Synthesis and Reactivity of Alkylzirconium Complexes Incorporating Asymmetrically Substituted *ansa* Ligands − X-ray Crystal Structure of [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Me)$}$(CH_2Ph)Cl$]

Antonio Antiñolo,[a] Rafael Fernández-Galán,[a] Beatriz Gallego,[a] Antonio Otero,*[a] Sanjiv Prashar,[b] and Ana M. Rodríguez[c]

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The monoalkyl complexes [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3R)$}$(R')Cl$] [R = Me, R′ = CH_2Ph (**1**); R = Me, R′ = CH_2SiMe_3 (**2**); R = *i*Pr, R′ = CH_2Ph (**3**); R = *i*Pr, R′ = CH_2SiMe_3 (**4**); R = $SiMe_3$, R′ = CH_2Ph (**5**); R = $SiMe_3$, R′ = CH_2SiMe_3 (**6**)] have been synthesized by the reaction of the corresponding *ansa*-metallocene dichloride complex and 1 equiv of the alkyl Grignard reagent. Dialkyl complexes with large alkyl groups only formed for the zirconocene complex containing the *ansa* ligand $Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$ and with the benzyl substituent giving [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}$(CH_2Ph)_2$] (**7**). When the alkyl substituent is CH_2SiMe_3 only the monoalkyl derivative, [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}$(CH_2SiMe_3)Cl$] (**8**), was formed. The insertion reaction of the isocyanide reagent $CNC_6H_3Me_2$-2,6 into the zirconium–carbon σ-bond of complexes **1**–**8** gave the corresponding η^2-iminoacyl compound [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3R)$}{η^2-R′C=$NC_6H_3Me_2$-2,6}Cl] [R = Me, R′ = CH_2Ph (**9**); R = Me, R′ = CH_2SiMe_3 (**10**); R = *i*Pr, R′ = CH_2Ph (**11**); R = *i*Pr, R′ = CH_2SiMe_3 (**12**); R = $SiMe_3$, R′ = CH_2Ph (**13**); R = $SiMe_3$, R′ = CH_2SiMe_3 (**14**); R = H, R′ = CH_2SiMe_3 (**16**)] and [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}{η^2-$PhCH_2C$=$NC_6H_3Me_2$-2,6}(CH_2Ph)] (**15**). The molecular structure of **1** has been determined by single-crystal X-ray diffraction studies.

Introduction

Zirconocene complexes are of considerable interest due to their synthetic and catalytic applications.[1] The relationship between the properties of different zirconocene catalysts and their molecular structures has been the subject of in-depth studies. The main emphasis of these studies has centred on the steric effects of various ring substituents and bridging units on the properties of the catalysts and their polymer products.[2] However, considerably less work has been carried out into the electronic effects that different ligands exert on the relative electron densities at the zirconium centre,[3] even though they will influence the reactivity of the catalysts.[4]

Although modifications of cyclopentadienyl ligands simultaneously change both the steric and electronic effects, a rational design of new olefin polymerization catalysts requires an approach in which the electron density at the metal atom and the shape of a coordination site can be predicted.[5] Recent studies have demonstrated that the incorporation of an *ansa* bridge may have a profound influence on the chemistry of metallocene systems.[6] The electrochemical properties of group-4 *ansa*-metallocene complexes have previously been reported[7] and indicate that a positive shift of E° occurs versus their non-*ansa* analogues. For example, the complex [Zr{$Me_2Si(\eta^5$-$C_5H_4)_2$}Cl_2] is reduced at a lesser negative potential than [$Zr(\eta^5$-$C_5H_5)_2Cl_2$] (by 0.1 V).[7a] Therefore it is well established that the electron density at the metal atom is modified by the alkyl group substituents of the cyclopentadienyl ligand. In methyl-substituted zirconocene dihalide complexes [$Zr(\eta^5$-$C_5H_{5-n}Me_n)_2Cl_2$] (n = 0−5) such trends were observed in shifts of electrochemical reduction potentials.[8] We have observed the same effect in our recently presented study on the electrochemistry of niobium(IV) dichloride complexes which contain the same *ansa* ligands as those discussed presently in this paper.[9]

Alkylzirconocene cations are currently of interest due to their role as single-site Ziegler−Natta olefin polymerization catalysis.[10] Common precursors to these cationic catalysts include dimethyl- and dibenzylzirconocenes which are stable species.[10,11]

[a] Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, Facultad de Químicas, Campus Universitario, 13071 Ciudad Real, Spain
Fax: (internat.) + 34-926/295-318
E-mail: Antonio.Otero@uclm.es
[b] Departamento de Tecnología Química, Ambiental y de los Materiales, E.S.C.E.T., Universidad Rey Juan Carlos, 28933 Móstoles (Madrid), Spain
[c] ETS Ingenieros Industriales, Avd. Camilo José Cela, 3, 13071 Ciudad Real, Spain

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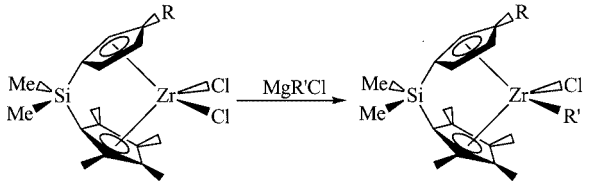
We recently developed a general synthesis of some $SiMe_2$-bridged asymmetric *ansa*-zirconocene complexes[12] and this series of highly active C_1-symmetric catalysts polymerize propylene with a high level of stereospecificity.[12b] Our research in this area is now focused on the elucidation of the mechanism of olefin polymerization as well as on the use of new types of metallocene complexes in stereoselective catalysis.[13]

In this paper we report our studies on the synthesis, characterization, and reactivity of new benzyl- and [(trimethylsilyl)methyl]zirconium derivatives containing asymmetric *ansa* ligands. Special attention is paid to the steric factors that govern the alkylation reactions due to the implication that this may have on the stereoselective mechanism in α-olefin polymerization.

Results and Discussion

The synthesis of the monoalkyl complexes, [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3R)$}(R′)Cl] [R = Me, R′ = CH_2Ph (**1**); R = Me, R′ = CH_2SiMe_3 (**2**); R = *i*Pr, R′ = CH_2Ph (**3**); R = *i*Pr, R′ = CH_2SiMe_3 (**4**); R = $SiMe_3$, R′ = CH_2Ph (**5**); R = $SiMe_3$, R′ = CH_2SiMe_3 (**6**)], was carried out by the reaction of 1 equiv. of the alkyl Grignard reagent with the corresponding *ansa*-metallocene dichloride derivative (Scheme 1).



R = Me, R' = CH_2Ph (**1**);
R = Me, R' = CH_2SiMe_3 (**2**);
R = *i*Pr, R' = CH_2Ph (**3**);
R = *i*Pr, R' = CH_2SiMe_3 (**4**);
R = $SiMe_3$, R' = CH_2Ph (**5**);
R = $SiMe_3$, R' = CH_2SiMe_3 (**6**)

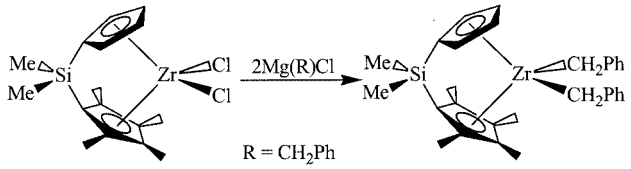
Scheme 1

The planar chirality exhibited by the *ansa*-zirconocene dichloride complexes, [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3R)$}Cl_2] (R = Me, *i*Pr, $SiMe_3$),[12] means that the two chloride positions are not equivalent. Thus, in the monoalkyl substitution reaction there exists the possibility of the formation of two stereoisomers. In all cases ^{1}H NMR spectroscopy revealed that only one of these isomers was present. In addition signals were observed for the nonequivalent methyl groups of the permethylated cyclopentadienyl moiety (4 singlets), the methyl groups of the $SiMe_2$ bridge (2 singlets), and the three protons of the monosubstituted cyclopentadienyl fragment (3 multiplets) (see Exp. Sect.). The methylene protons of the alkyl group (CH_2SiMe_3 or CH_2Ph) are diastereotopic due to the chiral nature of the metal centre and thus two doublets were observed in the ^{1}H NMR spectra of **1**−**6**. The signals corresponding to the differing alkyl groups (cyclopentadienyl- and metal-substituted) were also observed.

The corresponding dialkyl complexes were not obtained even when an excess of the alkylating reagent was used. This fact may be due to the bulky nature of the metal-bonded alkyl substituent or the presence of the β-alkyl substituent of the monosubstituted cyclopentadienyl moiety or indeed attributed to a combination of the two factors.

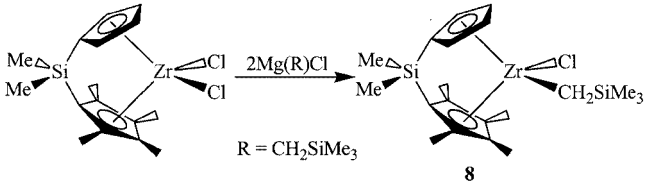
In the previously reported dimethyl complexes [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3R)$}Me_2] (R = H, Me, *i*Pr, $SiMe_3$), dialkyl substitution was shown to readily occur.[12b] The obvious reason for this reactivity can be attributed to the small size of the methyl group which allows the easy entry to the metal centre of two alkyl ligands which in addition also seem to be unaffected by the absence or presence of the β-cyclopentadienyl substituent.

For the *ansa*-zirconocene dichloride complex [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (i.e. no β-substituent present) the alkylation reaction with the benzyl group gave the disubstituted derivative, [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}$(CH_2Ph)_2$] (**7**) (Scheme 2). This indicates that in the case of benzylation that the conditioning factor leading to mono- or disubstitution corresponds to the nature of β-substitution in the *ansa*-cyclopentadienyl ligand.



Scheme 2

When the same reaction was carried out but using $Mg(CH_2SiMe_3)Cl$ as the alkylating agent only the monoalkyl derivative, [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}(CH_2SiMe_3)Cl] (**8**), was isolated (Scheme 3). Therefore we can infer that for the bulkier CH_2SiMe_3 ligand, its voluminous nature (and not the substituent present in the cyclopentadienyl moiety) is the primary factor in the steric demands imposed on the final product.



Scheme 3

The syntheses of bis(CH_2SiMe_3) derivatives of non-*ansa*-zirconocene complexes, [Zr(η^5-$C_5H_4R)_2(CH_2SiMe_3)_2$] (R = H, Me, Et, *i*Pr, *t*Bu), have been reported.[14] However, the attempted preparation of the hafnium analogue with R = *t*Bu proved unsuccessful and gave only the monosubstituted derivative [Hf(η^5-C_5H_4tBu)$_2(CH_2SiMe_3)$Cl].[14a] In addition, when the size of the alkyl ligand was increased to $CH(SiMe_3)_2$, only the synthesis of the monoalkyl deriva-

tives, $[Zr(\eta^5\text{-}C_5H_4R)_2\{CH(SiMe_3)_2\}Cl]$ (R = H, Me, Et, *i*Pr, *t*Bu, $SiMe_3$), was possible.[15] It seems obvious therefore that steric constraints and not electronic effects are responsible for the substitution reaction behaviour. In the *ansa* complexes where there is no free rotation of the C_5 rings, their substituents are located in fixed positions and thus those located in the β-positions will always influence sterically the reactions at the metal centre. In addition, one can imagine that the flexibility of the cyclopentadienyl rings in non-*ansa* derivatives makes them less sensitive to steric factors than their more rigid *ansa*-metallocene analogues and this may explain why we only obtained the monoalkyl compound $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}(CH_2SiMe_3)Cl]$ (**8**) and that dialkyl derivatives $[Zr(\eta^5\text{-}C_5H_4R)_2(CH_2SiMe_3)_2]$ (R = H, Me, Et, *i*Pr, *t*Bu)[15] could be readily formed for the non-*ansa* analogues.

For **7** and **8** ^{1}H NMR spectroscopy confirms the di- and monoalkyl substitution, respectively. The difference in symmetry of **7** (bis, C_s) and **8** (mono, C_1) is reflected in the ^{1}H NMR spectra. For the C_s symmetry in **7** only two signals were observed for the four protons of the unsubstituted cyclopentadienyl ring, two signals for the four methyl groups of the tetramethylcyclopentadienyl ring, one singlet for the two methyl groups of the *ansa*-$SiMe_2$ bridge, and one singlet for the methylene protons corresponding to the two benzyl ligands. For the C_1 symmetry in **8** four signals were observed for the four protons of the unsubstituted cyclopentadienyl ring, four signals for the four methyl groups of the tetramethylcyclopentadienyl ring, two singlets for the two methyl groups of the *ansa*-$SiMe_2$ bridge and two multiplets for the diastereoscopic methylene protons corresponding to the CH_2SiMe_3 ligand.

The molecular structure of **1** was established by single-crystal X-ray diffraction studies. The molecular structure and atomic numbering scheme are shown in Figure 1. Selected bond lengths and angles for **1** are given in Table 1.

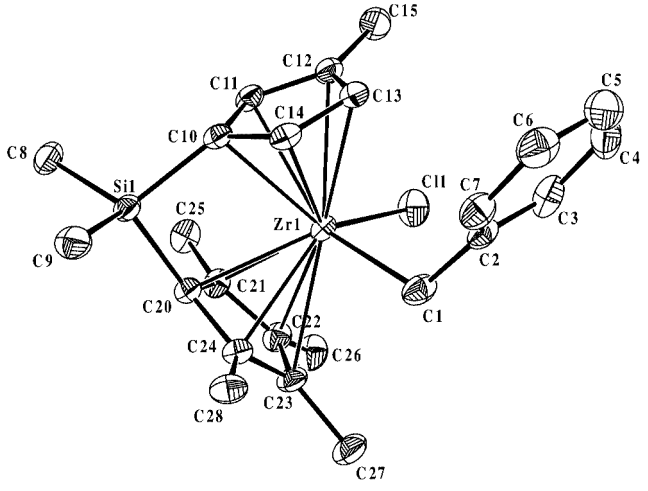


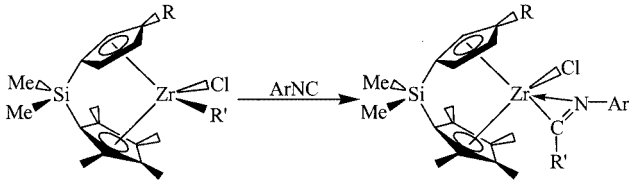
Figure 1. Molecular structure and atom-labeling scheme for $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)\}(CH_2Ph)Cl]$ (**1**) with thermal ellipsoids at 30% probability

The structure of **1** 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 atom in an η^5-mode. The environment of the zirconium atom is completed by a chlorine atom and the α-carbon atom of the benzyl group. The structure also reveals that the methyl substituent of the monosubstituted C_5 ring is orientated away from the benzyl group in a manner similar to that recently reported for imido *ansa*-niobocene complexes.[12a] The structural parameters of **1** are directly similar to those of its parent zirconocene dichloride complex $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)\}Cl_2]$.[12a]

Table 1. Selected bond lengths [Å] and angles [°] for **1**; Cent(1) and Cent(2) are the centroids of C(10)−C(14) and C(20)−C(24), respectively; * refers to the average bond length between Zr(1) and the carbon atoms of the C_5 ring of the corresponding cyclopentadienyl moiety

Zr(1)−Cent(1)	2.221
Zr(1)−Cent(2)	2.226
av Zr(1)−C[Cent(1)]*	2.525
av Zr(1)−C[Cent(2)]*	2.533
Zr(1)−Cl(1)	2.4261(9)
Zr(1)−C(1)	2.327(3)
C(1)−C(2)	1.475(4)
Cent(1)−Zr(1)−Cent(2)	126.50
Si(1)−C(10)−Cent(1)	162.02
Si(1)−C(20)−Cent(2)	162.23
C(10)−Si(1)−C(20)	94.72(11)
Cl(1)−Zr(1)−Cent(1)	109.43
Cl(1)−Zr(1)−Cent(2)	109.96
C(1)−Zr(1)−Cent(1)	106.94
C(1)−Zr(1)−Cent(2)	103.47
Cl(1)−Zr(1)−C(1)	95.90(9)
Zr(1)−C(1)−C(2)	118.3(2)

The reaction of the isocyanide reagent $CNC_6H_3Me_2$-2,6 with **1**−**8** has been studied (Scheme 4). The products of the insertion reactions $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)\}\{\eta^2\text{-}R'C{=}NC_6H_3Me_2\text{-}2,6\}Cl]$ [R = Me, R′ = CH_2Ph (**9**); R = Me, R′ = CH_2SiMe_3 (**10**); R = *i*Pr, R′ = CH_2Ph (**11**); R = *i*Pr, R′ = CH_2SiMe_3 (**12**); R = $SiMe_3$, R′ = CH_2Ph (**13**); R = $SiMe_3$, R′ = CH_2SiMe_3 (**14**); R = H, R′ = CH_2SiMe_3 (**16**)] and $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}\{\eta^2\text{-}PhCH_2C{=}NC_6H_3Me_2\text{-}2,6\}(CH_2Ph)]$ (**15**) were characterized by ^{1}H and ^{13}C NMR spectroscopy.



Ar = $C_6H_3Me_2$-2,6

R = Me, R' = CH_2Ph (**9**);
R = Me, R' = CH_2SiMe_3 (**10**);
R = *i*Pr, R' = CH_2Ph (**11**);
R = *i*Pr, R' = CH_2SiMe_3 (**12**);
R = $SiMe_3$, R' = CH_2Ph (**13**);
R = $SiMe_3$, R' = CH_2SiMe_3 (**14**)

Scheme 4

The migratory insertion of alkyl groups towards isocyanide ligands allows 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 **9**−**16** on the basis of IR and ^{13}C NMR spectroscopy which show the characteristic stretching vibration $\nu(C{=}N)$ at ca. 1600 cm^{-1} and iminoacyl quaternary carbon atom signal at $\delta \approx 250$ ppm, respectively. The ^1H NMR spectra of **9**−**16** in addition to the expected signals for the *ansa*-metallocene protons, gave signals corresponding to the iminoacyl alkyl group (see Exp. Sect.).

The iminoacyl group can position itself in two distinct conformations, the "proximal" or "N-outside" and the "distal" or "N-inside" configurations (see Figure 2). ^1H and ^{13}C NMR spectroscopic data indicate the presence of only one of the two 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 **9**−**16** 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.

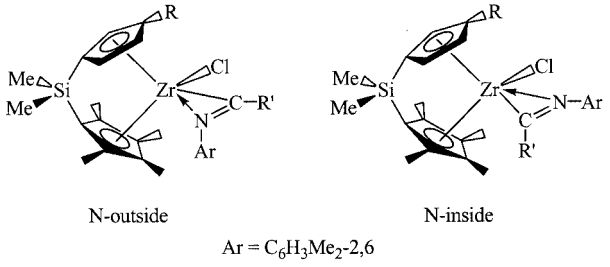


Figure 2. Two possible conformations for the (iminoacyl)metal complexes **9**−**16**

A second insertion was not observed even when stoichiometries other than 1:1 were tested.

Conclusions

In this paper we report our studies of the steric factors involved in the synthesis of alkylzirconocene complexes containing asymmetric *ansa* ligands. The preparation and characterization of mono- and dialkyl derivatives is described. The structural characterization of the monoalkyl complexes show the disposition of the β-alkyl substituent of the monosubstituted cyclopentadienyl moiety is such to orientate it away from the metal-bonded alkyl ligand. Insertion reactions with a bulky isocyanide, to give η^2-iminoacyl complexes, are also described.

Experimental Section

General Remarks: All reactions were performed using standard Schlenk tube techniques under dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Compounds [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3R)$}Cl_2] (R = H, Me, *i*Pr, $SiMe_3$) were prepared as described earlier.[12a] $Mg(CH_2Ph)Cl$, $Mg(CH_2SiMe_3)Cl$, and $CNC_6H_3Me_2$-2,6 were purchased from Aldrich and used directly. IR spectra were recorded with a Perkin−Elmer PE 883 IR spectrophotometer. ^1H and ^{13}C spectra were recorded with a Varian FT-300 spectrometer and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin−Elmer 2400 microanalyzer.

Preparation of [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Me)$}$(CH_2Ph)Cl$] (1): A 2 M solution of $Mg(CH_2Ph)Cl$ in THF (0.60 mL, 1.19 mmol) was added at −78 °C to a stirred solution of [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Me)$}Cl_2] (0.50 g, 1.19 mmol) in THF (50 mL). The solution was allowed to warm to room temperature and stirred for 6 h. The solvent was removed in vacuo and the remaining solid extracted in hexane. A orange crystalline solid was obtained by concentrating and cooling (−30 °C) the solution (0.45 g, 79%). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.19 and 0.28 (2 s, each 3 H, $SiMe_2$), 1.52, 1.58, 1.66, and 1.95 (4 s, each 3 H, C_5Me_4), 2.07 (s, 3 H, C_5H_3Me), 1.70 and 1.86 (2 d, $^2J_{H,H}$ = 18.9 Hz, each 1 H, CH_2Ph), 4.91, 5.06, and 5.47 (3 m, each 1 H, C_5H_3), 6.75−7.25 (m, 5 H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.5, −0.6 ($SiMe_2$), 11.2, 12.3, 14.6, 14.7 (C_5Me_4), 15.3 (C_5H_3Me), 38.2 (CH_2Ph), 102.1, 112.1, 113.9, 121.4, 134.9 (C_5H_3), 93.7, 121.9, 126.2, 131.1, 131.5 (C_5Me_4), 124.0, 126.9, 127.0, 128.5, 128.7, 153.6 (CH_2Ph) ppm. $C_{24}H_{31}ClSiZr$ (474.3): calcd. C 60.78, H 6.59; found C 60.59, H 6.54.

Preparation of [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Me)$}$(CH_2SiMe_3)Cl$] (2): A 1 M solution of $Mg(CH_2SiMe_3)Cl$ in Et_2O (0.96 mL, 0.96 mmol) was added at −78 °C to a stirred solution of [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Me)$}Cl_2] (0.40 g, 0.96 mmol) in THF (50 mL). The solution was allowed to warm to room temperature and stirred for 16 h. The resulting yellow solution was stirred under reflux for 2 h. The solvent was removed in vacuo and hexane added to the resulting solid. The mixture was filtered and the filtrate concentrated and cooled to −30 °C. The yellow solid that precipitated from the solution was isolated by filtration (0.37 g, 81%). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.23 (s, 9 H, CH_2SiMe_3), 0.29 and 0.34 (2 s, each 3 H, $SiMe_2$), 1.48, 1.65, 1.92, and 2.00 (4 s, each 3 H, C_5Me_4), 2.30 (s, 3 H, C_5H_3Me), 1.77 and 1.91 (2 d, $^2J_{H,H}$ = 21.6 Hz, each 1 H, CH_2SiMe_3), 5.02, 5.09, and 6.60 (3 m, each 1 H, C_5H_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.4, −0.7 ($SiMe_2$), 2.9 (CH_2SiMe_3), 12.2, 12.3, 14.5, 14.6 (C_5Me_4), 15.5 (C_5H_3Me), 42.1 (CH_2SiMe_3), 103.4, 111.4, 112.5, 122.8, 134.6 (C_5H_3), 93.7, 122.2, 122.5, 130.1, 131.6 (C_5Me_4) ppm. $C_{21}H_{35}ClSi_2Zr$ (470.4): calcd. C 53.62, H 7.50; found C 53.36, H 7.43.

Preparation of [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-C_5H_3*i*Pr)$}$(CH_2Ph)Cl$] (3): The synthesis of **3** was carried out in an identical manner to that of **1**: 2 M solution of $Mg(CH_2Ph)Cl$ in THF (0.38 mL, 0.76 mmol) and [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-C_5H_3*i*Pr)$}$Cl_2$] (0.34 g, 0.76 mmol). Yield 0.26 g, 69%. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.32 and 0.34 (2 s, each 3 H, $SiMe_2$), 1.03 and 1.07 (2 d, $^3J_{H,H}$ = 7.1 Hz, each 3 H, $HCMe_2$), 1.61, 1.67, 1.74, and 2.00 (4 s, each 3 H, C_5Me_4), 1.72 and 1.84 (2 d, $^2J_{H,H}$ = 17.2 Hz, each 1 H, CH_2Ph) 3.13 (sept, 1 H, $HCMe_2$), 5.05, 5.32, and 5.65 (3 m, each 1 H, C_5H_3), 6.88−7.33 (m, 5 H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.8, −0.3 ($SiMe_2$), 11.2, 12.4, 14.4, 14.8

(C_5Me_4), 22.1, 24.1 ($HCMe_2$), 28.0 ($HCMe_2$), 38.1 (CH_2Ph), 102.5, 110.9, 112.2, 121.4, 122.7 (C_5H_3), 94.1, 125.7, 126.1, 131.1, 131.8 (C_5Me_4), 122.6, 126.9, 127.0, 128.7, 128.8, 153.2 (CH_2Ph) ppm. $C_{26}H_{35}ClSiZr$ (502.3): calcd. C 62.17, H 7.02; found C 61.89, H 6.99.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$*i*Pr)}(CH$_2$SiMe$_3$)Cl] (4): The synthesis of **4** was carried out in an identical manner to that of **2**: 1 M solution of $Mg(CH_2SiMe_3)Cl$ in Et_2O (0.85 mL, 0.85 mmol) and [Zr{$Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3iPr)$}$Cl_2$] (0.38 g, 0.85 mmol). Yield 0.28 g, 65%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.23 (s, 9 H, CH_2SiMe_3), 0.44 and 0.55 (2 s, each 3 H, $SiMe_2$), 1.17 and 1.36 (2 d, $^3J_{H,H}$ = 6.8 Hz, each 3 H, $HCMe_2$), 1.72, 1.76, 1.86, and 1.90 (4 s, each 3 H, C_5Me_4), 1.80 and 1.94 (2 d, $^2J_{H,H}$ = 21.6 Hz, each 1 H, CH_2SiMe_3), 3.85 (sept, 1 H, $HCMe_2$), 5.30, 5.50, and 6.31 (3 m, each 1 H, C_5H_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −1.0, −0.4 ($SiMe_2$), 3.2 ($SiMe_3$), 12.4, 12.5, 15.1, 15.4 (C_5Me_4), 22.0, 24.4 ($HCMe_2$), 28.5 ($HCMe_2$), 44.0 (CH_2SiMe_3), 100.2, 112.4, 113.9, 120.6, 122.6 (C_5H_3), 98.4, 125.6, 126.8, 132.3, 132.4 (C_5Me_4) ppm. $C_{23}H_{39}ClSi_2Zr$ (498.4): calcd. C 55.43, H 7.89; found C 55.09, H 7.78.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$SiMe$_3$)}(CH$_2$Ph)Cl] (5): The synthesis of **5** was carried out in an identical manner to that of **1**: 2 M solution of $Mg(CH_2Ph)Cl$ in THF (0.32 mL, 0.64 mmol) and [Zr{$Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3SiMe_3)$}$Cl_2$] (0.30 g, 0.64 mmol). Yield 0.26 g, 76%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.27 (s, 9 H, $SiMe_3$), 0.32 and 0.39 (2 s, each 3 H, $SiMe_2$), 1.62, 1.73, 1.74, and 1.94 (4 s, each 3 H, C_5Me_4), 1.96 and 2.00 (2 d, $^2J_{H,H}$ = 18.5 Hz, each 1 H, CH_2Ph), 5.36, 5.71, and 5.90 (3 m, each 1 H, C_5H_3), 6.91−7.30 (m, 5 H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.9, −0.6 ($SiMe_2$), −0.5 ($SiMe_3$) 11.1, 12.6, 14.3, 14.9 (C_5Me_4), 38.15 (CH_2Ph), 108.0, 116.3, 117.2, 121.5, 123.4 (C_5H_3), 95.7, 129.3, 130.6, 133.1, 136.4 (C_5Me_4), 126.1, 127.4, 127.5, 128.8, 129.5, 152.8 (CH_2Ph) ppm. $C_{26}H_{37}ClSi_2Zr$ (532.4): calcd. C 58.65, H 7.00; found C 58.46, H 6.96.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$SiMe$_3$)}(CH$_2$SiMe$_3$)Cl] (6): The synthesis of **6** was carried out in an identical manner to that of **2**: 1 M solution of $Mg(CH_2SiMe_3)Cl$ in Et_2O (0.63 mL, 0.63 mmol) and [Zr{$Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3SiMe_3)$}$Cl_2$] (0.30 g, 0.63 mmol). Yield 0.28 g, 85%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.21 (s, 9 H, CH_2SiMe_3), −0.05 and 0.24 (2 s, each 3 H, $SiMe_2$), 0.41 (s, 9 H, $C_5H_3SiMe_3$), 1.60, 1.78, 1.85, and 1.92 (4 s, each 3 H, C_5Me_4), 1.81 and 1.98 (2 d, $^2J_{H,H}$ = 19.4 Hz, each 1 H, CH_2SiMe_3), 5.43, 5.91, and 7.30 (3 m, each 1 H, C_5H_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.9, −0.6 ($SiMe_2$), 0.0 (CH_2SiMe_3), 1.4 ($C_5H_3SiMe_3$), 12.2, 12.4, 15.1, 15.2 (C_5Me_4), 48.9 (CH_2SiMe_3), 107.9, 115.9, 118.9, 122.5, 126.5 (C_5H_3), 95.8, 124.3, 124.9, 130.7, 131.3 (C_5Me_4) ppm. $C_{23}H_{41}ClSi_3Zr$ (528.5): calcd. C 52.27, H 7.82; found C 52.00, H 7.74.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}(CH$_2$Ph)$_2$] (7): The synthesis of **7** was carried out in an identical manner to that of **1**: 2 M solution of $Mg(CH_2Ph)Cl$ in THF (0.74 mL, 1.48 mmol) and [Zr{$Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)$}$Cl_2$] (0.30 g, 0.74 mmol). Yield 0.30 g, 79%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.26 (s, 6 H, $SiMe_2$), 1.58 and 1.80 (2 s, each 6 H, C_5Me_4), 2.69 (s, 4 H, 2 × CH_2Ph), 5.06 and 6.14 (2 m, each 2 H, C_5H_4), 6.82−7.25 (m, 10 H, 2 × CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.6 ($SiMe_2$), 11.6, 14.6 (C_5Me_4), 38.1 (CH_2Ph), 100.5, 113.0, 121.1, (C_5H_4), 98.2, 124.4, 135.7 (C_5Me_4), 125.9, 126.8, 129.2, 153.7 (CH_2Ph) ppm. $C_{30}H_{36}SiZr$ (515.9): calcd. C 69.84, H 7.03; found C 69.66, H 6.91.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}(CH$_2$SiMe$_3$)Cl] (8): The synthesis of **8** was carried out in an identical manner to that of **2**: 1 M solution of $Mg(CH_2SiMe_3)Cl$ in Et_2O (0.74 mL, 0.74 mmol) and [Zr{$Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)$}$Cl_2$] (0.30 g, 0.74 mmol). Yield 0.25 g, 75%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.25 (s, 9 H, CH_2SiMe_3), 0.23 and 0.28 (2 s, each 3 H, $SiMe_2$), 1.43, 1.70, 1.86, and 1.95 (4 s, each 3 H, C_5Me_4), 1.79 and 1.95 (2 d, $^2J_{H,H}$ = 18.3 Hz, each 1 H, CH_2SiMe_3), 5.01, 5.48, 6.71, and 6.95 (4 m, each 1 H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.6, −0.5 ($SiMe_2$), 2.8 (CH_2SiMe_3), 12.1, 12.2, 14.5, 14.8 (C_5Me_4), 42.9 (CH_2SiMe_3), 104.4, 110.8, 111.5, 123.0, 123.7 (C_5H_4), 94.9, 123.9, 125.6, 130.8, 131.4 (C_5Me_4) ppm. $C_{20}H_{33}ClSi_2Zr$ (456.3): calcd. C 52.64, H 7.29; found C 52.29, H 7.23.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$Me)}{η^2-PhCH$_2$C=N(C$_6$H$_3$Me$_2$-2,6)}Cl] (9): 2,6-Dimethylphenyl isocyanide (0.14 g, 1.05 mmol) and **1** (0.50 g, 1.05 mmol) were dissolved in THF (100 mL). The resulting orange solution was stirred at room temperature for 18 h. The solvent was removed in vacuo and the remaining solid extracted with toluene (30 mL). An orange solid was obtained by concentrating (5 mL) and cooling (−30 °C) the solution (0.54 g, 84%). IR (Nujol): $\tilde{\nu}$ = 1590 ($\nu_{C=N}$) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.43 and 0.45 (2 s, each 3 H, $SiMe_2$), 1.46, 1.71, 1.88, and 1.97 (4 s, each 3 H, C_5Me_4), 2.03 (s, 3 H, C_5H_3Me), 2.17 and 2.20 (2 s, each 3 H, $C_6H_3Me_2$), 3.22 and 3.59 (2 d, $^2J_{H,H}$ = 18.0 Hz, each 1 H, CH_2Ph), 5.50, 5.62, and 5.73 (3 m, each 1 H, C_5H_3), 6.55 (2 H), 6.69 (1 H) (2 m, $C_6H_3Me_2$), 6.83−7.15 (m, 5 H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.7, −0.2 ($SiMe_2$), 12.4, 12.5, 15.1, 15.3, 15.5 (C_5Me_4, C_5H_3Me), 20.0, 20.1 ($C_6H_3Me_2$), 38.2 (CH_2Ph), 104.1, 104.4, 114.4, 119.4, 137.3 (C_5H_3), 108.0, 115.1, 120.9, 131.1, 134.9 (C_5Me_4), 125.6, 127.6, 127.7, 128.8, 128.9, 144.2 (CH_2Ph), 126.2, 126.3, 126.9, 127.0, 128.4, 128.7, 171.0 ($C_6H_3Me_2$), 246.7 (CCH_2Ph) ppm. $C_{33}H_{40}ClNSiZr$ (605.4): calcd. C 65.47, H 6.66, N 2.31; found C 65.21, H 6.58, N 2.29.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$Me)}{η^2-Me$_3$Si-CH$_2$C=N(C$_6$H$_3$Me$_2$-2,6)}Cl] (10): The synthesis of **10** was carried out in an identical manner to that of **9**: **2** (0.50 g, 1.06 mmol) and 2,6-dimethylphenyl isocyanide (0.14 g, 1.06 mmol). Yield 0.49 g, 77%. IR (Nujol): $\tilde{\nu}$ = 1620 ($\nu_{C=N}$) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = −0.05 (s, 9 H, CH_2SiMe_3), 0.50 and 0.54 (2 s, each 3 H, $SiMe_2$), 1.50, 1.89, 1.95, and 1.99 (4 s, each 3 H, C_5Me_4), 2.28 (s, 3 H, C_5H_3Me), 2.16 and 2.17 (2 s, each 3 H, $C_6H_3Me_2$), 1.95 and 2.41 (2 d, $^2J_{H,H}$ = 18.5 Hz, each 1 H, CH_2SiMe_3), 5.50, 5.62, and 5.73 (3 m, each 1 H, C_5H_3), 6.86 (s, 3 H, $C_6H_3Me_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.4, 0.3 ($SiMe_2$), 0.8 (CH_2SiMe_3), 12.5, 12.7, 14.8, 15.6, 15.8 (C_5Me_4, C_5H_3Me), 19.8, 20.7 ($C_6H_3Me_2$), 32.2 (CH_2SiMe_3), 100.2, 103.8, 113.5, 118.8, 130.7 (C_5H_3), 108.5, 114.7, 118.3, 130.2, 130.3 (C_5Me_4) 125.6, 127.3, 127.4, 128.3, 128.4, 144.2 ($C_6H_3Me_2$), 245.4 (CCH_2SiMe_3) ppm. $C_{30}H_{44}ClNSi_2Zr$ (601.5): calcd. C 59.90, H 7.37, N 2.33; found C 59.63, H 7.32, N 2.28.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$*i*Pr)}{η^2-PhCH$_2$C=N(C$_6$H$_3$Me$_2$-2,6)}Cl] (11): The synthesis of **11** was carried out in an identical manner to that of **9**: **3** (0.40 g, 0.80 mmol) and 2,6-dimethylphenyl isocyanide (0.10 g, 0.80 mmol). Yield 0.39 g, 78%. IR (Nujol): $\tilde{\nu}$ = 1605 ($\nu_{C=N}$) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.39 and 0.44 (2 s, each 3 H, $SiMe_2$), 0.99 and 1.25 (2 d, $^3J_{H,H}$ = 7.1 Hz, each 3 H, $HCMe_2$), 1.42, 1.69, 1.93, and 1.97 (4 s, each 3 H, C_5Me_4), 2.12 and 2.14 (2 s, each 3 H, $C_6H_3Me_2$), 3.12 and 3.76 (2 d, $^2J_{H,H}$ = 17.1 Hz, each 1 H, CH_2Ph), 3.35 (sept, 1 H, $HCMe_2$), 5.67 (2 H), 5.92 (1 H) (2 m, C_5H_3), 6.52 (2 H), 6.69

(1 H) (2 m, $C_6H_3Me_2$), 6.88−7.26 (m, 5 H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.6, −0.2 ($SiMe_2$), 12.4, 12.8, 15.0, 15.2 (C_5Me_4), 22.5, 24.6 ($HCMe_2$), 29.1 ($HCMe_2$), 39.3 (CH_2Ph), 19.5, 20.4 ($C_6H_3Me_2$), 100.7, 112.6, 114.1, 122.6, 123.4 (C_5H_3), 105.3, 126.7, 127.2, 133.4, 134.4 (C_5Me_4), 125.3, 127.4, 127.6, 128.8, 128.9, 152.2 (CH_2Ph), 126.1, 126.9, 127.0, 128.9, 129.0, 165.3 ($C_6H_3Me_2$), 246.3 (CCH_2Ph) ppm. $C_{35}H_{44}ClNSiZr$ (633.5): calcd. C 66.36, H 7.00, N 2.21; found C 66.01, H 6.91, N 2.18.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$*i*Pr)}{η^2-Me$_3$SiCH$_2$C=N(C$_6$H$_3$Me$_2$-2,6)}Cl] (12): The synthesis of **12** was carried out in an identical manner to that of **9**: **4** (0.45 g, 0.90 mmol) and 2,6-dimethylphenyl isocyanide (0.12 g, 0.90 mmol). Yield 0.43 g, 75% IR (Nujol): $\tilde{\nu}$ = 1570 ($\nu_{C=N}$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.35 and 0.39 (2s, each 3 H, $SiMe_2$), 0.25 (s, 9 H, CH_2SiMe_3), 1.05 and 1.33 (2 d, $^3J_{H,H}$ = 7.1 Hz, each 1 H, $HCMe_2$), 1.48, 1.72, 1.95, and 2.00 (4 s, each 3 H, C_5Me_4), 2.15 and 2.16 (2 s, each 3 H, $C_6H_3Me_2$), 3.01 and 3.54 (2 d, $^2J_{H,H}$ = 18.0 Hz, each 1 H, CH_2SiMe_3), 3.42 (sept, 1 H, $HCMe_2$), 5.60, 5.63, and 5.92 (3 m, each 1 H, C_5H_3), 6.60 (2 H), 6.84 (1 H) (2 m, $C_6H_3Me_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −1.0, −0.7 ($SiMe_2$), 2.6 ($SiMe_3$), 12.9, 13.0, 16.5, 16.6 (C_5Me_4), 22.7, 25.3 ($HCMe_2$), 30.0 ($HCMe_2$), 35.1 (CH_2SiMe_3), 19.3, 20.3 ($C_6H_3Me_2$), 98.7, 112.7, 114.9, 124.2, 125.6 (C_5H_3), 104.9, 125.8, 126.4, 133.8, 133.9 (C_5Me_4), 126.9, 127.8, 128.1, 131.4, 131.6, 160.7 ($C_6H_3Me_2$), 248.1 (CCH_2SiMe_3) ppm. $C_{32}H_{48}ClNSi_2Zr$ (629.6): calcd. C 61.05, H 7.68, N 2.22; found C 60.72, H 7.62, N 2.23.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$SiMe$_3$)}{η^2-PhCH$_2$C=N(C$_6$H$_3$Me$_2$-2,6)}Cl] (13): The synthesis of **13** was carried out in an identical manner to that of **9**: **5** (0.45 g, 0.85 mmol) and 2,6-dimethylphenyl isocyanide (0.11 g, 0.85 mmol). Yield 0.45 g, 81%. IR (Nujol): $\tilde{\nu}$ = 1590 ($\nu_{C=N}$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.31 (s, 9 H, $SiMe_3$), 0.37 and 0.41 (2 s, each 3 H, $SiMe_2$), 1.39, 1.59, 1.88, and 1.96 (4 s, each 3 H, C_5Me_4), 2.11 and 2.13 (2 s, each 3 H, $C_6H_3Me_2$), 3.03 and 3.85 (2 d, $^2J_{H,H}$ = 18.0 Hz, each 1 H, CH_2Ph), 5.81, 6.10, and 6.45 (3 m, each 1 H, C_5H_3), 6.56 (2 H), 6.70 (1 H) (m, $C_6H_3Me_2$), 6.88−7.26 (m, 5 H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.6, −0.3 ($SiMe_2$), 0.7 ($SiMe_3$), 11.9, 12.4, 15.0, 15.2 (C_5Me_4), 19.9, 20.5 ($C_6H_3Me_2$), 38.1 (CH_2Ph), 104.2, 108.0, 110.9, 118.3, 125.8 (C_5H_3), 107.2, 118.7, 119.6, 134.8, 135.7 (C_5Me_4), 125.6, 127.0, 127.1, 128.6, 128.7, 144.1 (CH_2Ph), 126.1, 126.9, 127.7, 129.2, 129.9, 171.0 ($C_6H_3Me_2$), 247.8 (CCH_2Ph) ppm. $C_{35}H_{46}ClNSi_2Zr$ (663.6): calcd. C 63.35, H 6.99, N 2.11; found C 63.17, H 6.94, N 2.10.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$SiMe$_3$)}{η^2-Me$_3$SiCH$_2$C=N(C$_6$H$_3$Me$_2$-2,6)}Cl] (14): The synthesis of **14** was carried out in an identical manner to that of **9**: **6** (0.40 g, 0.76 mmol) and 2,6-dimethylphenyl isocyanide (0.10 g, 0.76 mmol). Yield 0.40 g, 80%. IR (Nujol): $\tilde{\nu}$ = 1605 ($\nu_{C=N}$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.00 (s, 9 H, CH_2SiMe_3), 0.31 (s, 9 H, $SiMe_3$), 0.53 and 0.54 (2 s, each 3 H, $SiMe_2$), 1.39, 1.89, 1.96, and 2.04 (4 s, each 3 H, C_5Me_4), 2.14 and 2.16 (2 s, each 3 H, $C_6H_3Me_2$), 2.13 and 2.41 (2 d, $^2J_{H,H}$ = 12.5 Hz, each 1 H, CH_2SiMe_3), 5.85, 6.05, and 6.24 (3 m, each 1 H, C_5H_3), 6.85 (2 H), 7.11 (1 H) (m, $C_6H_3Me_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.0, 0.1 ($SiMe_2$), 0.6 (CH_2SiMe_3), 1.4 ($C_5H_3SiMe_3$), 12.1, 12.5, 14.8, 15.9 (C_5Me_4), 19.8, 21.0 ($C_6H_3Me_2$), 31.5 (CH_2SiMe_3), 103.9, 107.5, 109.8, 111.1, 115.3, 116.9 (C_5H_3), 103.9, 124.2, 125.0, 131.6, 132.4 (C_5Me_4), 125.5, 127.1, 127.5, 129.1, 129.8, 171.0 ($C_6H_3Me_2$), 246.4 (CCH_2SiMe_3) ppm. $C_{32}H_{50}ClNSi_3Zr$ (659.7): calcd. C 58.26, H 7.64, N 2.12; found C 57.97, H 7.57, N 2.08.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}{η^2-PhCH$_2$C=N(C$_6$H$_3$Me$_2$-2,6)}(CH$_2$Ph)] (15): The synthesis of **15** was carried out in an identical manner to that of **9**: **7** (0.30 g, 0.58 mmol) and 2,6-dimethylphenyl isocyanide (0.08 g, 0.58 mmol). Yield 0.30 g, 80%. IR (Nujol): $\tilde{\nu}$ = 1590 ($\nu_{C=N}$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.47 and 0.49 (2 s, each 3 H, $SiMe_2$), 1.39, 1.47, 1.83, and 1.77 (4 s, each 3 H, C_5Me_4), 2.06 and 2.07 (2 s, each 3 H, $C_6H_3Me_2$), 1.62 and 2.12 (2 d, $^2J_{H,H}$ = 16.5 Hz, each 1 H, CH_2Ph), 3.05 and 3.40 (2 d, $^2J_{H,H}$ = 18.4 Hz, each 1 H, $NCCH_2Ph$), 5.13, 5.46, 5.63, and 5.92 (4 m, each 1 H, C_5H_4), 6.78 (2 H), 6.87 (1 H) (m, $C_6H_3Me_2$), 6.90−7.26 (m, 10 H, 2 × CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.9, 0.3 ($SiMe_2$), 12.3, 12.4, 15.1, 15.4 (C_5Me_4), 19.5, 19.6 ($C_6H_3Me_2$), 38.2, 44.8 (CH_2Ph), 100.9, 112.4, 114.9, 118.4, 119.4 (C_5H_4), 106.0, 125.4, 125.6, 131.2, 134.8 (C_5Me_4), 125.0, 125.7, 127.0, 127.1, 128.6, 128.7, 141.9, 146.2 (CH_2Ph), 126.4, 126.7, 127.7, 128.9, 129.0, 156.6 ($C_6H_3Me_2$), 247.8 (CCH_2Ph) ppm. $C_{39}H_{45}NSiZr$ (647.1): calcd. C 72.39, H 7.01, N 2.16; found C 72.11, H 6.92, N 2.15.

Preparation of [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}{η^2-Me$_3$SiCH$_2$C=N(C$_6$H$_3$Me$_2$-2,6)}ZrCl] (16): The synthesis of **16** was carried out in an identical manner to that of **9**: **8** (0.25 g, 0.55 mmol) and 2,6-dimethylphenyl isocyanide (0.07 g, 0.55 mmol). Yield 0.25 g, 77%. IR (Nujol): $\tilde{\nu}$ = 1600 ($\nu_{C=N}$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = −0.09 (s, 9 H, CH_2SiMe_3), 0.51 and 0.54 (2 s, each 3 H, $SiMe_2$), 1.58, 1.81, 1.85, and 2.14 (4 s, each 3 H, C_5Me_4), 2.21 and 2.26 (2 s, each 3 H, $C_6H_3Me_2$), 3.79 and 3.96 (2 d, $^2J_{H,H}$ = 15.5 Hz, each 1 H, CH_2SiMe_3), 5.65, 5.97, 6.23, and 6.47 (3 m, each 1 H, C_5H_3), 6.86 (m, 3 H, $C_6H_3Me_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = −0.6, −0.2 ($SiMe_2$), 15.5 (CH_2SiMe_3), 12.4, 12.5, 15.1, 15.3 (C_5Me_4), 20.0, 20.1 ($C_6H_3Me_2$), 38.2 (CH_2SiMe_3), 101.9, 104.4, 114.4, 119.3, 125.6 (C_5H_3), 104.0, 131.0, 134.8, 137.2, 144.1 (C_5Me_4), 126.2, 126.9, 127.0, 128.8, 128.9, 171.2 ($C_6H_3Me_2$), 246.7 (CCH_2SiMe_3) ppm. $C_{29}H_{42}ClNSi_2Zr$ (587.50): calcd. C 59.29, H 7.21, N 2.38; found C 59.00, H 7.15, N 2.35.

Table 2. Crystal data and structure refinement for **1**

Empirical formula	$C_{24}H_{31}ClSiZr$
Formula mass	474.25
Temperature [K]	250(2)
Wavelength [Å]	0.71073
Crystal system, space group	triclinic, $P\bar{1}$
a [Å]	8.853(8)
b [Å]	11.134(3)
c [Å]	11.998(2)
α [°]	102.55(2)
β [°]	100.09(3)
γ [°]	90.23(4)
Volume [Å^3]	1135(1)
Z, calculated density [g/cm^3]	1, 1.387
Absorption coefficient [cm^{-1}]	6.61
F(000)	492
Crystal size [mm]	0.3 × 0.2 × 0.2
Limiting indices	$-11 \le h \le 11$ $-14 \le k \le 14$ $0 \le l \le 12$
Reflections collected/unique	5313/5057 [*R*(int) = 0.0366]
Data/restraints/parameters	5057/0/248
Goodness-of-fit on F^2	1.058
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0338, *wR*2 = 0.0879
R indices (all data)	*R*1 = 0.0468, *wR*2 = 0.0975
Largest diff. peak and hole [e·Å^{-3}]	0.444 and −0.798

X-ray Crystal-Structure Determination of [Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Me)$}$(CH_2Ph)Cl$] (1): Intensity data were collected with a NONIUS-MACH3 diffractometer equipped with a graphite monochromator and Mo-K_α radiation source (λ = 0.71073 Å) using an $\omega/2\theta$-scan technique. The final unit cell parameters were determined from 25 well-centered reflections and refined by least-squares methods. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using the SHELXS computer program[18] and refined on F^2 by full-matrix least squares (SHELXL-97).[19] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Weights were optimized in the final cycles. Crystallographic data are given in Table 2. CCDC-205931 contains 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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