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Insertion of isocyanides into zirconium–alkyl bonds of di-*ansa*-zirconocene complexes. X-ray molecular structure of $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl\{\eta^2\text{-}C(i\text{-}Pr)N(2,6\text{-}Me_2C_6H_3)\}]$

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Abstract

New dicyclopentadienyl iminoacyl zirconium complexes have been prepared and characterized by NMR spectroscopy. The reaction of $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me_2]$ with CNR (R = 2,6-$Me_2C_6H_3$, t-Bu) yields $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me(\eta^2\text{-}CMeNR)]$ (R = 2,6-$Me_2C_6H_3$, t-Bu), which reacts with a stoichiometric amount of water to give the μ-oxo dimers $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}(\eta^2\text{-}CMeNR)]_2(\mu\text{-}O)$ (R = 2,6-$Me_2C_6H_3$, t-Bu). The chloro neophyl complex $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl(CH_2CMe_2Ph)]$ and other β-hydrogen containing zirconium chloro alkyls $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}ClR]$ (R = Et, n-Pr, i-Pr) react with CN(2,6-$Me_2C_6H_3$) to yield the related chloro iminoacyl complexes $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl\{\eta^2\text{-}CRN(2,6\text{-}Me_2C_6H_3)\}]$ (R = Et, n-Pr, i-Pr), whereas no reaction was observed when CN(t-Bu) was used. All the new iminoacyl complexes were characterized by ^1H and ^{13}C NMR spectroscopy and the X-ray molecular structure of $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl\{\eta^2\text{-}C(i\text{-}Pr)N(2,6\text{-}Me_2C_6H_3)\}]$ was studied by diffraction methods to prove the expected 'inside' coordination of the iminoacyl nitrogen atom. © 1997 Elsevier Science S.A.

Keywords: Zirconium; Dicyclopentadienyl; Iminoacyl

1. Introduction

Migratory insertion of carbon monoxide and the isoelectronic isocyanide ligands is one of the most simple reactions in organometallic chemistry, but very useful in many stoichiometric and catalytic processes [1]. Reaction of many Group 4 metal-alkyls with different alkyl and aryl isocyanides has enabled the isolation and characterization of a large number of η^2-iminoacyl complexes [2]. We have recently reported extensive studies on the isolation and reactivity of η^2-iminoacyl tantalum complexes [3]. Several studies related to the insertion of isocyanides into dicyclopentadienyl zirconium-alkyls have also been reported [4]. The 'inside' or 'outside' coordination of the oxygen atom in acyl ligands generated by the carbonylation of organozirconocenes has been extensively studied [5–7] and energy profiles for coordination of CO and further isomerization have been estimated [5]. Analogous studies have also been extended to the insertion of isocyanides and the inside or outside coordination of the nitrogen atom in η^2-iminoacyl compounds [8–10]. Here we report the insertion of CNR (R = t-Bu, 2,6-$Me_2C_6H_3$) into the zirconium–alkyl bonds of $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}RX]$ (X = R = Me; X = Cl, R = Me, CH_2CMe_2Ph, Et, n-Pr, i-Pr) and the X-ray molecular structure of the i-propyl iminoacyl derivative.

2. Results and discussion

2.1. Preparative results

We have recently reported [11,12] the alkylation of the dichloro zirconocene containing the doubly-bridged bis(1,1',2,2'-dimethylsilanediyl)-η^5-dicyclopentadienyl ligand $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl_2]$ with lithium alkyls

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[1] X-ray diffraction studies.

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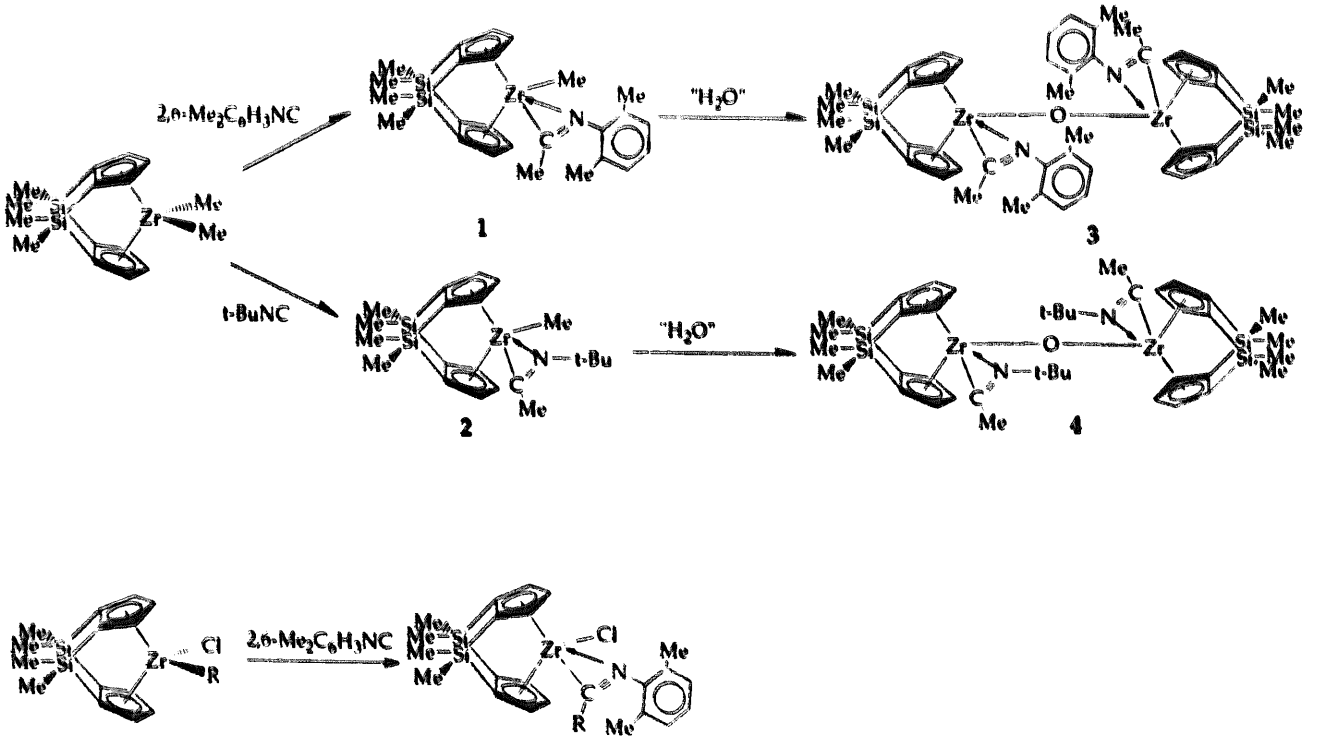
which leads to the β-hydrogen-free alkyl complexes $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}RX]$ (X = R = Me; X = Cl, R = CH_2CMe_2Ph). In similar reactions the much less stable β-hydrogen containing chloro-ethyl, n-propyl and i-propyl derivatives $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}ClR]$ (R = Et, n-Pr, i-Pr) were also prepared [13].

All of these compounds reacted with isocyanides to give the corresponding iminoacyl complexes. Reaction of a toluene solution of the dimethyl zirconium compound $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me_2]$ with one equivalent of CN(2,6-$Me_2C_6H_3$) at room temperature led to the methyl iminoacyl complex $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me\{\eta^2\text{-}CMeN(2,6\text{-}Me_2C_6H_3)\}]$ **1**, which did not react when heated with further additions of the isocyanide, as expected for an 18 electron zirconium compound containing the η^2-coordinated iminoacyl group. Similar behaviour was observed when CN(t-Bu) was used, leading to the iminoacyl complex $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me\{\eta^2\text{-}CMeN(t\text{-}Bu)\}]$ **2** (see Scheme 1). Both compounds **1** and **2** are extremely moisture sensitive and react with a stoichiometric amount of water to give the μ-oxo dimers $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}(\eta^2\text{-}CMeNR)]_2(\mu\text{-}O)$ (R = 2,6-$Me_2C_6H_3$ **3**, t-Bu **4**). Likewise reaction of CN(t-Bu) with the chloro neophyl complex under the same conditions led to the related chloro iminoacyl derivative $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl\{\eta^2\text{-}C(CH_2CMe_2Ph)[N(2,6\text{-}Me_2C_6H_3)]\}]$ **5**.

Likewise addition of one equivalent of CN(2,6-$Me_2C_6H_3$) to toluene solutions of the β-hydrogen containing chloro-ethyl, n-propyl and i-propyl zirconium complexes at room temperature led to the related iminoacyl derivatives $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl(\eta^2\text{-}CR\{N(2,6\text{-}Me_2C_6H_3)\})]$ (R = Et **6**, n-Pr **7**, i-Pr **8**), reactions being complete after stirring for 1 h. The chloro-i-propyl complex was used in situ to avoid isomerization. All of the chloro iminoacyl compounds show a remarkable thermal stability and can be manipulated in air without transformation for short periods, as expected for rather inert 18 electron species.

2.2. Structural characterization

All of the new iminoacyl complexes **2–8** show the ν(CN) absorption band between 1575 and 1610 cm^{-1} in their IR spectra and the NMR behaviour expected for C_s symmetrical molecules having equivalent cyclopentadienyl rings, but each showing non-equivalent ring protons and carbon atoms. Therefore their ^1H NMR spectra show four singlets between δ 0.39 and δ 1.02 for the four non-equivalent silicon bonded methyl groups located in the equatorial plane of symmetry along with the metal atom and the other three substituents, and three multiplets between δ 5.06 and δ 6.90 for the non-equivalent protons of the rings (see Section 3). The resonances due to the migrated alkyl group are shifted down-field with respect to the values observed for the starting metal bonded species. Similar behaviour is also



Scheme 1.

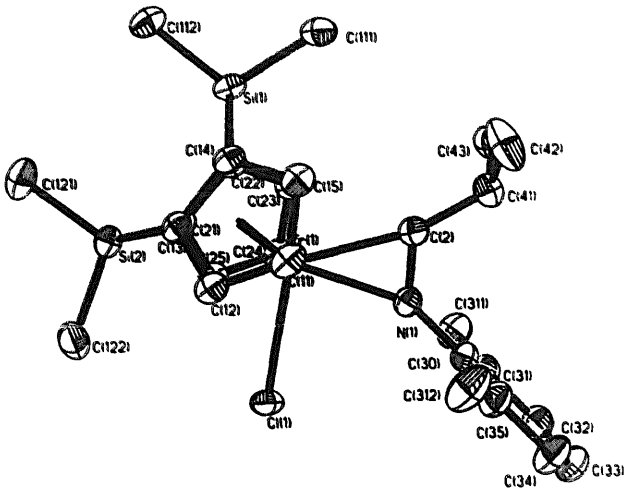


Fig. 1. Molecular structure of **8**.

observed in the ^{13}C NMR spectra, which show five signals for the ring carbon atoms and four resonances for the silicon carbon bonded atoms due to the chelating disposition of the dicyclopentadienyl ligand and the presence of three different substituents in the equatorial plane. Only one isomer is observed for all the new iminoacyl complexes, but from the spectral data it is not possible to distinguish the relative disposition of the two carbon and nitrogen coordinated atoms. For clarification we made a crystallographic study of the i-propyl compound $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl\{\eta^2\text{-}C(i\text{-}Pr)N(2,6\text{-}Me_2C_6H_3)\}]$ **8**.

Crystals of compound **8** suitable for X-ray diffraction studies were obtained from hexane. Fig. 1 shows the resulting molecular structure of **8**. Selected bond distances and angles are presented in Table 1.

The molecular structure is a typical metallocene system with the chlorine and the iminoacyl groups located aproximately in the plane bisecting the Cp–Zr–Cp unit. The coordination around the zirconium can be considered tetrahedral if the cyclopentadienyl rings and the iminoacyl system are taken as occupying only one coordination site. The two Cp rings are bonded by two $SiMe_2$ units leading to an eclipsed disposition. The central plane is defined by two silicon atoms from the doubly-bridged system and the metal atom. The N(1) atom is located in this plane, but Cl(1) is displaced by 0.043 Å and the C(2) and C(41) atoms are displaced by 0.062 Å and 0.2 Å respectively on the opposite side to the chorine. The i-propyl group is out of the plane.

The η^2-coordination of the iminoacyl group is similar to that found in $[ZrCp_2\{\eta^2\text{-}CMeN(t\text{-}Bu)\}(\mu\text{-}O,O'\text{-}O_2CHCF_3)ZrCp_2Me]$ [7]. The N(1)–C(2) distance 1.268 Å is consistent with a double bond and similar to the 1.255(5) Å found in the above mentioned complex, in contrast to N–C distances of 1.44 Å corresponding to single bonds found for η^2-amino– and amido–alkyl complexes [14–16]. The Zr(1)–N(1) distance 2.215(2) Å is quite similar to that found for the above mentioned dinuclear zirconium complex [2.216(4) Å] and the Zr–C(2)–N(1) angle 71.3(2)° is slightly smaller (74.0(3)°).

A more noticeable difference is observed in the Zr(1)–C(2) distance 2.267(3) Å, clearly longer than in the iminoacyl compound $[ZrCp_2\{\eta^2\text{-}CMeN(t\text{-}Bu)\}(\mu\text{-}O,O'\text{-}O_2CHCF_3)ZrCp_2Me]$ [7] 2.206(5) Å. This large distance in our case can probably be explained by the steric interaction of the methyl substituents of the i-propyl group with the Cp ring.

The nitrogen atom is located in an 'inside' position which is the more common for this type of iminoacyl ligand. The Zr–Cl distance is 2.532(1) Å, longer than in the starting dichloro complex [11] where the distances are 2.427(1) and 2.428(1) Å. The two Cp rings are planar and the distances from Zr to the planes are 2.233(2) Å in both cases. The distances from the Zr to the C atoms of the Cp rings range from 2.466(3) Å to 2.611(3) Å, the distances to the carbon atoms bonded to silicon being shorter. This feature was also observed in

Table 1
Selected bond lengths (Å) and bond angles (°) for compound **8**

Zr(1)–N(1)	2.215(2)	Zr(1)–C(2)	2.267(3)
Zr(1)–Cl(1)	2.532(1)	Zr(1)–C(11)	2.611(3)
Zr(1)–C(12)	2.566(3)	Zr(1)–C(13)	2.487(3)
Zr(1)–C(14)	2.487(3)	Zr(1)–C(15)	2.563(3)
Zr(1)–C(21)	2.496(3)	Zr(1)–C(22)	2.465(3)
Zr(1)–C(23)	2.554(3)	Zr(1)–C(24)	2.623(3)
Zr(1)–C(25)	2.588(3)	Si(1)–C(111)	1.856(4)
Si(1)–C(112)	1.868(3)	Si(1)–C(22)	1.873(3)
Si(1)–C(14)	1.887(3)	Si(2)–C(121)	1.859(4)
Si(2)–C(122)	1.859(4)	Si(2)–C(21)	1.882(3)
Si(2)–C(13)	1.884(3)	N(1)–C(2)	1.268(4)
N(1)–C(30)	1.440(4)	C(2)–C(41)	1.523(5)
C(41)–C(42)	1.521(6)	C(41)–C(43)	1.528(6)
C(31)–C(311)	1.507(6)	C(35)–C(312)	1.512(6)
Zr(1)–Cp1	2.239	Zr(1)–Cp2	2.239
N(1)–Zr(1)–C(2)	32.8(1)		
N(1)–Zr(1)–Cl(1)	80.53(7)		
C(2)–Zr(1)–Cl(1)	113.33(8)		
N(1)–C(2)–Zr(1)	71.3(2)		
N(1)–C(2)–C(41)	123.3(3)		
C(41)–C(2)–Zr(1)	165.0(3)		
C(35)–C(30)–N(1)	119.6(3)		
C(31)–C(30)–N(1)	119.1(3)		
C(42)–C(41)–C(2)	111.2(3)		
C(42)–C(41)–C(43)	112.4(4)		
C(2)–C(41)–C(43)	110.7(3)		
C(22)–Si(1)–C(14)	91.4(1)		
C(21)–Si(2)–C(13)	92.4(1)		
Cp1–Zr(1)–Cp2	118.0		
Cl(1)–Zr(1)–Cp1	105.7		
Cl(1)–Zr(1)–Cp2	104.3		
C(2)–Zr(1)–Cp1	106.6		
C(2)–Zr(1)–Cp2	109.1		
N(1)–Zr(1)–Cp1	119.1		
N(1)–Zr(1)–Cp2	118.5		

Cp1 is the centroid of C11, C12, C13, C14, C15.
Cp2 is the centroid of C21, C22, C23, C24, C25.

other cases [11]. The angle between the two planes is 109.4(9)° and the centroid–Zr–centroid angle is 118.0°, slightly smaller than in the starting dichloro compound. The phenyl group is planar and is located almost perpendicular to the Zr–Si(1)–Si(2) plane (angle 82.12(8)°).

3. Experimental

All manipulations were performed under an inert atmosphere (argon) using Schlenk and high vacuum line techniques or a VAC Model HE 63P glovebox. Solvents were purified by distillation from an appropriate drying/deoxygenating agent (sodium/benzophenone for diethyl ether, sodium for toluene, and sodium/potassium alloy for hexane).

The complexes $[Zr\{\mu\text{-}[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]\}Cl_2]$ [11] and $[Zr\{\mu\text{-}[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]\}ClR]$ [11–13] were prepared according to literature procedures. CN(t-Bu) and $CN(2,6\text{-}Me_2C_6H_3)$ (Aldrich) were obtained commercially.

NMR spectra were recorded on Varian Unity 300 and Varian Unity 500 Plus instruments (^1H and ^{13}C chemical shifts were referenced to external $SiMe_4$, δ = 0 ppm). IR spectra were performed in Nujol mulls on a Perkin–Elmer 883 spectrophotometer. Mass spectra were recorded on a Hewlett–Packard 5890 spectrometer. Elemental C and H analyses were carried out on a Perkin–Elmer 240B microanalyser.

3.1. Synthesis of $[Zr\{\mu\text{-}[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]\}Me\{\eta^2\text{-}CMeN(2,6\text{-}Me_2C_6H_3)\}]$ (1)

Toluene (30 ml) was added to a mixture of $[Zr\{\mu\text{-}[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]\}Me_2]$ (0.5 g, 1.37 mmol) and $CN(2,6\text{-}Me_2C_6H_3)$ (0.18 g, 1.37 mmol) at room temperature and then stirred for 1 h. The solvent was completely removed in vacuo to give a white–yellow solid. Recrystallization from hexane at −20 °C gave a white–yellow solid characterized as **1** (0.64 g, 94% yield). Anal. Found: C, 60.41; H, 6.40; N, 3.01. $C_{28}H_{33}Si_2ZrN$ Calc.: C, 60.67; H, 6.72; N, 2.83%. Mass spectrum m/z: M^+ −(Me) (3%); M^+ −[CMe=N(2,6-$Me_2C_6H_3$)] (2%); M^+ −[CMe=N(2,6-$Me_2C_6H_3$)]−(Me) (29%); M^+ is not observed. IR ν(C=N): 1582 cm^{-1}. ^1H NMR (C_6D_6): δ 6.89 (m, 3H, C_6H_3), δ 6.81 (m, 2H, C_5H_3), δ 6.32 (m, 2H, C_5H_3), δ 5.28 (m, 2H, C_5H_3), δ 1.95 (s, 3H, *Me*–C=N), δ 1.70 (s, 6H, 2,6-*Me*$_2$$C_6H_3$), δ 0.74 (s, 3H, Si*Me*$_2$), δ 0.68 (s, 3H, Si*Me*$_2$), δ 0.63 (s, 3H, Si*Me*$_2$), δ 0.62 (s, 3H, Si*Me*$_2$), δ 0.12 (s, 3H, Zr*Me*). ^{13}C NMR (C_6D_6): δ 243.75 (RN=*C*Me), δ 144.81 (C_6H_3), δ 141.74 (C_5H_3), δ 132.32 (C_5H_3), δ 129.28 (C_6H_3), δ 128.51 (C_6H_3), δ 125.11 (C_6H_3), δ 122.24 (C_5H_3), δ 110.15 (C_5H_3), δ 107.50 (C_5H_3), δ 24.84 (RN=C*Me*), δ 18.63 (2,6-*Me*$_2$–C_5H_3), δ 7.41 (Zr*Me*), δ 3.72 (Si*Me*$_2$), δ 3.52 (Si*Me*$_2$), δ −3.78 (Si*Me*$_2$), δ −3.8 (Si*Me*$_2$).

3.2. Synthesis of $[Zr\{\mu\text{-}[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]\}Me\{\eta^2\text{-}CMeN(t\text{-}Bu)\}]$ (2)

Toluene (30 ml) was added to a mixture of $[Zr\{\mu\text{-}[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]\}Me_2]$ (0.5 g, 1.37 mmol) and CN(t-Bu) (0.15 ml, 1.37 mmol) at room temperature and then stirred for 1 h. The solvent was completely removed in vacuo to give a white–yellow solid. Recrystallization from hexane at −20 °C gave a microcrystalline solid characterized as **2** (0.57 g, 93% yield). Anal. Found: C, 56.50; H, 7.07; N, 3.01. $C_{21}H_{33}Si_2ZrN$ Calc.: C, 56.44; H, 7.44; N, 3.13%. Mass spectrum m/z: M^+ −(Me) (17%); M^+ − Me (21%); M^+ −[CMe=N(t-Bu)] (12%); M^+ is not observed. IR ν(C=N): 1624 cm^{-1}. ^1H NMR (C_6D_6): δ 6.81 (m, 2H, C_5H_3), δ 6.17 (m, 2H, C_5H_3), δ 5.06 (m, 2H, C_5H_3), δ 2.28 (s, 3H, *Me*–C=N–R), δ 1.09 (s, 9H, *Me*$_3$C), δ 0.75 (s, 3H, Si*Me*$_2$), δ 0.69 (s, 3H, Si*Me*$_2$), δ 0.68 (s, 3H, Si*Me*$_2$), δ 0.57 (s, 3H, Si*Me*$_2$), δ 0.23 (s, 3H, Zr*Me*). ^{13}C NMR (C_6D_6): δ 233.30 (RN=*C*Me), δ 142.54 (C_5H_3), δ 133.47 (C_5H_3), δ 122.06 (C_5H_3), δ 105.74 (C_5H_3), δ 105.24 (C_5H_3), δ 62.02 (Me$_3$*C*), δ 30.11 (*Me*$_3$C), δ 24.50 (RN=C*Me*), δ 7.24 (Zr*Me*), δ 4.19 (Si*Me*$_2$), δ 4.11 (Si*Me*$_2$), δ −3.37 (Si*Me*$_2$), δ −3.58 (Si*Me*$_2$).

3.3. Synthesis of $[Zr\{\mu\text{-}[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]\}\{\eta^2\text{-}CMeN(2,6\text{-}Me_2C_6H_3)\}]_2(\mu\text{-}O)$ (3)

A solution of $[Zr\{\mu\text{-}[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]\}Me\{\eta^2\text{-}CMeN(2,6\text{-}Me_2C_6H_3)\}]$ (**1**) (0.35 g, 0.71 mmol) in toluene (20 ml) at room temperature was stirred for 48 h with a stoichiometric amount of water (0.007 ml, 0.35 mmol). The solvent was completely removed in vacuo to give a white–yellow solid characterized as **3** (0.22 g, 64% yield). Anal. Found: C, 58.55; H, 5.98; N, 3.28. $C_{48}H_{60}Si_4Zr_2N_2$ Calc.: C, 59.08; H, 6.2; N, 2.87%. Mass spectrum m/z: M^+ −(Me) (3%); M^+ −[CMe=N(2,6-$Me_2C_6H_3$)] (2%); M^+ −[CMe=N(2,6-$Me_2C_6H_3$)]−(Me) (29%); M^+ is not observed. IR ν(C=N): 1608 cm^{-1}. ^1H NMR (C_6D_6): δ 7.22 (m, 4H, C_5H_3), δ 6.90 (m, 6H, C_6H_3), δ 6.39 (m, 4H, C_5H_3), δ 5.48 (m, 4H, C_5H_3), δ 1.91 (s, 6H, *Me*–C=N), δ 1.84 (s, 12H, 2,6-*Me*$_2$$C_6H_3$), δ 0.97 (s, 6H, Si*Me*$_2$), δ 0.69 (s, 6H, Si*Me*$_2$), δ 0.67 (s, 6H, Si*Me*$_2$), δ 0.39 (s, 6H, Si*Me*$_2$). ^{13}C-RMN (C_6D_6): δ 298.80 (RN=*C*Me), δ 139.21 (C_5H_3), δ 137.92 (C_5H_3), δ 130.54 (C_5H_3), δ 128.55 (C_5H_3), δ 124.91 (C_5H_3), δ 138.07 (C_6H_3), δ 136.44 (C_6H_3), δ 117.43 (C_6H_3), δ 20.68 (RN=C*Me*), δ 16.85 (2,6-*Me*$_2$–C_5H_3), δ 0.36 (Si*Me*$_2$), δ 0.19 (Si*Me*$_2$), δ −3.56 (Si*Me*$_2$), δ −7.57 (Si*Me*$_2$).

3.4. Synthesis of [Zr{μ-[(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]}{η^2-CMeN(t-Bu)}]$_2$(μ-O) (4)

A solution of [Zr{μ-[(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]}Me{η^2-CMeN(t-Bu)}] (2) (0.35 g, 0.78 mmol) in toluene (20 ml) at room temperature was stirred for 48 h with a stoichiometric amount of water (0.007 ml, 0.39 mmol). The solvent was completely removed in vacuo to give a white–yellow solid characterized as 4 (0.22 g, 64% yield). Anal. Found: C, 54.39; H, 6.61; N, 3.39. $C_{40}H_{60}Si_4Zr_2N_2$ Calc.: C, 54.66; H, 6.82; N, 3.19%. Mass spectrum *m/z*: M^+ is not observed. IR ν(C=N): 1600 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.20 (m, 4H, C_5H_3), δ 6.22 (m, 4H, C_5H_3), δ 5.28 (m, 4H, C_5H_3), δ 2.19 (s, 6H, *Me*–C=N–R), δ 1.12 (s, 18H, Me_3C), δ 1.02 (s, 6H, Si*Me*$_2$), δ 1.00 (s, 6H, Si*Me*$_2$), δ 0.69 (s, 6H, Si*Me*$_2$), δ 0.68 (s, 6H, Si*Me*$_2$).

3.5. Synthesis of [ZrCl{μ-[(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]}{η^2-C(CH$_2$CMe$_2$(C$_6$H$_5$))N(2,6-Me$_2$C$_6$H$_3$)}] (5)

Toluene (30 ml) was added to a mixture of [Zr{μ-[(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]}Cl(CH$_2$CMe$_2$Ph)] (0.5 g, 0.99 mmol) and CN(2,6-Me$_2$C$_6$H$_3$) (0.13 g, 0.99 mmol) at room temperature and then stirred for 1 h. The solvent was completely removed in vacuo to give a white–yellow solid. Recrystallization from hexane at −20 °C gave a white–yellow solid characterized as 5 (0.59 g, 94% yield). Anal. Found: C, 62.56; H, 6.06; N, 2.83. $C_{33}H_{40}Si_2ZrNCl$ Calc.: C, 62.58; H, 6.32; N, 2.21%. Mass spectrum *m/z*: M^+ − [CMe=N(2,6-Me$_2$C$_6$H$_3$)] (14%); M^+ is not observed. IR ν(C=N): 1580 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.17 (m, 5H, CMe$_2$*Ph*), δ 7.12 (m, 2H, C_5H_3), δ 6.89 (m, 3H, C_6H_3), δ 6.23 (m, 2H, C_5H_3), δ 5.44 (m, 2H, C_5H_3), δ 3.15 (s, 2H, C*H*$_2$), δ 1.99 (s, 6H, 2,6-*Me*$_2$C$_6$H$_3$), δ 1.05 (s, 12H, C*Me*$_2$Ph), δ 0.98 (s, 3H, Si*Me*$_2$), δ 0.69 (s, 3H, Si*Me*$_2$), δ 0.64 (s, 3H, Si*Me*$_2$), δ 0.36 (s, 3H, Si*Me*$_2$). ^{13}C NMR (C_6D_6): δ 244.69 (RN=*C*Me), δ 148.86 (C_6H_3), δ 142.74 (C_5H_3), δ 129.60 (C_6H_3), δ 128.89 (C_6H_5), δ 128.68 (C_6H_5), δ 128.55 (C_6H_3), δ 126.66 (C_6H_3), δ 125.88 (C_6H_5), δ 125.74 (C_6H_5), δ 124.52 (C_5H_3), δ 110.94 (C_5H_3), δ 110.41 (C_5H_3), δ 107.52 (C_5H_3), δ 30.32 (*C*Me$_2$Ph), δ 29.45 (RN=C*C*H$_2$–), δ 19.71 (2,6-*Me*$_2$–C$_6$H$_3$), δ 3.43 (Si*Me*$_2$), δ 3.14 (Si*Me*$_2$), δ −3.38 (Si*Me*$_2$), δ −3.53 (Si*Me*$_2$).

3.6. Synthesis of [ZrCl{μ-[(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]}{η^2-C(CH$_2$–CH$_3$)N(2,6-Me$_2$C$_6$H$_3$)}] (6)

Toluene (30 ml) was added to a mixture of [Zr{μ-[(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]}Cl(CH$_2$–CH$_3$)] (0.5 g, 1.25 mmol) and CN(2,6-Me$_2$C$_6$H$_3$) (0.164 g, 1.25 mmol) at room temperature and then stirred for 1 h. The solvent was completely removed in vacuo to give a white–yellow solid. Recrystallization from hexane at −20 °C gave a white solid characterized as 6 (0.63 g, 95% yield). Anal. Found: C, 56.74; H, 6.18; N, 2.74. $C_{25}H_{32}Si_2ZrN$ Calc.: C, 56.74; H, 6.05; N, 2.64%. Mass spectrum *m/z*: [M^+] − (Et) (0.6%); [M^+] − (Et–CNR) (3%); [Et–CNR]$^+$ (60.6%). IR ν(C=N): 1585 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.21 (m, 2H, C_5H_3), δ 6.89 (m, 3H, C_6H_3), δ 6.60 (m, 2H, C_5H_3), δ 5.51 (m, 2H, C_5H_3), δ 2.40 (q, *J* = 7.69 Hz, 2H, C*H*$_2$CH$_3$), δ 1.88 (s, 6H, 2,6-*Me*$_2$C$_6$H$_3$), δ 0.98 (s, 3H, Si*Me*$_2$), δ 0.71 (s, 3H, Si*Me*$_2$), δ 0.68 (s, 3H, Si*Me*$_2$), δ 0.65 (t, *J* = 7.69 Hz, 2H, CH$_2$C*H*$_3$), δ 0.41 (s, 3H, Si*Me*$_2$). ^{13}C NMR (C_6D_6): δ 243.61 (RN=*C*Me), δ 143.7 (C_6H_3), δ 141.9 (C_5H_3), δ 129.4 (C_6H_3), δ 128.5 (C_6H_3), δ 125.6 (C_6H_3), δ 123.9 (C_5H_3), δ 111.4 (C_5H_3), δ 109.5 (C_5H_3), δ 108 (C_5H_3), δ 31.6 (–*C*H$_2$CH$_3$), δ 19.1 (2,6-*Me*$_2$–C$_6$H$_3$), δ 9.91 (CH$_2$*C*H$_3$), δ 3.3 (Si*Me*$_2$), δ 3.2 (Si*Me*$_2$), δ −3.6 (Si*Me*$_2$), δ −4.5 (Si*Me*$_2$).

3.7. Synthesis of [ZrCl{μ-[(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]}{η^2-C(CH$_2$–CH$_2$–CH$_3$)N(2,6-Me$_2$C$_6$H$_3$)}] (7)

Toluene (50 ml) was added to a mixture of [Zr{μ-[(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]}Cl(CH$_2$–CH$_2$–CH$_3$)] (0.5 g, 1.21 mmol) and CN(2,6-Me$_2$C$_6$H$_3$) (0.158 g, 1.21 mmol) at room temperature and then stirred for 1 h. The solvent was completely removed in vacuo to give a white–yellow solid. Recrystallization from hexane at −20 °C gave a white solid characterized as 7 (0.625 g, 95% yield). Anal. Found: C, 57.40; H, 6.32; N, 2.49. $C_{26}H_{34}Si_2ZrN$ Calc.: C, 57.46; H, 6.30; N, 2.57%. Mass spectrum *m/z*: [M^+] − (Pr) (2%); [M^+] − (Pr–CNR) (7.8%); [Pr–CNR]$^+$ (100%). IR ν(CN): 1585 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.22 (m, 2H, C_5H_3), δ 6.89 (m, 3H, C_6H_3), δ 6.62 (m, 2H, C_5H_3), δ 5.52 (m, 2H, C_5H_3), δ 2.47 (m, 2H, C*H*$_2$CH$_2$CH$_3$), δ 1.91 (s, 6H, 2,6-*Me*$_2$C$_6$H$_3$), δ 1.27 (m, 2H, CH$_2$C*H*$_2$CH$_3$), δ 0.99 (s, 3H, Si*Me*$_2$), δ 0.72 (s, 3H, Si*Me*$_2$), δ 0.69 (s, 3H, Si*Me*$_2$), δ 0.58 (t, 3H, CH$_2$CH$_2$C*H*$_3$), δ 0.43 (s, 3H, Si*Me*$_2$). ^{13}C NMR (C_6D_6): δ 242.8 (RN=*C*Me), δ 143.9 (C_6H_3), δ 142 (C_5H_3), δ 129.6 (C_6H_3), δ 128.6 (C_6H_3), δ 125.6 (C_6H_3), δ 124.1 (C_5H_3), δ 111.4 (C_5H_3), δ 109.4 (C_5H_3), δ 108 (C_5H_3), δ 40.8 (–*C*H$_2$CH$_2$CH$_3$), δ 19.3 (–CH$_2$*C*H$_2$CH$_3$), δ 19.2 (2,6-*Me*$_2$–C$_6$H$_3$), δ 14.7 (–CH$_2$CH$_2$*C*H$_3$), δ 3.3 (Si*Me*$_2$), δ 3.2 (Si*Me*$_2$), δ −3.6 (Si*Me*$_2$), δ −4.5 (Si*Me*$_2$).

3.8. Synthesis of [ZrCl{μ-[(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]}{η^2-C(CH–(CH$_3$)$_2$)N(2,6-Me$_2$C$_6$H$_3$)}] (8)

A 2 M solution of MgCl(i-Pr) in THF (1 ml, 1.98 mmol) at −78 °C was added to a solution of [ZrCl$_2${μ-(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$}] (0.8 g, 1.98 mmol) in THF (25 ml) at ca. −78 °C and the mixture was stirred for 2 h at 10 °C. The solvent was completely removed in vacuo. A solution of CN(2,6-Me$_2$C$_6$H$_3$) (0.26 g,

1.98 mmol) in toluene (50 ml) at room temperature was added to the mixture and then stirred for 1.5 h. The solvent was completely removed in vacuo to give a white–yellow solid. Recrystallization from hexane at −20 °C gave a white–yellow crystalline solid characterized as **8** (1.0 g, 94% yield). Anal. Found: C, 57.34; H, 6.297; N, 2.77. $C_{26}H_{34}Si_2ZrN$ Calc.: C, 57.47; H, 6.30; N, 2.58%. Mass spectrum *m/z*: $[M^+]$ − (i-Pr) (4.6%); $[M^+]$ − (i-Pr–CNR) (10.4%); $[i\text{-Pr–CNR}]^+$ (100%). IR ν_s(CN): 1575 cm^{-1}. ^1H NMR (C_6D_6): δ 7.23 (m, 2H, C_5H_3), δ 6.89 (m, 3H, C_6H_3), δ 6.84 (m, 2H, C_5H_3), δ 5.54 (m, 2H, C_5H_3), δ 2.69 (spt, J = 6.96 Hz, 1H, $CH(CH_3)_2$), δ 1.87 (s, 6H, 2,6-$Me_2C_6H_3$), δ 1.02 (s, 3H, SiMe_2), δ 0.9 (d, J = 6.96 Hz, 6H, $CH(CH_3)_2$), δ 0.73 (s, 3H, SiMe_2), δ 0.68 (s, 3H, SiMe_2), δ 0.48 (s, 3H, SiMe_2). ^{13}C NMR (C_6D_6): δ 244.2 (RN=*C*Me), δ 143.7 (C_6H_3), δ 142.5 (C_5H_3), δ 129.5 (C_6H_3), δ 128.4 (C_6H_3), δ 125.5 (C_6H_3), δ 122.5 (C_5H_3), δ 110.9 (C_5H_3), δ 110.5 (C_5H_3), δ 107.8 (C_5H_3), δ 38 ($CH(CH_3)_2$), δ 19.5 ($CH(CH_3)_2$), δ 19.3 (2,6-Me_2–C_6H_3), δ 3.51 (SiMe_2), δ 3.36 (SiMe_2), δ −3.04 (SiMe_2), δ −3.5 (SiMe_2).

Table 2
Crystal data and structure refinement for compound **8**

Empirical formula	$ZrClSi_2NC_{26}H_{34}$
Crystal size (mm^3)	0.2 × 0.3 × 0.3
Colour	Yellow-pale
Crystal habit	Prismatic
Formula weight	543.4
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 9.655(1) Å
	b = 11.949(1) Å
	c = 12.227(1) Å
	α = 108.38(1)°
	β = 92.08(1)°
	γ = 91.49(1)°
Volume (Å^3)	1336.7(2)
Z	2
Density (calc.) ($g\,cm^{-3}$)	1.350
Absorption coefficient (cm^{-1})	6.15
F(000)	564
θ range for data collection (°)	2.08 to 24.97
Index ranges	$-11 \le h \le 11$, $-14 \le k \le 13$, $0 \le l \le 14$
Reflections collected	4942
Independent reflections	4699 (R_{int} = 0.0212)
Reflections observed with $I > 2\sigma(I)$	4095
Absorption correction	N/A
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4699/0/280
Goodness-of-fit on F^2	1.085
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0378, wR_2 = 0.1019
R indices (all data)	R_1 = 0.0470, wR_2 = 0.1084
Largest difference peak and hole (e Å^{-3})	1.172 and −0.738
Weighting scheme (calc.)	$w = 1/[\sigma^2(F_o^2) + (0.0745P)^2 + 0.4115P]$
	$P = (F_o^2 + 2F_c^2)/3$

3.9. X-ray structural determination for compound 8

Crystallographic and experimental details of the crystal structure determinations are given in Table 2. Suitable crystals of complex **8** were mounted on an Enraf–Nonius CAD4 automatic four-circle diffractometer with bisecting geometry, equipped with a graphite-oriented monochromator and Mo Kα radiation (λ = 0.71073 Å). Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made.

The structure was solved by direct methods (SHELXS 90) [17] and refined by full-matrix least-squares against F^2 (SHELXL 93) [18]. All non-hydrogen atoms were refined anisotropically. In the last cycle of refinement the hydrogen atoms were positioned geometrically and refined using a riding model with fixed thermal parameters (U = 0.08 Å^2).

Calculations were carried out on an ALPHA AXP (Digital) workstation.

4. Supplementary material available

Tables of anisotropic thermal parameters for non-hydrogen atoms (Table 1), hydrogen coordinates (Table 2), coordinates for non-hydrogen atoms (Table 3), complete lists of bond lengths and angles (Table 4, 2 pages) and observed and calculated structure factors (11 pages).

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