radiation, λ = 1.54178 Å) operating at 50 kV and 100 mA, using ω/2θ scan-technique. Absorption corrections were applied using the SADABS program [21]. The structure was solved using the SHELXTL structure determination package [22] by direct methods and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, and refined in the riding model. Weights were optimized in the final cycles. Crystallographic data are given in Table 4.

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Appendix A. Supplementary material

Crystallographic data for the structural analyses of **1b**, **1c** and **3b** have been deposited with the Cambridge Crystallographic Data Centre, CCDC-287186, CCDC-287187 and CCDC-287188. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.02.039.

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