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FULL PAPER

Mono- and di-cyclopentadienyl zirconium derivatives containing the dimethylsilylcyclopentadienyl ligand. Agostic linear Si–H–Zr interaction in the molecular structure of $[Zr\{\eta^5\text{-}C_5H_4(SiMe_2H)\}Cl_3]_2$ †

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Dimethylsilyl substituted mono- and di-cyclopentadienyl zirconium chlorides have been prepared and their reactions with amido and alkyl reagents studied. The silylcyclopentadienes $C_5H_5(SiMe_2H)$ **1**, $C_5H_4(SiMe_2H)_2$ **2** and $C_5H_4(SiMe_3)(SiMe_2H)$ **3** can be prepared by reaction of $Na(C_5H_5)$ with the appropriate chlorosilane reagent. The lithium salt $Li[C_5H_4(SiMe_2H)]$ reacts with $ZrCl_4$ or $[Zr(C_5H_5)Cl_3]$ to give the metallocene complexes $[Zr(C_5H_4R)\{C_5H_4(SiMe_2H)\}Cl_2]$ (R = $SiMe_2H$ **4** or H **5**) whereas the reaction of the disilylcyclopentadiene $C_5H_4(SiMe_2H)_2$ with $ZrCl_4$ afforded the monocyclopentadienyl complex $[Zr\{C_5H_4(SiMe_2H)\}Cl_3]$ **6**, which exchanges the Si–H and Zr–Cl bonds. The reaction of **6** with lithium amides produces different products depending on the basicity of the nitrogen atom and the steric demands of its amido substituents. The reaction with $LiN(SiMe_3)_2$ and $LiNH(2,6\text{-}Me_2C_6H_3)$ afforded the corresponding amido zirconium complexes $[Zr\{C_5H_4(SiMe_2H)\}(NRR')Cl_2]$ (R = R′ = $SiMe_3$ **7**; R = H, R′ = 2,6-$Me_2C_6H_3$ **8**), but in the case of the reaction with LiNH^{t}Bu the known cyclopentadienylsilylamido derivative $[Zr(\eta^5,\eta^1\text{-}C_5H_4SiMe_2N^tBu)Cl_2]$ was formed. The monoamido, diamido and dialkyl dicyclopentadienyl complexes $[Zr(C_5H_4R)\{C_5H_4(SiMe_2H)\}X(Y)]$ (R = $SiMe_2H$ **9** or H **10**, X = Cl, Y = NH^{t}Bu; R = $SiMe_2H$ **11** or H **12**, X = Y = NH^{t}Bu; R = $SiMe_2H$ **13** or H **14**, X = Y = Me) have been synthesized by reaction of **4** and **5** with the appropriate amido or methyl reagent. Compound **9** reacts with a stoichiometric amount of water with selective hydrolysis of the Zr–amido bond to give the corresponding μ-oxo dinuclear complex $[\{Zr[C_5H_4(SiMe_2H)]_2Cl\}_2(\mu\text{-}O)]$ **15**. The molecular structure of $[Zr\{C_5H_4(SiMe_2H)\}Cl_3]$ **6** was established by X-ray crystallography. Compound **6** is a dimer, in the solid state, in which dimerization occurs through Zr–H–Si agostic interactions and two chloride bridges.

Introduction

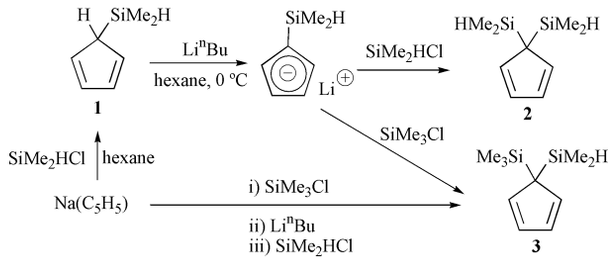
The Si–H bond, which is relatively strong and has low polarity, does not normally react spontaneously with unsaturated molecules. An exception to this rule is the reaction of silanes with enamines. It is normally necessary to use catalysts to obtain useful reaction rates under ambient conditions. One of the most useful methods to synthesize organosilicon compounds involves transition metal catalysts to achieve olefin hydrosilylation. Representative catalysts for hydrosilylation are derived from Group 8–10 late transition metals and Group 4 early transition metals.[1] Recent results have revealed that metallocene complexes of titanium and zirconium are active precursors for olefin hydrosilylation.[2] Complexes containing both hydride and silyl ligands which are formed by oxidative addition of Si–H bonds to transition metals are important intermediates in such processes.[3,4] We are interested in the formation of zirconium complexes where the Si–H unit is not bonded directly to the metal in order to study the influence of the metal centre and the feasibility of using these systems to break the Si–H bond under such conditions. With appropriate silyl substitution, cyclopentadienyl ligands form a large variety of monocyclopentadienyl and dicyclopentadienyl derivatives of Group 4 metals.[5] Hence, Cp systems provide suitable precursors to introduce the Si–H fragment into the side chain of a Cp ligand and subsequently its inclusion in organometallic zirconium compounds. We present here the synthesis and reactivity of some mono- and di-cyclopentadienyl zirconium complexes containing the dimethylsilylcyclopentadienyl ligand $[C_5H_4(SiMe_2H)]$.

Results and discussion

Synthesis and characterization

The reaction of $Na(C_5H_5)$ with one equivalent of chlorodimethylsilane $SiMe_2HCl$ in hexane gave a yellow oil, in *ca.* 80% yield, which was characterized as $C_5H_5(SiMe_2H)$ **1**.[6] The silylcyclopentadiene **1** exists as a mixture of three isomers, as evidenced by its NMR data. Treatment of a solution of **1** in hexane with Li^{n}Bu at 0 °C afforded a suspension of the white insoluble lithium salt $Li[C_5H_4(SiMe_2H)]$ which, after the addition of one equivalent of chlorodimethylsilane, afforded a yellow liquid corresponding to the 1,1-bis(dimethylsilyl)cyclopentadiene compound $C_5H_4(SiMe_2H)_2$ **2** (72% yield), characterized by NMR as a single isomer. $Li[C_5H_4(SiMe_2H)]$ did not form a dimer, unlike the unstable salt $Li[C_5H_4(SiMe_2Cl)]$[5] which dimerized through an intermediate silylene species. An analogous reaction of the lithium salt $Li[C_5H_4(SiMe_2H)]$ with chlorotrimethylsilane gave the bis(silyl)cyclopentadiene compound $C_5H_4(SiMe_3)(SiMe_2H)$ **3** (69% yield). An alternative method for the synthesis of **3** used the reaction of $Na(C_5H_5)$ with $SiMe_3Cl$ and subsequent treatment with Li^{n}Bu and $SiMe_2HCl$ (Scheme 1). The ^{1}H NMR spectra (C_6D_6, room

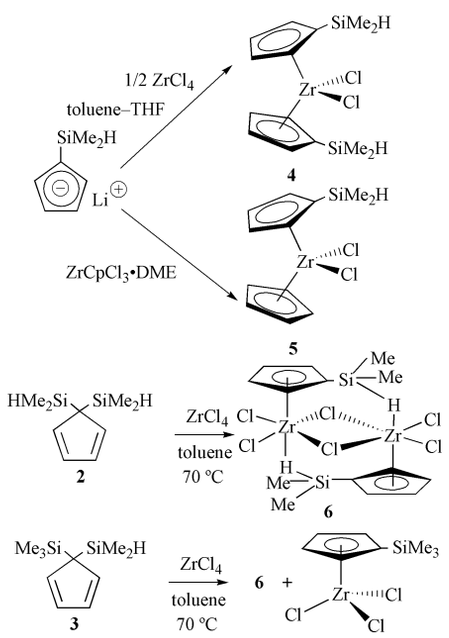
† Dedicated to Professor Rafael Usón on the occasion of his 75th birthday.
‡ For X-ray diffraction studies.



Scheme 1

temperature) of compounds **1**–**3** exhibited resonances corresponding to an AA′BB′ spin system between δ 6.30 and 6.90, assigned to the diene protons, and for **1** a weak broad signal at δ 3.27 corresponding to the sp^3-C bonded proton was also observed. The dimethylsilyl protons showed one doublet ($^3J_{H\text{-}H}$ = 2.9–3.6 Hz), shifted to high field, for the methyl groups and a multiplet located at δ 3.91 for **1**, 4.27 for **2** and 4.26 for **3**, attributed to the Si–H bond. These spectroscopic data are consistent with the formation of only one possible isomer for compounds **2** and **3** with both silyl substituents located over the sp^3 carbon ring, as evidenced by the absence of alyllic proton signals in the ^{1}H NMR spectra.

Treatment of $ZrCl_4$ with two equivalents of Li[$C_5H_4(SiMe_2H)$] in a mixture of toluene–THF at room temperature gave the expected dicyclopentadienyl complex [Zr{$C_5H_4(SiMe_2H)$}$_2Cl_2$] **4**, while the reaction of one equivalent of the lithium salt with [Zr(C_5H_5)Cl_3]·DME afforded the mixed metallocene complex [Zr(C_5H_5){$C_5H_4(SiMe_2H)$}Cl_2] **5**. Compounds **4** and **5** were obtained as off-white microcrystals in *ca.* 70–75% yield (Scheme 2).

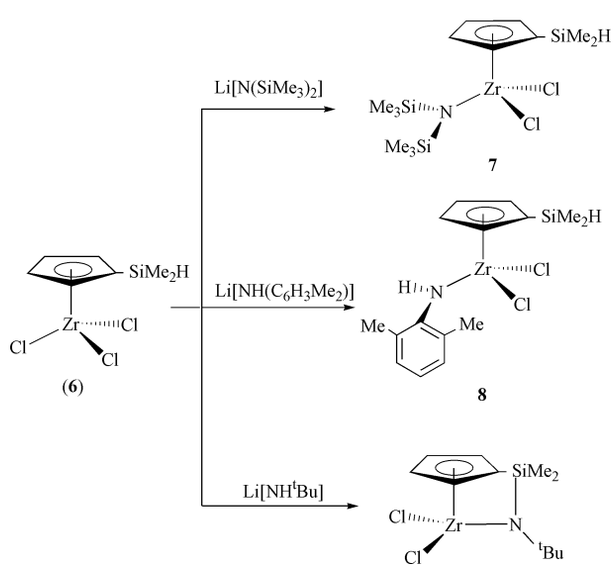


Scheme 2

The reaction of $ZrCl_4$ with one equivalent of the disilylcyclopentadiene **2** in toluene at 70 °C produced the monocyclopentadienyl derivative [Zr{$C_5H_4(SiMe_2H)$}Cl_3] **6** as pale yellow crystals (Scheme 2). However, when this reaction mixture was stirred for a longer period of time, the Si–H hydrogen atom was replaced by chlorine to afford [Zr{C_5H_4($SiMe_2$Cl)}Cl_3], previously prepared by an alternative method.[7] This process must result from an Si–H and Zr–Cl bond interchange.[8] This behaviour contrasts with that observed for the dicyclopentadienyl derivatives **4** and **5**, where the Si–H bonds remain unchanged under the same conditions. Attempts to prepare complex **6** *via* the reaction of $ZrCl_4$ with the cyclopentadiene $C_5H_4(SiMe_2H)(SiMe_3)$ afforded mainly a mixture of **6** and the well characterized compound [Zr{$C_5H_4(SiMe_3)$}Cl_3].[9] This latter result indicates that the two silyl substituents, $SiMe_3$ and $SiMe_2H$, behave analogously as leaving groups in reactions of this type. In contrast the cyclopentadiene $C_5H_4(SiMe_2Cl)$-($SiMe_3$) reacts with $ZrCl_4$ with elimination of $SiMe_3Cl$ and selective formation of [Zr{$C_5H_4(SiMe_2Cl)$}Cl_3].[7] The monocyclopentadienyl complex **6** is very moisture sensitive but it can be stored under rigorously dry conditions for months, whereas the dicyclopentadienyl derivatives **4** and **5** can be handled in air for a few minutes without decomposition. These compounds are soluble in aromatic hydrocarbons and chlorinated solvents but insoluble in alkanes and they have been characterized by the usual techniques, and the crystal structure of **6** has been determined by X-ray diffraction methods.

The Si–H IR stretching frequencies were measured at 2117 cm^{-1} for the dicyclopentadienyl derivatives and at 2066 cm^{-1} for the monocyclopentadienyl compound **6**. The latter indicates a slight weakening in the Si–H bond,[10] consistent with the Si–H–Zr agostic interaction observed in the solid state (X-ray diffraction study). The ^{1}H NMR (C_6D_6) spectra of complexes **4**–**6** show AA′BB′ spin systems for the substituted cyclopentadienyl ring protons and one singlet for the C_5H_5 group protons of **5**. For the $SiMe_2H$ fragment the spectra showed one doublet for the two methyl groups and one septet in the range δ 4.4–4.6 with $^3J_{HH}$ = 3.6–4.0 Hz for the Si–H proton, resulting from vicinal coupling and indicating no perturbation of the Si–H environment in solution. The similar NMR spectroscopic behaviour observed for the "Si–H" proton in compounds **4**–**6** suggests no Si–H–Zr agostic interaction for **6** in solution in contrast with this interaction observed in the solid state (X-ray diffraction study). The ^{13}C NMR spectra were consistent with the presence of a $C_5H_4(SiMe_2H)$ group in which the ring C_{ipso} atom resonances were shielded with respect to the signals of the other ring carbon atoms.

Reactions of the mono- and di-cyclopentadienyl complexes with lithium amides have been studied. Compound **6** reacts in hexane at room temperature with 1 equivalent of LiR (R = N($SiMe_3$)$_2$ or NH(2,6-$Me_2C_6H_3$)) to give the amido compounds [Zr{$C_5H_4(SiMe_2H)$}{N($SiMe_3$)$_2$}Cl_2] **7** and [Zr{C_5H_4-($SiMe_2H$)}{NH(2,6-$Me_2C_6H_3$)}Cl_2] **8** as yellow oils in 75–80% yield (Scheme 3). Complexes **7** and **8** are very moisture sensitive

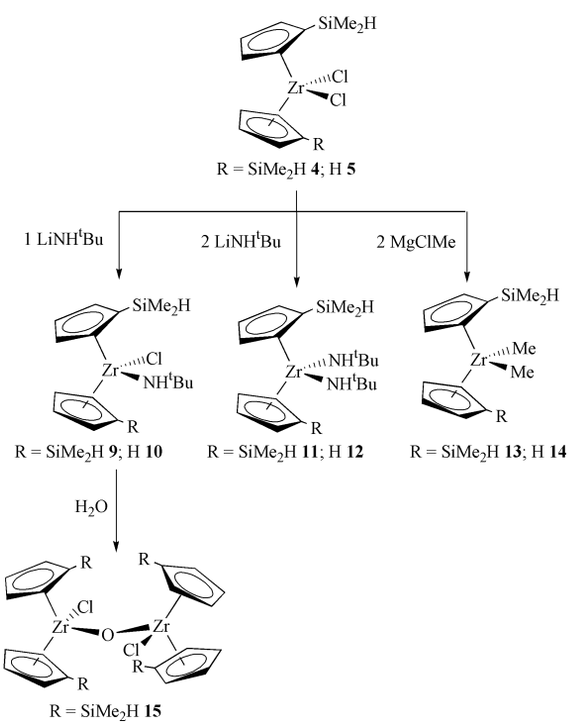


Scheme 3

but thermally stable and remain unchanged even after heating at 100 °C in a C_6D_6 solution. This behaviour is similar to that observed for the analogous complex [Zr{$C_5H_4(SiMe_2Cl)$}-{N($SiMe_3$)$_2$}Cl_2] previously described.[11] Compound **8** always

contained a small amount of impurity, the free amine $H_2N(C_6H_3Me_2$-2,6). However, when **6** was treated with Li(NH^{t}Bu) the previously reported cyclopentadienylsilylamido derivative [Zr(η^5,η^1-$C_5H_4SiMe_2N^tBu$)Cl_2][11,12] was obtained in 56% yield after recrystallization in cooled toluene. We propose the reactions of the monocyclopentadienyl compound **6** with lithium amides produce, in a first step, the zirconium amido derivatives in which the silicon atom can extend its coordination number through intramolecular coordination of the nitrogen atom of the Zr–NR_2 group. Such an interaction would form an intermediate five-coordinated silicon that could enhance its reactivity towards nucleophilic substitution reactions compared with four-coordinated silicon compounds,[13] as observed in the reaction of **6** with Li(NH^{t}Bu). In the case of complex **7**, the steric demands of the $SiMe_3$ groups may prevent such a five-coordinated silicon arrangement by nitrogen coordination, and in **8** this effect may be attributed to the weaker Lewis base properties of the amido fragment "Zr–NH($C_6H_3Me_2$)" compared with "Zr–NH^{t}Bu". On this basis, reactions of cyclopentadienyl Group 4 complexes that contain M–Cl bonds and "$SiMe_2X$" (X = Cl or H) Cp substituents with different lithium amides LiNHR or alternatively with primary amines in the presence of NEt_3 are convenient routes to cyclopentadienylsilylamido derivatives.[5,11]

Analogous reactions of the dicyclopentadienyl compounds **4** and **5** with 1 or 2 equivalents of the amido reagent Li(NH^{t}Bu) in hexane gave the mono- and bis-amido complexes [Zr{C_5H_4-($SiMe_2H$)}(C_5H_4R)(NH^{t}Bu)Cl] (R = $SiMe_2H$ **9** or H **10**) and [Zr{$C_5H_4(SiMe_2H)$}(C_5H_4R)(NH^{t}Bu)$_2$] (R = $SiMe_2H$ **11** or H **12**) respectively. Likewise, reaction of complexes **4** and **5** with 2 equivalents of MgClMe afforded the dimethyl compounds [Zr{$C_5H_4(SiMe_2H)$}(C_5H_4R)Me_2] (R = $SiMe_2H$ **13** or H **14**) in high yield (Scheme 4). Compounds **9**–**14** were obtained as very



Scheme 4

moisture sensitive yellow oils which were very soluble in all common solvents. Compound **9** reacts with a stoichiometric amount of water with selective hydrolysis of the Zr–amido bond to give the corresponding μ-oxo dinuclear complex [{Zr[$C_5H_4(SiMe_2H)$]$_2$Cl}$_2$(μ-O)] **15** (Scheme 4).

The infrared data for compounds **7**–**15** show Si–H stretching frequencies at values greater than 2100 cm^{-1}, the expected region of hydrosilanes.[10] The ^{1}H and ^{13}C NMR spectra (C_6D_6 and $CDCl_3$) of the amido and methyl compounds described are consistent with the presence of a $C_5H_4(SiMe_2H)$ ligand bonded to zirconium. The ^{1}H NMR spectra of the monocyclopentadienyl derivatives **7** and **8** show one AA′BB′ spin system for the cyclopentadienyl protons, and one doublet and one septet ($^3J_{H\text{-}H}$ = 3.7 Hz) for the methylsilicon and Si–H of the silylcyclopentadienyl substituent respectively. The resonances for the amido groups were in the expected region of the spectrum. The ^{1}H NMR spectra (C_6D_6) of complexes **9** and **10** show one ABCD spin system for the silyl substituted cyclopentadienyl ring protons (five resonances in the ^{13}C NMR spectra were observed for the corresponding carbon atoms) resulting from the asymmetry afforded by the presence of two different groups (Cl and NH^{t}Bu) attached to zirconium. Compounds **11**–**14** display AA′BB′ spin systems for the silyl substituted cyclopentadienyl protons consistent with the presence of two equivalent σ ligands at the bent metallocene wedge (three resonances in the ^{13}C NMR spectra were observed for the corresponding carbon atoms). Compounds **10**, **12** and **14** also exhibit a singlet associated with the C_5H_5 protons. The $SiMe_2H$ fragment protons appear as one doublet for the methyl groups for compounds **11**–**14** whereas for **9** and **10** two doublets appear, corresponding to the diastereotopic methyl groups which result from the chiral zirconium atom. One septet is observed for the Si–H hydrogen in the region expected for silicon hydride resonances.[10] The ^{1}H NMR spectra of the amido complexes **9**–**12** all display resonances in the range δ 1.19–1.28 for the *tert*-butyl protons, and **13** and **14** exhibited singlets at δ −0.03 and −0.09 for the methyl protons, and at δ 30.8 and 30.6 for the methyl carbons in their ^{13}C NMR spectra. Broad signals at δ 6.31, 4.04 and 3.88 are attributed to the N–H proton in the monoamido **9** and the bisamido compounds **11** and **12** respectively. The presence of the $SiMe_2H$ substituent in the cyclopentadienyl ligand does not significantly change the chemical shifts of the cyclopentadienyl and methylzirconium protons compared with the analogous system [Zr(C_5H_5)$_2X_2$] (X = Cl or Me).[14] The ^{1}H NMR spectrum of complex **15** shows the expected ABCD spin system along with two doublets for the methyl groups and a multiplet for the hydrogen of the $SiMe_2H$ fragment.

Molecular structure of [Zr($C_5H_4SiMe_2H$)Cl_3]$_2$ 6

Crystals of **6** suitable for X-ray diffraction were obtained by slow cooling of a hexane solution at −30 °C. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1.

The X-ray determination shows **6** as a dimer of two [Zr{η^5-$C_5H_4(SiMe_2H)$}Cl_3] units. The coordination around the zirconium atom corresponds to a distorted octahedral environment with the dimethylsilylcyclopentadienyl ligand occupying one site, four chlorine atoms defining the equatorial positions (two of which act as terminal atoms and two bridge the adjacent zirconium atoms) and with one hydride located at the remaining site. This hydride is located in the axial position *trans* to the cyclopentadienyl ring and is bonded to the silicon of the neighbouring silyl substituent group of the other cyclopentadienyl ligand. The metal atom is located 0.706 Å above the plane defined by the chloride substituents. The terminal Zr–Cl bond distances are slightly different (Zr(1)–Cl(1), 2.3999(8) and Zr(1)–Cl(2), 2.4124(8) Å) and shorter than the two Zr–Cl bridging distances (Zr(1)–Cl(3), 2.6146(7) Å and Zr(1)–Cl(3a), 2.6112(8) Å). The Zr–Cp(centroid) bond distance of 2.1906 Å compares well with the values reported for other similar mono- and bis-cyclopentadienyl complexes.[14a,16] The dimeric structure of **6** is similar to that observed for the analogous silyl monosubstituted cyclopentadienyl complex [Zr{η^5-$C_5H_4(SiMe_2OH)$}Cl_3]$_2$[17] or other crowded monocyclopentadienyl compounds such as [Zr(η^5-C_5Me_5)Cl_3]$_2$[18] or [Zr{η^5-$C_5H_3(SiMe_2P^iPr_2)$-1,3}Cl_3]$_2$[19] in contrast with the monomeric structure found in the very sterically encumbered mono-

Table 1 Selected bond lengths (Å) and angles (°) for **6**

Zr(1)–Cl(1)	2.3999(8)	Si(1)–C(7)	1.841(4)
Zr(1)–Cl(2)	2.4124(8)	Si(1)–C(6)	1.845(4)
Zr(1)–C(5)	2.483(3)	Si(1)–C(1)	1.875(3)
Zr(1)–C(2)	2.496(3)	C(1)–C(2)	1.424(4)
Zr(1)–C(1)	2.499(3)	C(1)–C(5)	1.423(4)
Zr(1)–C(4)	2.501(3)	C(4)–C(5)	1.397(5)
Zr(1)–C(3)	2.510(3)	C(4)–C(3)	1.400(6)
Zr(1)–Cl(3a)	2.6112(8)	C(2)–C(3)	1.408((5)
Zr(1)–Cl(3)	2.6146(7)	Zr(1a)–H(1)	2.28(3)
Cl(3)–Zr(1a)	2.6113(8)	Si(1)–H(1)	1.47(2)
Zr(1)–Cp(1)	2.1906		
Cl(1)–Zr(1)–Cl(2)	93.61(3)	C(2)–C(1)–Si(1)	126.3(2)
Cl(1)–Zr(1)–Cl(3a)	85.57(3)	C(5)–C(1)–Si(1)	127.8(2)
Cl(2)–Zr(1)–Cl(3a)	146.13(3)	C(5)–C(4)–C(3)	108.2(3)
Cl(1)–Zr(1)–Cl(3)	145.76(3)	C(3)–C(2)–C(1)	108.9(3)
Cl(2)–Zr(1)–Cl(3)	85.37(3)	C(4)–C(5)–C(1)	109.3(3)
Cl(3a)–Zr(1)–Cl(3)	76.98(2)	C(4)–C(3)–C(2)	107.9(3)
Zr(1a)–Cl(3)–Zr(1)	103.02(2)	Cl(1)–Zr(1)–Cp(1)	108.68
C(7)–Si(1)–C(6)	114.6(2)	Cl(2)–Zr(1)–Cp(1)	107.67
C(7)–Si(1)–C(1)	111.05(16)	Cl(3)–Zr(1)–Cp(1)	104.17
C(6)–Si(1)–C(1)	109.77(19)	Zr(1)–Cl(3)–Zr(1a)	103.02
C(2)–C(1)–C(5)	105.7(3)	Si(1)–H(1)–Zr(1a)	158.3

Symmetry transformation used to generate equivalent atoms: (a) $-x$, $-y$, $-z+1$. Cp(1) is the centroid of C(1), C(2), C(3), C(4), C(5).

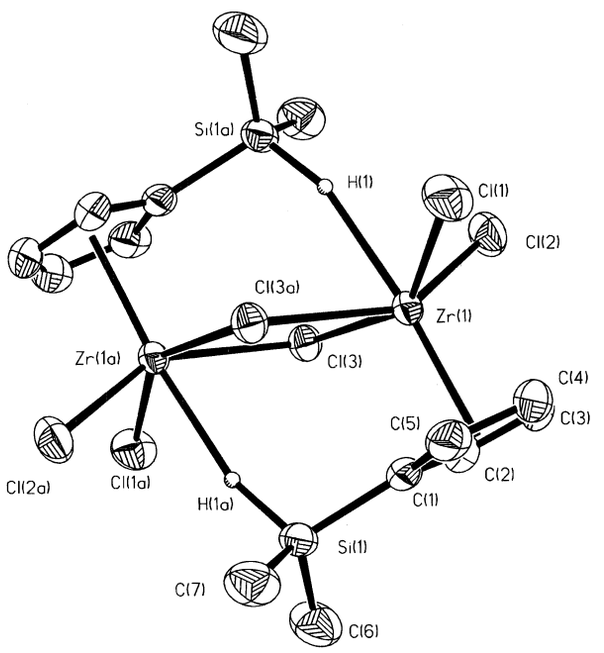


Fig. 1 An ORTEP[15] drawing of the molecular structure of compound **6** together with the atomic labelling scheme.

cyclopentadienyl derivative [Zr(diborna-Cp)Cl_3] {diborna-Cp = dibornacyclopentadienyl = (1*R*,5*R*,8*S*,11*S*)-η^5-1,5,14,14,-15,15-hexamethylpentacyclo[9.2.1.1^{5,8}.0^{2,10}.0^{4,9}]pentadeca-3,-$\Delta^{2,10}$-dienyl}[20] or the polymeric structure found in [Zr(η^5-C_5H_5)Cl_3].[16a] The most interesting feature of the structure is the Si–H–Zr interaction in relation to the presence of a non-classical interaction between zirconium and the silicon hydride. The Si–H distance of 1.47(2) Å is in the range expected for typical Si–H bond distances (1.48 Å) as found for the complex [Zr(C_5H_5)$_2$($SiHPh_2$)(μ-H)]$_2$.[21] The Zr–H distance of 2.28(3) Å is longer than the terminal Zr–H bond distance of previously characterized complexes such as [Zr(C_5H_5)$_2$(H)($SiPh_3$)(PMe_3)], which is 1.94(5) Å,[4] or for a bridging zirconium hydride as in [Zr(C_5H_5)$_2$($SiHPh_2$)(μ-H)]$_2$ (1.96(3) and 2.01(2) Å)[21] or [Zr-{$Me_2C(C_5H_4)$(Flu)}Cl(μ-H)]$_2$ (Flu = fluorenyl) (1.83(3) and 2.03(3) Å),[22] but shorter than the sum of the van der Waals radii and reflects an interaction between hydrogen and the zirconium centre. This distance is in the range found in [ZrCp_2(X)-(R^1C=CR^2H)], X = Cl, 2.29 Å; Br, 2.19 Å,[23] and [{Zr(C_5H_4Me)$_2$-(Et)(PMe_3)}(BPh_4)] where the Zr–H distance was 2.16 Å,[24] and where β-agostic H–Zr interactions have been proposed. An analogous bond distance was also found in [Zr(C_5H_5)$_2$-{N^{t}Bu($SiMe_2H$)}Cl] [2.266(3) Å][10] whereas in our case the hydrogen atom is bonded to a similar silyl moiety with a short Zr–Si distance, suggesting an interaction between the two atoms (explained by an η^2-silane bonding mode), in contrast with compound **6** in which the Zr–H–Si bond angle (158.3°) rules out this type of zirconium–silicon interaction. In the case of [Zr(C_5H_5)$_2$N^{t}Bu($SiMe_2H$)}Cl] the Zr–H interaction explains the small elongation observed in the bond length of Zr–Cl and Zr–Cp, whereas for **6** such elongation does not occur, probably because its structural disposition contributes to electronic stabilization of the dimeric form. A similar bridged species with Ti–H–Si–Ti is $Cp_2Ti(\mu$-H-SiHPh)$_2$$TiCp_2$[25] in which dimerization occurs *via* two Ti–H–Si bonds with a closer angle value of 117(2)°. The Si–C distances show the expected values for normal single-bond lengths (≈1.82–1.90 Å).[26] Thus, the crystallographic data for **6** indicate that an agostic interaction with a near linear Si–H–Zr disposition is present, consistent with the infrared data. However the NMR spectroscopic data discussed above suggest that this interaction must be weak in solution and probably broken by solvent effects.

Conclusion

The synthesis of the silylcyclopentadienes $C_5H_5(SiMe_2H)$, $C_5H_4(SiMe_2H)_2$ and $C_5H_4(SiMe_3)(SiMe_2H)$ and silyl substituted mono- and di-cyclopentadienyl zirconium derivatives of type [Zr{$C_5H_4(SiMe_2H)$}Cl_3] and [Zr(C_5H_4R){$C_5H_4(SiMe_2H)$}Cl_2] (R = $SiMe_2H$ or H) is described. The reaction of the mono-cyclopentadienyl complex with lithium amides depends on the basicity of the nitrogen atom and the steric effects of its substituents. Consequently the reactions with LiN($SiMe_3$)$_2$ and LiNHAr afforded the corresponding complexes [Zr{C_5H_4-($SiMe_2H$)}(NRR′)Cl_2] (R = R′ = $SiMe_3$; R = H, R′ = Ar) but in the case of LiNH^{t}Bu the known silylamido derivative [Zr(η^5,η^1-$C_5H_4SiMe_2N^tBu$)Cl_2] was formed probably through a hypervalent silicon hydride intermediate. The dicyclopentadienyl monoamido, bisamido and dialkyl zirconium derivatives [Zr(C_5H_4R){$C_5H_4(SiMe_2H)$}X(Y)] (R = $SiMe_2H$ or H, X = Y = NH^{t}Bu or Me; X = Cl, Y = NH^{t}Bu) have been synthesized without affecting the original tetravalent silicon environment. The molecular structure of [Zr{$C_5H_4(SiMe_2H)$}Cl_3] has been determined by X-ray diffraction methods which show that the dimeric structure is adopted through a pair of almost agostic Zr–H–Si interactions and two chloride bridges.

Experimental

General considerations

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glove-box model HE-63 or MBraun. Solvents were purified by distillation under argon from an appropriate drying agent (sodium for toluene, sodium–potassium alloy for hexane and sodium–benzophenone for THF). [$ZrCpCl_3$]·DME[27] and the lithium reagent LiN-($SiMe_3$)$_2$[28] were prepared by known procedures. LiNHR (R = 2,6-Me_2Ph or ^{t}Bu) was prepared in hexane in almost quantitative yield from NH_2R and Li^{n}Bu (Aldrich, 1.6 M in hexane). $ZrCl_4$ (Aldrich), and $SiMe_2HCl$ (Fluka) were obtained commercially. C, H and N microanalyses were performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyser. NMR spectra, at 25 °C, were recorded on a Varian Unity 300 spectrometer (usually ^{1}H at 300 MHz and ^{13}C at 75 MHz). ^{1}H and ^{13}C chemical shifts are reported in δ units relative to TMS standard.

Preparations

$C_5H_5(SiMe_2H)$ 1. $SiMe_2HCl$ (17.4 mL, 0.16 mol) was added at −78 °C to a suspension of $Na(C_5H_5)$ (14.1 g, 0.16 mol) in 150 mL of hexane. The reaction mixture was warmed to room temperature and stirred for 18 h. After filtration the volatiles were removed under reduced pressure, to give a yellow oil which was characterized as **1** (19.37 mL, 15.98 g, 0.13 mol, 80%) ($d = 0.825$ g mL^{-1}). ^{1}H NMR (200 MHz, C_6D_6): δ −0.13 (d, 6H, $SiMe_2$, $^3J_{H\text{-}H} = 3.0$ Hz), 3.27 (br, 1H, C_{sp^3}–H), 3.91 (m, 1H, Si–H), 6.30–6.90 (br, 4H, C_5H_5). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.03 (d, 6H, $SiMe_2$, $^3J_{H\text{-}H} = 3.1$ Hz), 3.45 (br, 1H, C_{sp^3}–H), 3.76 (m, 1H, Si–H), 6.46–6.75 (br, 4H, C_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$): δ −5.0 ($SiMe_2$), 45.6 (C_5H_5–C_{sp^3}), 130.8, 133.2 (C_5H_5).

$C_5H_4(SiMe_2H)_2$ 2. Li^{n}Bu (100 mL, 0.16 mol) was added dropwise to a vigorously stirred solution of **1** (24.18 g, 0.16 mol) in 150 mL of hexane at −78 °C. After the addition was complete the reaction mixture was stirred overnight and a white precipitate formed. After filtration the white solid was washed with cold hexane and characterized as Li[C_5H_4-($SiMe_2H$)] (20.48 g, 0.16 mol, 98%). $SiMe_2HCl$ (17.4 mL, 0.16 mol) was added to a suspension of the lithium salt (20.48 g, 0.16 mol) in 130 mL of hexane at −78 °C and the reaction mixture slowly warmed to room temperature and stirred for 12 h. Filtration gave a yellow solution and the solvent was removed to give a yellow oil characterized as **2** (21.01 g, 23.71 mL, 0.11 mol, 72%) ($d = 0.886$ g mL^{-1}). ^{1}H NMR (300 MHz, C_6D_6): δ −0.03 (d, 12H, $2SiMe_2$, $^3J_{H\text{-}H} = 2.9$ Hz), 4.27 (m, 2H, 2Si–H), 6.50, 6.74 (AA′BB′ spin system, 2 × 2H, C_5H_4). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.03 (d, 12H, $2SiMe_2$, $^3J_{H\text{-}H} = 2.9$ Hz), 3.99 (m, 2H, 2Si–H), 6.53, 6.72 (AA′BB′ spin system, 2 × 2H, C_5H_4). ^{13}C NMR (75 MHz, $CDCl_3$): δ −4.9 ($SiMe_2$), 65.8 (C_5H_4–C_{ipso}), 131.4, 134.9 (C_5H_4).

$C_5H_4(SiMe_3)(SiMe_2H)$ 3. Li^{n}Bu (100 mL, 0.16 mol) was added dropwise to a vigorously stirred solution of **1** (24.18 g, 0.16 mol) in 150 mL of hexane at −78 °C. After the addition was complete the reaction mixture was stirred overnight and a white precipitate formed. After filtration the white solid was washed with cold hexane and characterized as Li[C_5H_4-($SiMe_2H$)] (20.48 g, 0.16 mol, 98%). $SiMe_3Cl$ (20.22 mL, 0.16 mol, 17.33 g) was added to a suspension of the lithium salt Li[$C_5H_4(SiMe_2H)$] (20.48 g, 0.16 mol) in 200 mL of hexane at −78 °C and the reaction mixture slowly warmed to room temperature and stirred for 15 h. Filtration gave a yellow solution and the solvent was removed to give a yellow oil characterized as **3** (21.68 g, 0.11 mol, 69%). ^{1}H NMR (300 MHz, C_6D_6): δ −0.08 (d, 6H, $SiMe_2$, $^3J_{H\text{-}H} = 3.6$ Hz), −0.01 (s, 9H, $SiMe_3$), 4.26 (m, 1H, Si–H), 6.45, 6.74 (AA′BB′ spin system, 2 × 2H, C_5H_4). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.07 (d, 6H, $SiMe_2$, $^3J_{H\text{-}H} = 3.3$ Hz), −0.03 (s, 9H, $SiMe_3$), 4.00 (m, 1H, Si–H), 6.51, 6.70 (AA′BB′ spin system, 2 × 2H, C_5H_4).

[$Zr\{C_5H_4(SiMe_2H)\}_2Cl_2$] 4. A solution of Li[$C_5H_4(SiMe_2H)$] (3.08 g, 23.60 mmol) in 15 mL of THF was added dropwise, at −78 °C, to a suspension of $ZrCl_4$ (2.75 g, 11.80 mmol) in 40 mL of toluene. The reaction mixture was slowly warmed to room temperature and stirred for 17 h. After complete removal of the solvent under vacuum an oil was obtained which was extracted into hexane (40 mL). The resulting solution was concentrated and cooled to −36 °C to give a crystalline white solid characterized as **4** (3.27 g, 8.02 mmol, 68%). Calc. for $C_{14}H_{22}Cl_2Si_2Zr$: C, 41.16; H, 5.39. Found: C, 41.50; H, 5.39%. ^{1}H NMR (300 MHz, C_6D_6): δ 0.30 (d, 12H, $2SiMe_2$, $^3J_{H\text{-}H} = 4.0$), 4.62 (septet, 2H, 2Si–H, $^3J_{H\text{-}H} = 4.0$ Hz), 5.99, 6.40 (AA′BB′ spin system, 2 × 4H, $2C_5H_4$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.35 (d, 12H, $2SiMe_2$, $^3J_{H\text{-}H} = 4.0$), 4.43 (septet, 2H, 2Si–H, $^3J_{H\text{-}H} = 4.0$ Hz), 6.51, 6.70 (AA′BB′ spin system, 2 × 4H, $2C_5H_4$). ^{13}C NMR (75 MHz, $CDCl_3$): δ −3.3 ($SiMe_2$), 117.4 (C_5H_4), 121.1 (C_5H_4–C_{ipso}), 126.1 (C_5H_4).

[$Zr(C_5H_5)\{C_5H_4(SiMe_2H)\}Cl_2$] 5. A solution of Li[$C_5H_4$-($SiMe_2H$)] (1.42 g, 10.85 mmol) in 10 mL of THF was added dropwise, at −30 °C, to a suspension of [$ZrCpCl_3$]·DME (3.83 g, 10.85 mmol) in 35 mL of THF. The reaction mixture was maintained at room temperature with stirring for 12 h. The solvent was removed under vacuum to give a sticky solid, which was extracted into toluene. After filtration, the solution was concentrated to 25 mL and cooled to −36 °C to give a white microcrystalline solid characterized as **5** (2.85 g, 8.14 mmol, 75%). Calc. for $C_{12}H_{16}Cl_2SiZr$: C, 41.12; H, 4.57. Found: C, 40.62; H, 4.68%. ^{1}H NMR (300 MHz, C_6D_6): δ 0.27 (d, 6H, $SiMe_2$, $^3J_{H\text{-}H} = 3.7$), 4.62 (septet, 1H, Si–H, $^3J_{H\text{-}H} = 3.7$ Hz), 5.92, 6.32 (AA′BB′ spin system, 2 × 2H, C_5H_4), 5.96 (s, 5H, C_5H_5). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.35 (d, 6H, $SiMe_2$, $^3J_{H\text{-}H} = 3.7$), 4.42 (septet, 1H, Si–H, $^3J_{H\text{-}H} = 3.7$ Hz), 6.54, 6.74 (AA′BB′ spin system, 2 × 2H, C_5H_4), 6.45 (s, 5H, C_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$): δ −3.2 ($SiMe_2$), 116.1 (C_5H_5), 117.9 (C_5H_4), 120.7 (C_5H_4–C_{ipso}), 125.8 (C_5H_4).

[$Zr\{C_5H_4(SiMe_2H)\}Cl_3$] 6. $C_5H_4(SiMe_2H)_2$ **2** (1.52 g, 1.71 mL, 8.31 mmol) was added dropwise to a suspension of $ZrCl_4$ (2.13 g, 9.14 mmol) in 50 mL of toluene. The Schlenk vessel was connected to a bubbler and the reaction mixture warmed slowly to 70 °C with vigorous stirring. As the temperature increased the $ZrCl_4$ reacted to form a brown solution. The solution was filtered and cooled to −36 °C to give a pale yellow powder. Recrystallization from toluene gave **6** as pale yellow crystals (1.33 g, 4.15 mmol, 50%). Calc. for $C_7H_{11}Cl_3SiZr$: C, 26.19; H, 3.43. Found: C, 26.47; H, 3.47%. ^{1}H NMR (300 MHz, C_6D_6): δ 0.17 (d, 6H, $SiMe_2$, $^3J_{H\text{-}H} = 3.6$), 4.50 (septet, 1H, Si–H, $^3J_{H\text{-}H} = 3.6$ Hz), 6.27, 6.34 (AA′BB′ spin system, 2 × 2H, C_5H_4). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.44 (d, 6H, $SiMe_2$, $^3J_{H\text{-}H} = 3.6$), 4.49 (septet, 1H, Si–H, $^3J_{H\text{-}H} = 3.6$ Hz), 6.98, 7.02 (AA′BB′ spin system, 2 × 2H, C_5H_4). ^{13}C NMR (75 MHz, $CDCl_3$): δ −3.6 ($SiMe_2$), 123.6 (C_5H_4–C_{ipso}), 124.6, 126.8 (C_5H_4).

[$Zr\{C_5H_4(SiMe_2H)\}\{N(SiMe_3)_2\}Cl_2$] 7. Hexane (20 mL) was added at room temperature to a mixture of **6** (0.5 g, 1.56 mmol) and $LiN(SiMe_3)_2$ (0.26 g, 1.56 mmol) in a Schlenk vessel in a glove-box. The reaction mixture was stirred for 13 h. After filtration the solvent was removed to give **7** as a yellow oil (0.55 g, 1.25 mmol, 80%). Calc. for $C_{13}H_{29}Cl_2NSi_3Zr$: C, 35.02; H, 6.51; N, 3.14. Found: C, 35.47; H, 6.41; N, 3.79%. ^{1}H NMR (300 MHz, C_6D_6): δ 0.24 (s, 18H, $2SiMe_3$), 0.31 (d, 6H, $SiMe_2$, $^3J_{H\text{-}H} = 3.7$), 4.71 (septet, 1H, Si–H, $^3J_{H\text{-}H} = 3.7$ Hz), 6.35, 6.50 (AA′BB′ spin system, 2 × 2H, C_5H_4). ^{13}C NMR (50 MHz, C_6D_6): δ −3.5 ($SiMe_2$), 5.1 ($SiMe_3$), 118.5, 124.0 (C_5H_4), 126.1 (C_5H_4–C_{ipso}).

[$Zr\{C_5H_4(SiMe_2H)\}\{NH(2,6\text{-}Me_2C_6H_3)\}Cl_2$] 8. Hexane (25 mL) was added to a mixture of LiNHAr (0.20 g, 1.56 mmol) and **6** (0.5 g, 1.56 mmol). The resulting solution was stirring for 13 h at room temperature in a glove-box. After filtration the volatiles were removed under reduced pressure to give a pale brown oil characterized as **8** (0.47 g, 1.17 mmol, 75%). ^{1}H NMR (300 MHz, C_6D_6): δ 0.07 (d, 6H, $SiMe_2$, $^3J_{H\text{-}H} = 3.7$), 2.51 (s, 6H, *Me*$_2$Ph), 4.36 (septet, 1H, Si–H, $^3J_{H\text{-}H} = 3.7$ Hz), 6.22, 6.30 (AA′BB′ spin system, 2 × 2H, C_5H_4), 6.83 (t, 1H, *para*-C_6H_3), 6.96 (d, 2H, *meta*-C_6H_3).

[$Zr(\eta^5,\eta^1\text{-}C_5H_4SiMe_2N^tBu)Cl_2$]. A solution of Li(NH^{t}Bu) (0.34 g, 4.26 mmol) in 30 mL of hexane was quickly added to a cooled (−60 °C) suspension of **6** (1.37 g, 4.26 mmol) in 30 mL of hexane. The reaction mixture was slowly warmed to room temperature and stirred for 8 h. After filtration, the resulting solution was concentrated under reduced pressure and cooled to −40 °C to give a pale microcrystalline solid which was characterized as the previously reported [$Zr(\eta^5,\eta^1\text{-}C_5H_4$-$SiMe_2N^tBu)Cl_2$]. A second crop of product was obtained after concentration of the mother liquor. After recrystallization from

toluene at −40 °C, 0.85 g (2.38 mmol, 56%) of the cyclopentadienylsilylamido compound was obtained.

[Zr{$C_5H_4(SiMe_2H)$}$_2$(NH^{t}Bu)Cl] 9. A solution of **4** (1.00 g, 2.45 mmol) and LiNH^{t}Bu (0.20 g, 2.50 mmol) in 90 mL of hexane at room temperature was stirred for 17 h. After filtration the solvent was removed under vacuum to give **9** as a pale orange oil (0.85 g, 1.91 mmol, 78%). Calc. for $C_{18}H_{32}ClNSi_2Zr$: C, 48.56; H, 7.19; N, 3.15. Found: C, 49.12; H, 7.26; N, 3.85%. ^{1}H NMR (200 MHz, C_6D_6): δ 0.27 (d, 6H, 2SiMe, $^3J_{H\text{-}H}$ = 3.7), 0.31 (d, 6H, 2SiMe, $^3J_{H\text{-}H}$ = 3.7), 1.22 (s, 9H, ^{t}Bu), 4.62 (septet, 2H, 2Si–H, $^3J_{H\text{-}H}$ = 3.7 Hz), 6.04, 6.21, 6.20, 6.37 (ABCD spin system, 4 × 2H, 2C_5H_4), 6.31 (br, 1H, N–H). ^{13}C NMR (75 MHz, C_6D_6): δ −2.7 (SiMe), −2.4 (SiMe), 33.9 (C(*C*H$_3$)$_3$), 58.2 (*C*(CH$_3$)$_3$), 113.6, 114.4 (C_5H_4), 115.4 (C_5H_4–C_{ipso}), 121.5, 122.5 (C_5H_4).

[Zr(C_5H_5){$C_5H_4(SiMe_2H)$}(NH^{t}Bu)Cl] 10. A solution of **5** (1.00 g, 2.85 mmol) and LiNH^{t}Bu (0.23 g, 2.95 mmol) in 90 mL of hexane was stirred at room temperature for 18 h. After filtration the solvent was removed under vacuum to give **10** as a yellow oil (0.88 g, 2.28 mmol, 80%). Calc. for $C_{16}H_{26}ClNSiZr$: C, 49.64; H, 6.72; N, 3.62. Found: C; 49.77; H, 6.72; N, 4.47%. ^{1}H NMR (300 MHz, C_6D_6): δ 0.21 (d, 3H, SiMe, $^3J_{H\text{-}H}$ = 3.7), 0.28 (d, 3H, SiMe, $^3J_{H\text{-}H}$ = 3.7), 1.19 (s, 9H, ^{t}Bu), 4.59 (septet, 1H, Si–H, $^3J_{H\text{-}H}$ = 3.7 Hz), 5.98 (s, 5H, C_5H_5), 5.88, 6.01, 6.07, 6.26 (ABCD spin system, 4 × 1H, C_5H_4). ^{13}C NMR (75 MHz, C_6D_6): δ −2.9 (SiMe), −2.7 (SiMe), 33.6 (C(*C*H$_3$)$_3$), 58.2 (*C*(CH$_3$)$_3$), 112.1 (C_5H_5), 112.9 (C_5H_4), 114.8 (C_5H_4–C_{ipso}), 115.7, 120.6, 122.7 (C_5H_4).

[Zr{$C_5H_4(SiMe_2H)$}$_2$(NH^{t}Bu)$_2$] 11. Hexane (90 mL) was added to a mixture of **4** (1.00 g, 2.45 mmol) and LiNH^{t}Bu (0.42 g, 5.38 mmol). The reaction mixture was stirred for 18 h. After filtration the solvent was completely removed *in vacuo* to give a yellow oil characterized as **11** (1.00 g, 2.08 mmol, 85%). ^{1}H NMR (300 MHz, C_6D_6): δ 0.27 (d, 12H, 2SiMe$_2$, $^3J_{H\text{-}H}$ = 3.7), 1.28 (s, 18H, 2 ^{t}Bu), 4.04 (br, 2H, 2N–H), 4.63 (septet, 2H, 2Si–H, $^3J_{H\text{-}H}$ = 3.7 Hz), 6.18, 6.23 (AA′BB′ spin system, 2 × 4H, 2C_5H_4). ^{13}C NMR (75 MHz, C_6D_6): δ −2.6 (SiMe$_2$), 31.2 (C(*C*H$_3$)$_3$), 55.5 (*C*(CH$_3$)$_3$), 112.0 (C_5H_4), 112.3 (C_5H_4–C_{ipso}), 120.3 (C_5H_4).

[Zr(C_5H_5){$C_5H_4(SiMe_2H)$}(NH^{t}Bu)$_2$] 12. Hexane (100 mL) was added to a mixture of **5** (1.00 g, 2.85 mmol) and LiNH^{t}Bu (0.54 g, 6.84 mmol). The reaction mixture was stirred for 18 h. After filtration the solvent was completely removed *in vacuo* to give a yellow oil characterized as **12** (0.94 g, 2.22 mmol, 78%). Calc. for $C_{20}H_{36}N_2SiZr$: C, 56.67; H, 8.51; N, 6.61. Found: C; 56.12; H, 8.33; N, 6.49%. ^{1}H NMR (300 MHz, C_6D_6): δ 0.24 (d, 6H, SiMe$_2$, $^3J_{H\text{-}H}$ = 3.7), 1.25 (s, 18H, 2^{t}Bu), 3.88 (br, 2H, 2N–H), 4.60 (septet, 1H, Si–H, $^3J_{H\text{-}H}$ = 3.7 Hz), 5.92 (s, 5H, C_5H_5), 6.09 (m, 4H, C_5H_4). ^{13}C NMR (75 MHz, C_6D_6): δ −2.5 (SiMe$_2$), 34.4 (C(*C*H$_3$)$_3$), 55.5 (*C*(CH$_3$)$_3$), 109.0 (C_5H_4–C_{ipso}), 110.3 (C_5H_5), 112.3, 120.3 (C_5H_4).

[Zr{$C_5H_4(SiMe_2H)$}$_2$Me$_2$] 13. MgClMe (2.99 mL of a 3 M solution in THF, 8.99 mmol) was added to a suspension of **4** (1.74 g, 4.28 mmol) in 70 mL of diethyl ether at −30 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 h. After filtration, the volatiles were removed under reduced pressure to give **13** as a yellow oil (1.16 g, 3.17 mmol, 74%). Calc. for $C_{16}H_{28}Si_2Zr$: C, 52.26; H, 7.62. Found: C, 52.69; H, 7.80%. ^{1}H NMR (300 MHz, C_6D_6): δ −0.03 (s, 6H, ZrMe$_2$), 0.20 (d, 12H, 2SiMe$_2$, $^3J_{H\text{-}H}$ = 3.6), 4.49 (septet, 2H, 2Si–H, $^3J_{H\text{-}H}$ = 3.6 Hz), 5.96, 6.10 (AA′BB′ spin system, 2 × 4H, 2C_5H_4). ^{13}C NMR (50 MHz, C_6D_6): δ −2.9 (SiMe$_2$), 30.8 (ZrMe$_2$), 114.1 (C_5H_4), 114.7 (C_5H_4–C_{ipso}), 118.4 (C_5H_4).

[Zr(C_5H_5){$C_5H_4(SiMe_2H)$}Me$_2$] 14. MgClMe (1.99 mL of a 3 M solution in THF, 5.99 mmol) was added to a suspension of **5** (1.00 g, 2.85 mmol) in 60 mL of diethyl ether at −30 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 h. After filtration, the volatiles were removed under reduced pressure to give **14** as a yellow oil (0.66 g, 2.14 mmol, 75%). Calc. for $C_{14}H_{22}SiZr$: C, 54.32; H, 7.11. Found: C, 53.79; H, 6.83%. ^{1}H NMR (300 MHz, C_6D_6): δ −0.09 (s, 6H, ZrMe$_2$), 0.16 (d, 6H, SiMe$_2$, $^3J_{H\text{-}H}$ = 3.6), 4.43 (septet, 1H, Si–H, $^3J_{H\text{-}H}$ = 3.7 Hz), 5.79 (s, 5H, C_5H_5), 5.90, 5.98 (AA′BB′ spin system, 2 × 2H, C_5H_4). ^{13}C NMR (75 MHz, C_6D_6): δ −3.0 (SiMe$_2$), 30.6 (ZrMe$_2$), 110.7 (C_5H_5), 111.1 (C_5H_4–C_{ipso}), 114.3, 117.9 (C_5H_4).

[{Zr[$C_5H_4(SiMe_2H)$]$_2$Cl}$_2$(μ-O)] 15. A solution of **9** (0.85 g, 1.91 mmol) in 90 mL of hexane was stirred at room temperature for 17 h in air. The resulting solution was filtered and the solvent removed *in vacuo* to give a yellow-brown oil characterized as **15** (0.94 g, 1.24 mmol, 65%). Calc. for $C_{28}H_{44}Cl_2OSi_4Zr_2$: C, 44.11; H, 5.77. Found: C, 43.45; H, 5.80%. ^{1}H NMR (300 MHz, C_6D_6): δ 0.35 (d, 12H, 4SiMe, $^3J_{H\text{-}H}$ = 4.0), 0.37 (d, 12H, 4SiMe, $^3J_{H\text{-}H}$ = 3.7 Hz), 4.73 (m, 4H, 4Si–H), 6.31, 6.47, 6.46, 6.71 (ABCD spin system, 4 × 4H, 4C_5H_4). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.38 (d, 12H, 4SiMe, $^3J_{H\text{-}H}$ = 3.0), 0.40 (d, 12H, 4SiMe, $^3J_{H\text{-}H}$ = 3.6 Hz), 4.54 (m, 4H, 4Si–H), 6.39, 6.40, 6.54, 6.60 (ABCD spin system, 4 × 4H, 4C_5H_4). ^{13}C NMR (75 MHz, C_6D_6): δ −3.3, −2.8 (SiMe), 114.4 (C_5H_4), 116.2 (C_5H_4–C_{ipso}), 119.3, 122.8, 125.6 (C_5H_4).

Table 2 Crystal, experimental data and structure refinement for compound **6**

Formula	$C_{14}H_{22}Cl_6Si_2Zr_2$
M_w	641.64
Symmetry, space group	Monoclinic, $P2_1/n$
a/Å	7.010(1)
b/Å	17.674(1)
c/Å	9.648(1)
β/deg	102.56(1)
V/Å^3	1166.7(2)
Z	2
μ/cm^{-1}	16.80
No. reflections	
measured	2737
independent	2536 (R_{int} = 0.0156)
observed	2009 ($I > 2\sigma(I)$)
Final $R1$, $wR2$ indices ($I > 2\sigma(I)$)	0.0267, 0.0618
all data	0.0482, 0.0677

X-Ray diffraction analysis for complex 6

Crystals of compound **6** were obtained by crystallization from hexane. A suitably sized crystal sealed in a Lindemann tube was mounted in an Enraf-Nonius CAD 4 automatic four-circle diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Crystallographic and experimental details are summarized in Table 2. 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)[29] and refined by least squares against F^2 (SHELXL 93).[30] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms located and refined isotropically. Calculations were carried out on an ALPHA AXP (Digital) workstation.

CCDC reference number 155168.

See http://www.rsc.org/suppdata/dt/b0/b010221k/ for crystallographic data in CIF or other electronic format.

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