Structural Analysis of Zincocenes with Substituted Cyclopentadienyl Rings

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Abstract: New zincocenes [ZnCp′₂] (2–5) with substituted cyclopentadienyl ligands C₅Me₄H, C₅Me₄tBu, C₅Me₄SiMe₂tBu and C₅Me₄SiMe₃, respectively, have been prepared by the reaction of ZnCl₂ with the appropriate Cp′-transfer reagent. For a comparative structural study, the known [Zn(C₅H₄SiMe₃)₂] (1), has also been investigated, along with the mixed-ring zincocenes [Zn(C₅Me₅)(C₅Me₄SiMe₃)] (6) and [Zn(C₅Me₅)(C₅H₄SiMe₃)] (7), the last two obtained by conproportionation of [Zn(C₅Me₅)₂] with 5 or 1, as appropriate. All new compounds were characterised by NMR spectroscopy, and by X-ray methods, with the exception of 7, which yields a side-product (C) upon attempted crystallisation. Compounds 5 and 6 were also investigated by ¹³C CPMAS NMR spectroscopy. Zincocenes 1 and 2 have infinite chain structures with bridging Cp′ ligands, while 3 and 4 exhibit slipped-sandwich geometries. Compounds 5 and 6 have rigid, η⁵/η¹(σ) structures, in which the monohapto C₅Me₄SiMe₃ ligand is bound to zinc through the silyl-bearing carbon atom, forming a

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Zn–C bond of comparable strength to the Zn–Me bond in ZnMe₂. Zincocene 5 has dynamic behaviour in solution, but a rigid η⁵/η¹(σ) structure in the solid state, as revealed by ¹³C CPMAS NMR studies, whereas for 6 the different nature of the Cp′ ligands and of the ring substituents of the η¹-Cp′ group (Me and SiMe₃) have permitted observation for the first time of the rigid η⁵/η¹ solution structure. Iminoacyl compounds of composition [Zn(η⁵-C₅Me₄R)(η¹-C(NXyl)C₅Me₄R)] resulting from the reactions of some of the above zincocenes and CNXyl (Xyl= 2,6-dimethylphenylisocyanide) have also been obtained and characterised.

Introduction

Nearly six decades after the preparation of ferrocene[1] and the recognition of its sandwich structure,[2] study of metallo-cenes continues to be an important research theme. Cyclopentadienyl derivatives of most elements of the periodic table are known, including many main group elements, as well as the lanthanides and accessible actinides.[3–5] A large

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variety of cyclopentadienyl ligands may be used,[6] ranging from the parent C_5H_5 and its alkyl-substituted derivatives, exemplified by the widely utilised C_5Me_5, to the bulkier, so-called supracyclopentadienyls,[6b] for example, C_5Ph_5 and C_5iPr_5. Recently, perarylated cyclopentadienyls C_5Ar_5 of substituted aryl groups,[7] for instance $Ar = 4-nBu-C_6H_4$, or $3,5-tBu_2C_6H_3$, referred to as superbulky cyclopentadienyls, have imparted renewed impetus to the field by providing unexpected structures and reactivity, as well as remarkable stability to their corresponding metallocenes.[8]

With few exceptions, transition-metal metallocenes $[MCp_2']$ (Cp′ is used in this paper as a general representation for a cyclopentadienyl ligand) have a ferrocene-type structure (**a**). In the analogous metallocenes of divalent f
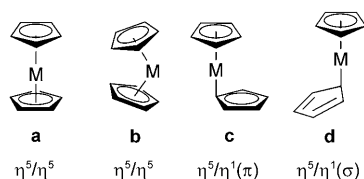
elements, the rings coordinate also in the η^5 fashion, although unusually bent structures are typically observed (**b**; see also reference [8a] for somewhat different geometries). Cyclopentadienyl derivatives of the main-group elements offer a rich structural diversity since they may adopt a variety of structures, including the slipped-sandwich geometry **c**.

This structure is often represented as $\eta^5/\eta^1(\pi)$, in which $\eta^1(\pi)$ implies metal coordination through one carbon atom of the ring by means of the π cloud and consequently planar or nearly planar coordination geometry of the sp^2-hybridised carbon atom, giving an essentially parallel arrangement of the two Cp′ ligands.

Zincocenes conform to this structural assortment. In contrast, the recent isolation of the Zn−Zn bonded dimetallocenes, $[Zn_2(\eta^5-C_5Me_5)_2]$ and $[Zn_2(\eta^5-C_5Me_4Et)_2]$[9] places them, for the time being, in an unique position among all metallocenes. A common feature of zincocenes is their low hapticity count, often η^1 or η^2. Thus, in the solid state the parent zincocene, $[Zn(C_5H_5)_2]$, features a structure consisting of an infinite chain of zinc atoms bridged by C_5H_5 groups, with each zinc atom surrounded by one terminal and two bridging ligands, all with η^2 binding.[10a] In the gas-phase[10b] the molecules have the $\eta^5/\eta^1(\pi)$ coordination **c**, which is also characteristic of beryllocenes.[11] The molecular zincocenes $[Zn(C_5Me_5)_2]$,[12a,b] $[Zn(C_5Me_4Ph)_2]$[12b] and $[Zn-(C_5iPr_4H)_2]$,[12c] have a slipped-sandwich geometry too, while zincocenes of 1,2-diaza-3,5-diborolyl ligands have a $\eta^1(\pi)/\eta^1(\pi)$, or η^3/η^3 coordination.[13] Even in an *ansa*-zincocene recently reported by Erker and co-workers, in which the rigidity of the ligand might be expected to enforce higher hapticity, the coordination of the two indenyl units is of the $\eta^1/\eta^2(\sigma,\pi)$ type.[14]

Continuing our investigations of main-group metallocenes and with the objective of broadening the scope of our previous work on beryllocenes, which resulted in the structural characterization of $[Be(C_5Me_5)_2]$, $[Be(C_5Me_4H)_2]$ and $[Be(C_5Me_5)(C_5Me_4H)]$,[11a] we have undertaken a systematic study of the structures of new zincocenes, of both polymeric and monomeric nature. Our original aim was the synthesis and characterization of a zincocene with a rigid $\eta^5/\eta^1(\sigma)$ structure (**d**). Here we give a full report of these findings[15] and provide synthetic, reactivity and structural data for new zincocenes derived from the C_5Me_5, C_5Me_4H, C_5Me_4tBu, $C_5Me_4SiMe_2tBu$, and $C_5Me_4SiMe_3$ rings. For the sake of completeness, the previously reported compound $[Zn(C_5H_4SiMe_3)_2]$, shown by Haaland et al. to posses an $\eta^5/\eta^1(\sigma)$ structure in the gas phase,[12a] has also been characterised by X-ray crystallography.

Results and Discussion

Most beryllocenes and zincocenes known to date exhibit the slipped-sandwich structure[11,12] **c**. In the gas phase $[Zn(C_5H_4SiMe_3)_2]$ (**1**), was shown by Haaland and co-workers[12a] to have $\eta^5/\eta^1(\sigma)$ coordination of the Cp′ rings, with the zinc atom bonded to the silyl-bearing carbon atom of the η^1 ligand, a Zn−C bond length of 1.95 Å and an angle of 110° between the Zn−C bond and the ring plane. Since the solid-state structure of **1** has not been reported, we considered of interest its determination by X-ray crystallography. Zincocene **1** was prepared by a slight modification of the literature procedure,[12a] reacting $LiC_5H_4SiMe_3$ and $ZnCl_2$ in tetrahydrofuran (THF) for 12 h. Following evaporation of the solvent under vacuum, extraction with pentane and crystallization afforded the desired metallocene with spectroscopic features identical to those already published.[12a] For the sake of completion, it is worth mentioning that the two rings of **1** are equivalent in solution (see below for the dynamic behaviour of these molecules) and yield ^1H NMR resonances with $\delta = 0.05$ (SiMe$_3$), 6.26 and 6.61 ppm (CH). In the $^{13}C\{^1H\}$ NMR spectrum corresponding resonances are found at $\delta = -0.2$ (SiMe$_3$), 114.5 and 117.7 ppm (CH), while the silicon-bound carbon atom resonates at 87.2 ppm. As discussed later for related compounds these chemical shift values are intermediate between those corresponding to the two rings of a rigid structure, with η^1 and η^5 cyclopentadienyls.

As for the parent zincocene $[Zn(C_5H_5)_2]$,[10a] compound **1** has a polymeric structure in the solid state that consists of infinite chains of zinc atoms bridged by $C_5H_4SiMe_3$ ligands. The asymmetric unit consists of two zinc atoms that are not equivalent by symmetry, each coordinated to three Cp′ ligands in a slightly different manner. Each zinc atom (Figure 1) has one terminal and two bridging Cp′ groups. For example, with reference to Zn1, the terminal ring is bound in $\eta^1(\pi)$ fashion or close to it. Thus, the Zn1−C3 distance of 2.060(9) Å and the angle of about 99.7° formed by the Zn1−C3 bond with the plane of this ring are typical for this type of coordination.[12] The distances between Zn1 and the carbon atoms C4 (2.533(9) Å) and C2 (ca. 2.71 Å) may
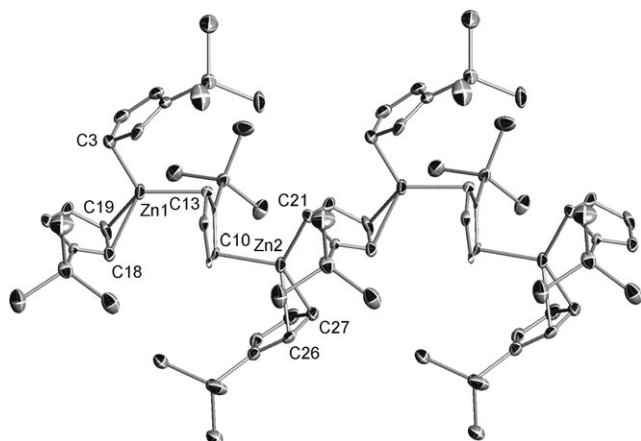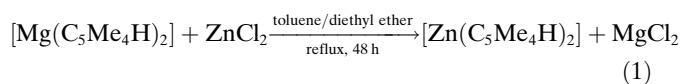
Figure 1. Schematic drawing of the structure of [Zn(C$_5$H$_4$SiMe$_3$)$_2$] (**1**), showing two units of the chain and the coordination of Zn1.

be considered nonbonding, particularly the latter. The two Cp′ rings that bridge Zn1 with neighbouring zinc atoms (formed by atoms C9–C13) can be approximately described as η^1(π) bonded, with a Zn1−C13 separation of 2.171(8) Å and a Zn1-C13-ring plane angle close to 90°, while the other Cp′ binds to zinc as η^2(π) (Zn1−C18 = 2.259(9) Å; Zn1−C19 = 2.303(9) Å; dihedral angle between planes Zn1-C18-C19 and C17-to-C21 of ca. 94°). Interestingly and at a variance with the gas phase structure,[12a] in the solid-state the Zn−Cp′ coordination involves only the α and the β carbon atoms and not the silyl-bound carbon atom.

To prevent aggregation of the ZnCp′$_2$ units in the solid-state structures of zincocenes, we next concentrated our attention on the bulkier, tetrasubstituted C$_5$Me$_4$H ligand and prepared [Zn(C$_5$Me$_4$H)$_2$] (**2**). However, as discussed below, compound **2** has also an infinite chain structure in the solid state. The conventional synthesis applicable to other zincocenes[12] including **1**, consisting in the room temperature reaction of ZnCl$_2$ and MC$_5$Me$_4$H (M = Li, Na, K) gave compound **2** in very low yields. Notwithstanding, the use of [Mg(C$_5$Me$_4$H)$_2$][16] as the cyclopentadienyl transfer reagent,[3a, 17] allows the formation of octamethylzincocene in good isolated yields [Eq. (1), ca. 60 %]. Compound **2** is obtained as a yellowish crystalline solid, soluble in common, nonpolar organic solvents and very sensitive to oxygen and moisture. In spite of the different coordination of the two C$_5$Me$_4$H ligands expected for **2**, (presumably one η^5 and the other η^1) only one set of resonances can be found for the two Cp′ groups down to −90°, both in the ^{1}H and the ^{13}C{^{1}H} NMR spectra.

$$[Mg(C_5Me_4H)_2] + ZnCl_2 \xrightarrow[\text{reflux, 48 h}]{\text{toluene/diethyl ether}} [Zn(C_5Me_4H)_2] + MgCl_2 \tag{1}$$

Metallocenes with slipped-sandwich structures η^5/η^1(π) are highly fluxional molecules. Molecular dynamic calculations for [Be(C$_5$H$_5$)$_2$][18] have identified two very facile processes, namely the so-called molecular inversion that

exchanges the roles of the two rings, from η^5 to η^1 and vice versa, and a 1,5-sigmatropic shift of the Be(η^5-C$_5$H$_5$) entity around the periphery of the η^1-C$_5$H$_5$ ring. The two rearrangements have very low activation energy and, consistent with such low energetic barriers, all beryllocenes and zincocenes known exhibit fluxional behaviour, both in solution[11, 12, 14] and in the solid state.[19, 20] Accordingly, the ^{1}H NMR spectra of **2** shows only three signals for the two C$_5$Me$_4$H rings at 1.84 and 1.95 (Me groups) and 4.31 ppm (CH). In the ^{13}C{^{1}H} NMR spectrum the corresponding resonances are found at δ 10.4 and 12.6 (CMe), 73.7 (CH) and 118.7 and 120.8 ppm (CMe).

As shown in Figure 2, the solid-state structure of **2** consists also of infinite chains of zinc atoms bridged by C$_5$Me$_4$H ligands, in a manner similar to **1** and the parent [Zn(C$_5$H$_5$)$_2$].
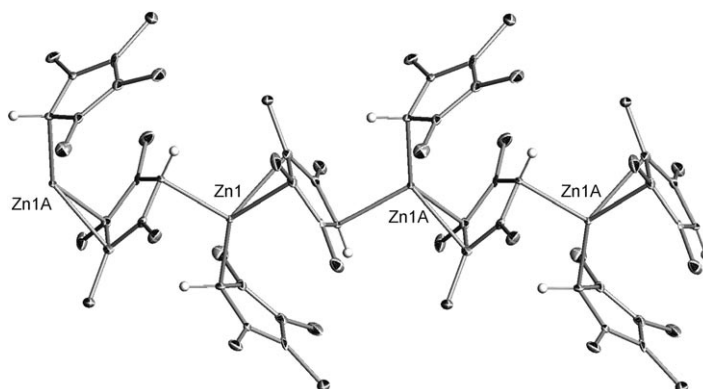

Figure 2. ORTEP drawing for [Zn(C$_5$Me$_4$H)$_2$] (**2**), showing four units of the chain and coordination of Zn1.

Each Zn atom has a terminal C$_5$Me$_4$H group with η^1 coordination through the unique methine carbon atom of the ring, presumably to form the strongest Zn−C bond possible. For Zn1, the Zn1−C1 bond has a length of 2.030(7) Å and the coordination approaches η^1(σ), as suggested by the Zn1-C1-ring plane angle of 122.7°. Each of the bridging C$_5$Me$_4$H ligands is coordinated in an η^1(π) fashion to one zinc atom and in an η^2(π) fashion to the other (Figure 2). For example, the ring that contains C10 is η^1(π)-bound to Zn1 (Zn1-C10 = 2.214(7) Å; Zn1-C10-ring angle of 90.2°) and η^2(π) to neighbouring Zn1A. The ring encompassing C15 and C16 joins to Zn1 through these two carbon atoms, with distances of 2.324(8) and 2.267(8) Å, respectively. The dihedral angle between this Cp′ group and the Zn1-C15-C16 plane is 98.2°. Since decamethylzincocene is a monomer in the solid state, it is evident that a seemingly small change in the ligand from C$_5$Me$_5$ to C$_5$Me$_4$H brings about a significant structural change. This is not, however, an unusual observation. There are related examples in metallocene chemistry, a notorious one being the difference in the coordination of N$_2$ to {Zr(η^5-Cp′)$_2$} units in the compounds [{Zr(η^5-C$_5$Me$_5$)$_2$(κ^1-N$_2$)}$_2$(μ$_2$,κ^1,κ^1-N$_2$)][21a] and [{Zr(η^5-C$_5$Me$_4$H)$_2$}$_2$(μ$_2$,κ^2,κ^2-N$_2$)],[21b] which determines that in their reaction with H$_2$ only the C$_5$Me$_4$H derivative yields ammonia.[21b]

In the search for a molecular zincocene with a rigid $\eta^5/\eta^1(\sigma)$ structure, for which the two low-energy fluxional processes cited above as characteristic of beryllocenes and zincocenes could have sufficiently high energetic barriers to prevent their observation at room temperature, we have prepared new zincocenes [ZnCp'$_2$] (3–5), containing the ligands C$_5$Me$_4$tBu, C$_5$Me$_4$SiMe$_2$tBu and C$_5$Me$_4$SiMe$_3$, respectively. In addition, the mixed complex [Zn(η^5-C$_5$Me$_5$)(η^1-C$_5$Me$_4$SiMe$_3$)] (6) was also obtained, and characterised by X-ray crystallographic studies. The known structures of [Zn-(C$_5$Me$_5$)$_2$][12a,b] and [Zn(C$_5$iPr$_4$H)$_2$] hint that the C$_5$Me$_4$tBu derivative 3 would have a similar slip sandwich geometry, but for the silyl-substituted Cp' ligands their corresponding zincocenes could exhibit the alternative $\eta^5/\eta^1(\sigma)$ coordination of the rings. Following Beattie and Nugent,[22] $\eta^1(\sigma)$ coordination gives a strong M–C bond that may compensate the loss of delocalization energy of the π-system associated with the η^5 binding mode. Elements like B, Si or C itself, that form strong element–carbon bonds, favour $\eta^1(\sigma)$ coordination at the expense of the loss of delocalization energy and indeed, in the gas phase, the molecules of [Zn(C$_5$H$_4$SiMe$_3$)$_2$] exhibit $\eta^5/\eta^1(\sigma)$ coordination, with the monohapto ring binding to zinc through the SiMe$_3$-substituted carbon atom.[12a] Moreover, [B(C$_5$Me$_5$)$_2$]$^+$ is, to our knowledge, the only bis(cyclopentadienyl) compound known that features $\eta^5/\eta^1(\sigma)$ binding of the Cp' ligands.[23] Knowledge of structural characteristics of silyl-substituted cyclopentadienyls and of some of their complexes encourage additionally perusal of this approach. For instance, [Hg(C$_5$Me$_4$SiMe$_2$tBu)$_2$], which contains two η^1-Cp' groups bonded to Hg through C-SiMe$_2$tBu, was the first example of a nonfluxional mercury cyclopentadienyl complex,[24] and [Hg(C$_5$Me$_4$SiMe$_3$)$_2$] and [Hg(C$_5$H$_4$SiMe$_3$)$_2$] were subsequently found to have rigid solution structures with sigma Hg–C-(SiMe$_3$) bonds.[25] Possibly, the more electropositive silicon atom favours concentration of the Cp' negative charge on its adjacent carbon atom, which can therefore form a relatively strong Hg–C bond.

Regarding substituted cyclopentadienyls, a strong preference for SiR$_3$ groups to occupy allylic positions is evident[26] and this has been explained theoretically in terms of hyperconjugative π-aromaticity that affects the relative stability of the possible isomers.[27] As a result, the C$_\alpha$C$_\beta$ and C$_\beta$C$_\beta$ bond lengths of the ring tend to equalise, indicating increased delocalization and reduced diene character. To gain further support for this hypothesis, the fully substituted cyclopentadiene C$_5$Me$_4$(SiMe$_3$)$_2$ was prepared according to Scheme 1 and shown to exist as the geminal isomer, with the two SiMe$_3$ occupying allylic positions. Its ^{1}H NMR spectrum shows the expected resonances at $\delta = 0.01$ (SiMe$_3$), 1.83 and 1.97 ppm (CMe).
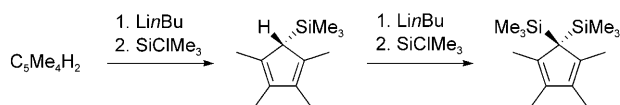
Scheme 1. Synthesis of C$_5$Me$_4$(SiMe$_3$)$_2$.

Corresponding ^{13}C{^{1}H} NMR signals appear at $\delta = -0.3$, 11.1 and 15.2 ppm, while the quaternary ring carbon nuclei resonate at 55.6 (CSiMe$_3$), 133.9 and 136.8 ppm (CMe).

Zincocenes [Zn(C$_5$Me$_4$tBu)$_2$] (3) and [Zn(C$_5$Me$_4$SiMe$_3$)$_2$] (5) were prepared by the reaction of ZnCl$_2$ with the corresponding KCp' [Eq. (2)], whereas the C$_5$Me$_4$SiMe$_2$tBu analogue 4, was obtained similarly by using LiCp' as the cyclopentadienyl transfer reagent.

$$ZnCl_2 + 2\,[K(C_5Me_4R)] \xrightarrow{\text{THF, 20\,°C}} [Zn(C_5Me_4R)_2] + 2\,KCl \quad (2)$$
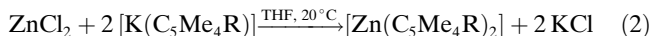
Compounds 3–5 are crystalline, colourless solids, soluble in common organic solvents, such as hydrocarbon and ether solvents, and are very sensitive to oxygen and water, decomposing instantly upon exposure to air. In spite of the bulkiness of the cyclopentadienyl rings, they exhibit dynamic behaviour that can not be slowed down by cooling at −90 °C. Their ^{1}H and ^{13}C{^{1}H} NMR spectra consist of only one set of resonances for the two rings. For instance, in the case of 5, ^{1}H NMR signals are found at $\delta = 0.14$ (SiMe$_3$), 1.96 and 2.04 ppm (α- and β-CMe). In the ^{13}C{^{1}H} NMR spectrum, the Me groups resonate at $\delta = 1.3$ (SiMe$_3$), 10.8 and 14.0 ppm (CMe) and these resonances are accompanied by others at $\delta = 78.7$ (CSiMe$_3$), 122.7 and 125.0 ppm (C$_\alpha$ and C$_\beta$). Clearly, the molecular inversion process that exchanges the two rings[18] is very fast in solution, even at −90 °C. Similar fluxional behaviour has been found for other zincocenes,[12] notably for [Zn(C$_5$Me$_5$)$_2$]. Recent variable-temperature ^{13}C CPMAS NMR studies on this compound[20] reveal spectra that are characterised by only two lines, which arise from the methyl and the quaternary ring carbon nuclei (10.9 and 110.8 ppm, respectively), indicating fast molecular inversion rates (as well as fast sigmatropic rearrangement) and only below −70 °C do the two rings become inequivalent in the solid state. Activation energies of about 21 and 11 kJ mol^{-1} were obtained for the sigmatropic shift and molecular inversion processes, respectively.[20]

In contrast with this behaviour, the SiMe$_3$-substituted zincocene 5 in the solid state exhibits inequivalent, rigid η^5 and η^1 rings, as revealed by the ^{13}C CPMAS NMR studies. Thus the signal for the silicon-bound carbon atom of the η^1 ring appears at $\delta = 59.3$ ppm (note the similarity with the chemical shift value of $\delta = 55.6$ ppm found for the corresponding carbon atom in the cyclopentadiene C$_5$Me$_4$(SiMe$_3$)$_2$ discussed above), while the corresponding resonance for the η^5 ligand is recorded at $\delta = 94.5$ ppm. These two values are in good accord with the average solution value of $\delta = 78.7$ ppm. Similarly, the quaternary carbon nuclei, CMe, of the two rings resonate at $\delta = 114.7$ and 118.0 ppm (η^1 ligand) and 129 and 130 ppm (η^5-C$_5$Me$_4$SiMe$_3$), once more in good accord with solution average values. Again, we note the similarity of these δ values of the {Zn–η^1-C$_5$Me$_4$SiMe$_3$} group with those found for C$_5$Me$_4$(SiMe$_3$)$_2$ ($\delta = 133.9$ and 136.8 ppm).

X-ray studies on the metallocenes 3–5 disclose their monomeric nature, with slip sandwich geometry for 3 and 4 and a structure that closely approaches the target $\eta^5/\eta^1(\sigma)$

coordination in the case of silyl-substituted **5**. Figure 3 shows drawings of the structures of **3** and **4**, both characterised by parallel cyclopentadienyl rings. Similar to other slipped-sandwich structures,[12] one half of the molecules crystal-
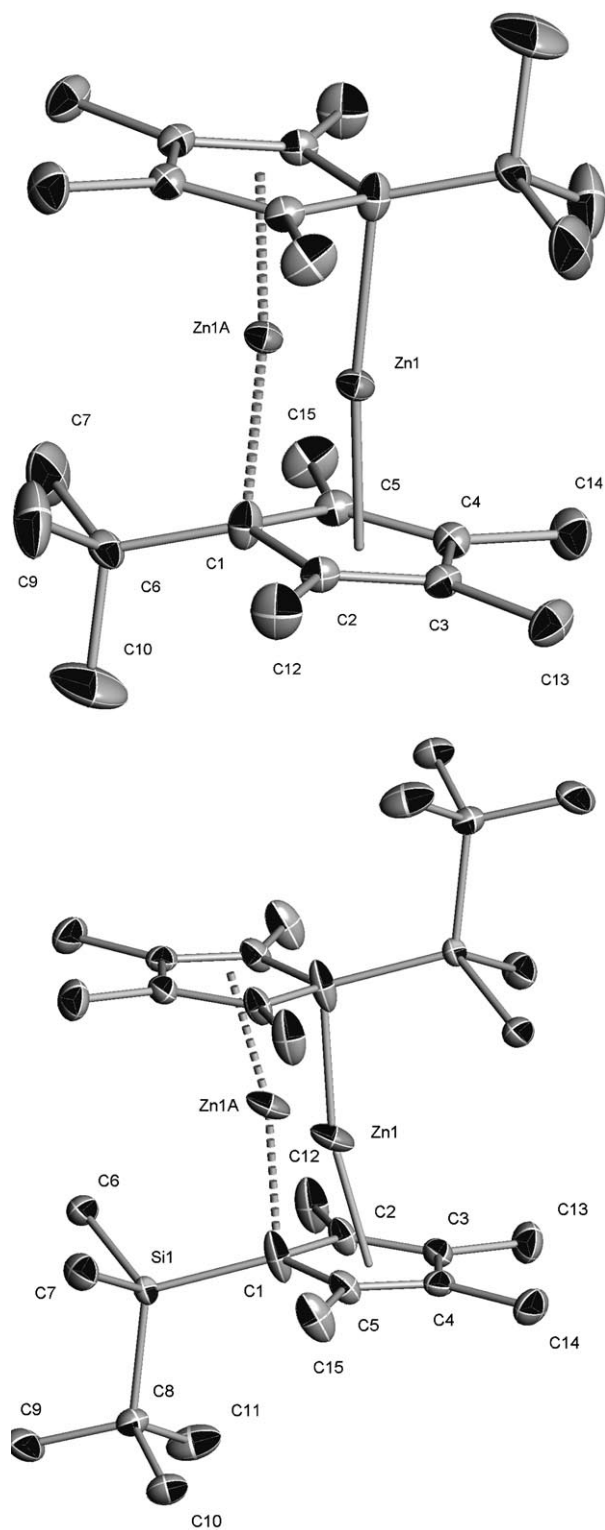
lises with the zinc atoms in one of the equivalent sites and the other half in the other position, although this does not imply any kind of atomic movement or interchange. The Zn–C bond length to the η^1-ring amounts 2.159(2) Å for **3** and 2.201(3) Å for **4**, and whereas they are somewhat shorter than corresponding distance in $[Zn(C_5iPr_4H)_2]$ (2.223(4) Å),[12c] they are significantly longer than the Zn–Me bonds in $ZnMe_2$ (1.930(2) Å)[28] and $[Zn(\eta^5\text{-}C_5Me_5)Me]$ (1.94 Å).[29] The Zn–C bonds in **3** and **4** are almost perpendicular to the planes of the η^1 rings (angles of 94.3 and 98.2°, respectively).

The structure of the $SiMe_3$-substituted zincocene **5** is noticeably different (Figure 4) as it is characterised by non-parallel cyclopentadienyl ligands (angle of ca. 18°), with η^5
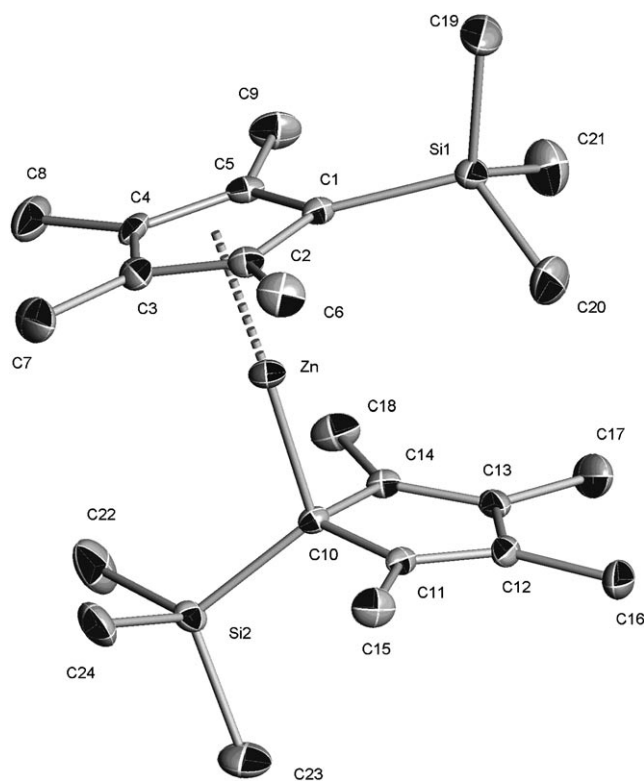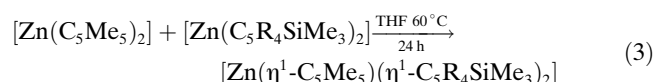

Figure 4. X-ray structure of $[Zn(C_5Me_4SiMe_3)_2]$ (**5**) with H atoms omitted for clarity.

and η^1 coordination. The monohapto Cp′ binds to zinc through the $CSiMe_3$ atom forming a relatively short, and therefore strong, Zn–C bond of length 1.953(3) Å, practically identical to the Zn–Me bonds mentioned above. Comparison with $[B(C_5Me_5)_2]^+$, which features $\eta^5/\eta^1(\sigma)$ coordination,[23] is appropriate. In the zincocene the Zn-C10-Si2 and the Zn-C10-ring angles of 112 and 110°, respectively, are similar to related angles in the boron cation (112 and 114°, respectively). In spite of the identity of the rings, the latter species has a rigid structure in solution that is in accord with the $\eta^5/\eta^1(\sigma)$ formulation, whereas as already mentioned, the two rings of compound **5** are equivalent down to −90 °C, suggesting that while the $\eta^5/\eta^1(\sigma)$ description is very close, it

Figure 3. ORTEP structures of $[Zn(C_5Me_4tBu)_2]$ (**3**) and $[Zn(C_5Me_4SiMe_2tBu)_2]$ (**4**).

is not fully attained. Thus, coordination of C10 approaches tetrahedral, albeit with some deviation as revealed by Zn-C10-C11 and Zn-C10-C14 angles of approximately 102°, somewhat smaller than the 109.5° tetrahedral value. The Zn-C10-ring angle of about 110° is also smaller than the 125° value expected for a tetrahedrally coordinated ring carbon atom.[22]

The preference of the silyl-substituted carbon atom of these Cp′ rings to coordinate to Zn in a η^1 fashion suggested that a mixed zincocene with C_5Me_5 and $C_5Me_4SiMe_3$ cyclopentadienyl ligands would present η^5 coordination of the former and η^1 binding of the latter. Accordingly, the new zincocenes $[Zn(C_5Me_5)(C_5R_4SiMe_3)]$ were prepared for R = Me (**6**) and R = H (**7**) by the conproportionation reaction shown in Equation (3).

$$[Zn(C_5Me_5)_2] + [Zn(C_5R_4SiMe_3)_2] \xrightarrow[24\,h]{THF\,60\,°C} \\ [Zn(\eta^1\text{-}C_5Me_5)(\eta^1\text{-}C_5R_4SiMe_3)_2] \quad (3)$$

Compound **6** is formed as a yellowish oil of spectroscopic purity, and is also very reactive towards oxygen and water. Crystallization of this compound proved rather elusive, but the use of dioxane provided crystals suitable for X-ray crystallography. The existence in the molecules of **6** of two different rings and the nature of the η^1 ring, with Me and SiMe_3 substituents of different electronic characteristics, result in a rigid solution structure with the anticipated η^5-C_5Me_5 coordination, attested by the observation of a $^{13}C\{^1H\}$ signal at $\delta = 107.4$ ppm, characteristic of the $\{Zn(\eta^5\text{-}C_5Me_5)\}$ units.[9,20,29] Furthermore, the $C_5Me_4SiMe_3$ ligand gives rise to ring carbon resonances at $\delta = 51.4$ (CSiMe_3; note the similarity with the $\delta = 59.3$ ppm value found for the related carbon atom in **5** in the solid state), 130.3 and 130.4 ppm (CMe). The ^{13}C CPMAS NMR spectrum of **6** is very similar to the solution spectrum indicating identical solution and solid-state molecular structures. The CSiMe_3 nucleus resonates at $\delta = 59.6$, while the CMe nuclei of this ring appear as a somewhat broad signal at $\delta = 130.8$ ppm, due to accidental overlap. For the η^5-C_5Me_5 group the quaternary ring carbon nuclei are found at $\delta = 108.1$ ppm. Thus, compound **6** has a $[Zn(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_4SiMe_3)]$ structure both in solution and in the solid state, and this structure is rigid, indicating high energetic barriers for both the molecular inversion and the sigmatropic rearrangements that pervade zincocene (and beryllocene) chemistry.

The molecular structure of **6** was determined in the solid state by X-ray crystallography and is shown in Figure 5. Coordination of the pentahapto C_5Me_5 ring is symmetrical, with Zn—C distances clustering in a narrow range, namely, 2.19–2.25 Å. As expected, the $C_5Me_4SiMe_3$ ligand coordinates through the CSiMe_3 carbon atom, yielding a Zn—C bond length (Zn1—C1 in Figure 5) of 1.96 Å, identical within experimental error to the analogous distance in **5**. Bond angles around C1 have similar values too, hence coordination of this ring is very close to $\eta^1(\sigma)$. However, while the Cp′-Zn-C10 unit in **5** is practically linear (angle of ca. 177°) the bend angle in **6** is significantly smaller (ca. 164°). The
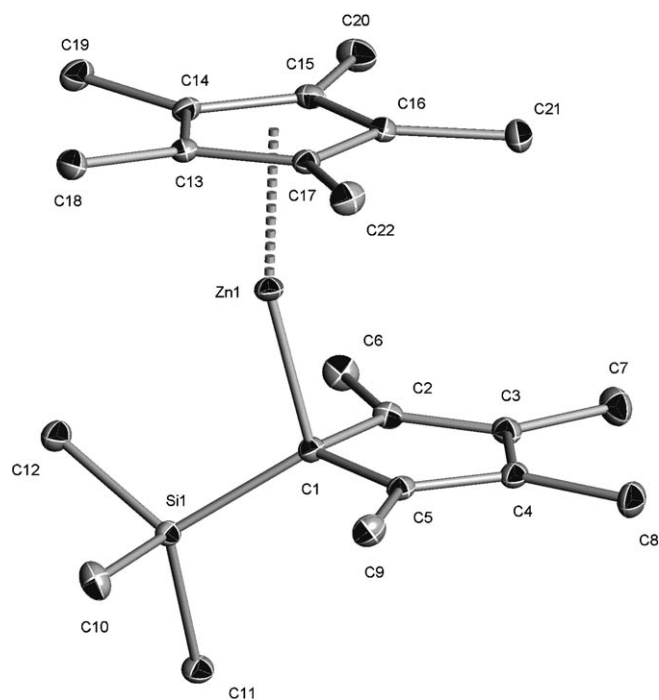

Figure 5. X-ray structure of $[Zn(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_4SiMe_3)]$ (**6**). H atoms have been omitted.

bend angles in metallocenes depend on different properties, among them the size of the ring substituents. It is probable that the deviations found in **6** are due to packing effects associated with steric interactions between ring substituents[30] and not to electronic effects (see below).

A final, relevant structural comment pertinent to the coordination of the η^1-Cp′ ligand in these compounds concerns with the values of the C—C bond lengths within the ring. As shown in Scheme 2, for complex **3** with a slipped-sandwich
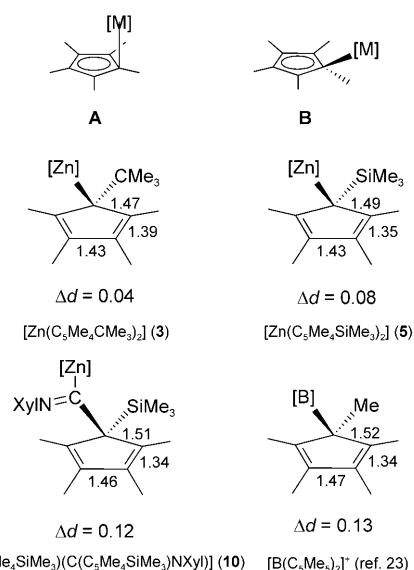

Scheme 2. C—C distances (in Å) within the η^1 ring of zincocenes **3** and **5** and some related compounds.

geometry, and therefore with the Zn−C bond nearly perpendicular to the ring and significant π-electron delocalization, the difference Δd between the $C_{\alpha\beta}$ and $C_{\beta\beta}$ bonds is of only 0.04 Å and the distance between C_α and the zinc-bound carbon atom C_{ipso}, is somewhat smaller (1.47 Å) than expected for a single C−C bond. These data are in accord with expectations for a structure of type **A**. On the opposite side, in the decamethylborocenium cation structurally characterised by Cowley and co-workers,[23] the C_{ipso}−C_α distance is about 1.52 Å, typical of a single bond, and a Δd value of 0.13 Å, indicative of a localised 1,3-diene structure, **B**. The same holds for the Cp′ ring part of the iminoacyl functionality of compound **10** (vide infra), while for zincocene **5** that has a structure close to $\eta^1(\sigma)$, Δd amounts 0.08 Å. This value is significantly smaller than those in $[B(C_5Me_5)_2]^+$ and iminoacyl **10** (0.12 Å, see Scheme 2), and intermediate between these two and that of 0.04 Å corresponding to **3** (0.05 Å in **4** also with slip sandwich geometry). Thus, in accord with Nyulászi and Schleyer's proposal,[27a] the electropositive $SiMe_3$ and $Zn(\eta^5$-Cp′) substituents at the ipso carbon of **5** (Pauling's electronegativity values for C, Si and Zn are 2.5, 1.9 and 1.7, respectively) permit this carbon atom to have coordination geometry close to tetrahedral, and hence to form a strong Zn−C bond, while at the same time introducing a small degree of electron delocalization within the ring. The same reasoning applies to the $C_5Me_4SiMe_3$ group of **6**, characterised by similar structural parameters ($\Delta d = 0.09$ Å). Proximate silicon groups can perturb the π-system of unsaturated hydrocarbons.[27b]

With respect to compound **7**, synthesised as in Equation (3) R=H, normal workup of the reaction mixture permits its isolation as a yellow solid with spectroscopic purity. The C_5Me_5 group gives rise to a $^{13}C\{^1H\}$ resonance at $\delta = 108.1$ ppm, suggestive of η^5-coordination, whereas the $C_5H_4SiMe_3$ group yields signals at $\delta = 69.7$ (CSiMe_3), 111.6 and 123.0 ppm (C_β and C_α ring carbon atoms) that are in accord with monohapto coordination through the CSiMe_3 carbon atom. Hence $(\eta^5$-$C_5Me_5)Zn(\eta^1$-$C_5H_4SiMe_3)$ formulation can be proposed for **7** from these data. Similarly to other zincocenes like $[Zn(C_5Me_5)_2]$[12a,b] and **6** (vide supra), which are difficult to crystallise, attempts to obtain crystals of **7** suitable for analytical and X-ray determinations proved unsuccessful and the use of dioxane, utilised with fortune in the case of **6**, provided instead a dimeric, mixed cyclopentadienyl/(cyclopentadienyl)oxy derivative, containing η^1-$C_5H_4SiMe_3$ and μ_2-C_5Me_5O ligands, the latter resulting, most probably, from accidental, partial oxidation of **7**. Indeed, the ^1H NMR spectrum of this crystalline material **C** is very different from that recorded for **7**. Since an X-ray analysis reveals the structure schematically represented in **C**, this compound was not further investigated (an ORTEP perspective view of the molecules of this complex is included in the Supporting Information).

C
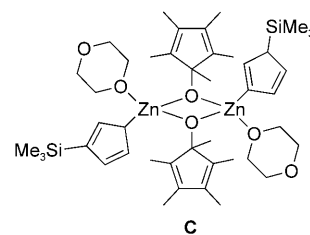
A closely related compound of composition $[Zn_2(C_5Me_5)_2(OC_5Me_5)_2]$, with three-coordinate zinc atoms, terminal η^1-C_5Me_5 and bridging OC_5Me_5 ligands, was obtained upon attempting crystallization of $[Zn(C_5Me_5)_2]$.[31] Structural data for this compound may be obtained from the Cambridge Structural Database (CCDC 228381). Concerning the structure of **C**, it suffices to note that $C_5H_4SiMe_3$ is bonded to Zn through a β-carbon atom in a $\eta^1(\pi)$ fashion, as denoted by the relatively long Zn−C bond of 2.04 Å, comparable to those in **1** and also in **3** and **4**.

DFT and DFT/MM calculations on selected zincocene models: Theoretical calculations by using DFT methods (B3LYP/LANL2DZ+6-31G(d)) on the models $[Zn(\eta^5$-$C_5H_5)(\eta^1$-$C_5Me_4R)]$ for R=CMe_3, $SiMe_3$ and SiH_3, and others, have been reported in a preliminary communication.[15] In good accord with the experimental results the model $[Zn(C_5H_5)(C_5Me_4tBu)]$ was predicted to have a slipped-sandwich geometry, characterised by a Zn-C(CMe_3)-ring angle of 97.4° (experimental value for **3** is 94.4°), while the model complex $[Zn(C_5H_5)(C_5Me_4SiMe_3)]$, containing a Zn−C($SiMe_3$) bond, has a Zn-C($SiMe_3$)-ring angle of 106° (experimental value for **5** is 110°). DFT calculations on $[Zn(C_5H_5)(C_5Me_4SiH_3)]$ also resulted in a $\eta^5/\eta^1(\sigma)$ structure, leading to the conclusion that the presence of a silyl group substituent on a cyclopentadienyl ring favours the adoption of a nonslip sandwich structure.

However, X-ray studies of compound **4**, containing a bulky $SiMe_2tBu$ substituent on the cyclopentadienyl ring, shows that it has a slipped-sandwich structure too, with the Zn atom disordered between two equivalent positions, a Zn-C1-C5 angle of 94.6° and the two rings parallel. We therefore performed a more systematic DFT study of the effect of different silyl substituents on the structures of zincocenes.

Table 1 shows selected bond lengths, angles and dihedral angles for the calculated $[Zn(\eta^5$-Cp)(η^1-$CpH_4R)]$ (R=SiH_3, SiH_2Me, $SiHMe_2$, $SiMe_3$, SiH_2tBu and $SiMe_2tBu$) model complexes. A more complete table is given as Supporting Information.

Table 1. Bond lengths [Å], angles [°] and dihedral angles [°] for $[Zn(\eta^5$-Cp)(η^1-$CpH_4R)]$ model complexes. DFT calculations.

	R=SiH_3	R=SiH_2Me[a]	R=$SiHMe_2$	R=$SiMe_3$	R=SiH_2tBu[b]	R=$SiMe_2tBu$
Zn−C_a	2.058	2.059	2.059	2.062	2.067	2.073
Zn-C_a-C_b[c]	96.2	95.3	94.7[d]	93.5	93.1	90.1
Zn-C_a-Cp′$_{centr}$[d]	100.0	98.9	97.6	95.6	95.1	90.5

[a] NImag=1. 11.1 i cm^{-1} [b] NImag=1. 4.5 i cm^{-1} [c] Average C_a−C_b, C_a−$C_{b'}$ [d] Average Zn-C_a-C_b, Zn-C_a-$C_{b'}$.

It can be observed that Zn−C distances and Zn-C-C angles are dependent on the substituents of the silyl group. In good agreement with the experimental results, the calculation of the model zincocene with the largest silyl substituent (SiMe$_2$tBu) results in the longest Zn−C distance (2.073 Å) and the true slipped-sandwich structure, with a Zn-C-C angle of 90.1°. Reduction of the size of the substituents on the silyl group gives rise to a nonslipped-sandwich structure, with the smaller SiH$_3$ silyl substituent providing the shortest Zn−C distance (2.058 Å) and the largest Zn-C-C angle (96.2°). The calculated structures of other silyl substituents lie between these two extreme cases.

It seems probable that the reduced bond strength in **4**, doubtless related to the substitution of a Me group in the SiMe$_3$ unit for tBu, which is bulkier and has a stronger inductive effect than the Me group, causes adoption of a slipped-sandwich structure, since the weakness of the Zn−C bond demands a larger contribution of the aromaticity to the global energy of the compound.

It seems therefore clear that not only the change of an alkyl group (e.g., Me, iPr, tBu) by SiMe$_3$ in the Cp′ ligand, but also a change in the nature of the silyl substituents may have considerable influence in the structure of the zincocenes. To determine if the reasons behind the adoption of a slipped-sandwich structure in the silyl-substituted zincocenes are due to differences in electronic or steric effects, we performed DFT/MM calculations on the same set of complexes using the IMOMM method, a variation of ONIOM. These calculations neglect the electronic effects for some points of the molecule (the substituents on the silicon atom), while maintaining the steric effect for the whole molecule. Comparison of DFT and DFT/MM results can be used for evaluation of steric and electronic effects.[32] Selected results of bond distances and angles are given in Table 2. A more detailed table can be found as Supporting Information.

Table 2. Bond lengths [Å], angles [°] and dihedral angles [°] for [Zn(η^5-Cp)(η^1-CpH$_4$R)] model complexes. DFT/MM calculations.

	R = SiH$_3$	R = SiH$_2$Me	R = SiHMe$_2$	R = SiMe$_3$	R = SiH$_2$tBu	R = SiMe$_2$tBu
Zn−C$_a$	2.058	2.055	2.054	2.053	2.062	2.060
Zn-C$_a$-C$_b$	96.1	97.2	97.2	97.6	94.6	95.0
Zn-C$_a$-Cp′$_{centr}$	99.9	101.8	101.7	102.5	97.6	98.2

It is clear from these data that the experimental slipped-sandwich structure of the SiMe$_2$tBu containing zincocene **4** is not reproduced by the ONIOM calculation. Therefore, it can be concluded that the differences observed in the structures of silyl-substituted zincocenes cannot be attributed to changes in the bulkiness of the substituent of the silyl group, but to electronic effects. Also a comparison of the data in Tables 1 and 2 can help to further refine the analysis. The discrepancy is particularly noticeable in the series SiH$_3$, SiH$_2$Me, SiHMe$_2$, SiMe$_3$. As more hydrogen atoms are replaced by methyl groups the trend in the pure DFT calculations is an increase in the Zn−C distance and a decrease of
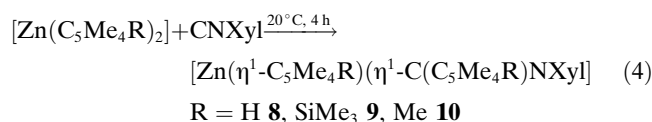
the Zn-C$_a$-C$_b$ and Zn-C$_a$-Cp′$_{centr}$ angles. These trends are inverted in the DFT/MM calculation.

Therefore, for the geometrical distortion being discussed, the role of the methyl substituents on silyl is essentially electronic. Their pure steric effect would go in the opposite direction. Similar variations are found for the introduction of a tBu substituent. In the pairs SiH$_3$, SiH$_2$tBu and SiMe$_3$, SiMe$_2$tBu, the trends in the geometrical parameters are properly reproduced by the DFT/MM calculation. That is, when a methyl is replaced by a tert-butyl, the Zn−C distance increases and the Zn-C$_a$-C$_b$ and Zn-C$_a$-Cp′$_{centr}$ angles decrease. The strongly electron donor tBu substituent reduces the capacity of the Si atom to stabilise the Cp′ ring negative charge on the Si-bound carbon atom and weakens the Zn−C bond.

Zinc iminoacyls from the reactions of zincocenes and CNXyl: Notwithstanding the importance of organic isocyanides in transition-metal chemistry, particularly as models for CO insertion reactions, their influence in the chemistry of metallocene and other compounds of the main-group elements is rather limited. Naturally, there are literature reports on their reactivity, some examples being the formation of adducts of alkaline earth metallocenes, [M(C$_5$Me$_5$)$_2$-(CNXyl)$_2$] (M = Mg, Ca, Sr, Ba; Xyl = 2,6-dimethylphenylisocyanide) reported by Burns and Andersen,[33] the double insertion of CNtBu in the metallocene [Al(C$_5$Me$_4$H)$_3$],[34] or the insertion of various isonitriles into Si−B bonds.[35]

We have previously reported the reactions of some beryllocenes with CNXyl to give the corresponding iminoacyls.[36] In view of the similarity of beryllocenes and zincocenes, and considering in particular the relative weakness of their M-η^1-Cp′ bond, we have performed the reactions of **2** and **5** with CNXyl [Eq. (4)].

$$[Zn(C_5Me_4R)_2] + CNXyl \xrightarrow{20\,°C,\ 4\,h}$$
$$[Zn(\eta^1\text{-}C_5Me_4R)(\eta^1\text{-}C(C_5Me_4R)NXyl] \quad (4)$$
$$R = H\ \mathbf{8},\ SiMe_3\ \mathbf{9},\ Me\ \mathbf{10}$$

Prior to this study, and in order to facilitate investigation of the dynamic behaviour of [Zn(C$_5$Me$_5$)$_2$] in the solid state,[20] its analogous iminoacyl **10** was also prepared. Its X-ray structure is reported here, together with those of **8** and **9**.

Iminoacyl formation is a facile reaction of these metallocenes and yields the desired compounds in quantitative yield by spectroscopy (>80% isolated yields). Complexes **8–10** are yellow crystalline solids that feature an IR band around 1580–1590 cm^{-1}, due to ν(C=N) of the iminoacyl linkage. This is associated with a ^{13}C{^{1}H} resonance at about δ = 200 ppm, attributed to the metal-bound iminoacyl carbon atom. For compound **9**, in which the η^5-C$_5$Me$_4$SiMe$_3$ group evidently cannot participate in the molecular inversion rearrangement characteristic of its metallocene precursor **5**; the ^{13}C{^{1}H} resonance of the CSiMe$_3$ nucleus appears at δ = 96.4 ppm, a chemical shift value very similar to that of

$\delta = 94.5$ ppm found for the η^5-ring of **5** in the ^{13}C CPMAS NMR spectrum (vide supra).

The solid-state structures of the three iminoacyls **8**–**10** were investigated by X-ray crystallography. Since the three structures are very similar, only the ORTEP representation of **9** is provided in Figure 6.
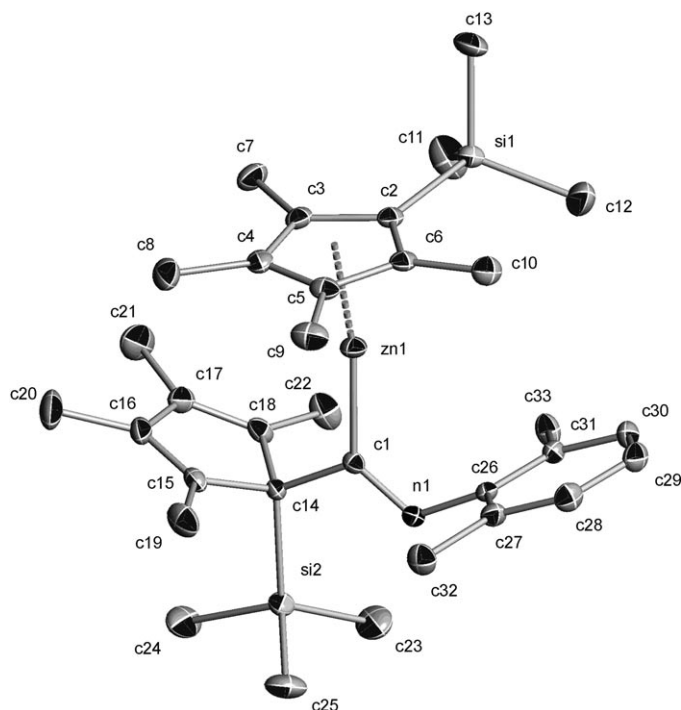

Figure 6. ORTEP perspective view of the molecules of iminoacyl **9**, [Zn(η^5-C$_5$Me$_4$SiMe$_3$)(η^1-C(NXyl)C$_5$Me$_4$SiMe$_3$)].

In the three compounds, the Zn−C bond to the iminoacyl has a length of about 1.95 Å, identical to the sigma Zn−C bonds of metallocenes **5** and **6**. Another structural feature worthy of note, in this case in connection with the bend angle of approximately 164° found for **6**, refers to the values for the corresponding angles in iminoacyls **8**–**10**.

For the least bulky Cp′, that is, C$_5$Me$_4$H in iminoacyl **8**, the Cp$_{centr}$-Zn-C$_{iminoacyl}$ angle is almost linear (176°), but decreases for the C$_5$Me$_5$ derivative **10** to 172° and becomes even smaller for the bulkiest Cp′ ring, C$_5$Me$_4$SiMe$_3$ in **9** (165°, therefore identical to that in **6**). This observation reinforces our view that the bending in metallocene **6** is not electronic in origin, but it is due instead to packing effects that result from steric repulsion between the substituents of the rings.

Conclusions

The structural diversity characteristic of main-group metallocenes appears in zincocenes, as these metallocenes may exhibit, in addition to the low hapticity coordination distinctive of polymeric zincocenes (i.e. those with low degree of substitution or without substituents, like Zn(C$_5$H$_5$)$_2$, **1** and **2**), a variety of structures encompassing the dimetallocene sandwich structure of [Zn$_2$(η^5-C$_5$Me$_5$)$_2$], the unusual slipped-sandwich geometry, now enlarged with the synthesis of **3** and **4**, and the unprecedented $\eta^5/\eta^1(\sigma)$ coordination exhibited by **5** and **6**. It is clear from the results reported in this paper that stabilization of the last type of geometry is possible thanks to the effect exerted by the SiMe$_3$ ring substituent, which allows the formation of a Zn−C bond of strength comparable to the Zn−Me bonds of ZnMe$_2$. In compound **5**, Zn(C$_5$Me$_4$SiMe$_3$)$_2$, the different electronic characteristics of the Me and SiMe$_3$ substituents[37] slows down the 1,5-sigmatropic shift theoretically studied for Be(C$_5$H$_5$)$_2$[18] and experimentally investigated in the solid state by NMR methods for beryllocenes[19] and for [Zn(C$_5$Me$_5$)$_2$].[20] While for the latter compound molecular inversion is fast down to −90°C, **5** has a rigid structure in the solid state at room temperature, consisting of one η^5- and one η^1-C$_5$Me$_4$SiMe$_3$ groups. The different nature of the two Cp′ rings in **6**, coupled with the above-mentioned facts, permit observation for the first time of a zincocene that has a rigid sandwich structure in solution.

Experimental Section

X-ray structure analysis for 1–6 and 8–10: A summary of crystallographic data and structure refinement results for zincocenes are given in Table 3. Crystals coated with dry perfluoropolyether were mounted on a glass fibre and fixed in a cold nitrogen stream ($T = 100(2)$ or 173(2) K). Intensity data were collected on a Bruker-Nonius X8 Apex-II CCD diffractometer (**1**, **2**, **6** and **8**) or a Bruker SMART 1k CCD diffractometer (**3**, **4**, **5**, **9** and **10**), both equipped with a Mo$_{K\alpha1}$ radiation ($\lambda = 0.71073$ Å) source and graphite monochromator. The data were reduced (SAINT) and corrected for Lorentz polarisation and absorption effects by multiscan method (SADABS).[38,39] The structures were solved by direct methods (SIR-2002)[40] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.14)[41] minimizing $w[F_o^2 - F_c^2]^2$. All nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions (except for H1 and H10 in compound **1**, which were included in the refinement from observed positions and full isotropically refined); first they were calculated and allowed to ride on the attached carbon atoms with the isotropic temperature factors (U_{iso} values) and then fixed at 1.2 times (1.5 times for methyl groups) the U_{eq} values of the corresponding carbon atoms. CCDC-697628 (**1**), 697629 (**2**), 697630 (**4**). 697631 (**6**), 697633 (**8**), 697634 (**9**) and 697635 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details: The electronic structure and geometries of the zincocene model complexes were computed with pure DFT and DFF/MM methods. The pure density functional theory (DFT) calculations used the B3LYP functional[42,43] level and the LANL2DZ basis set[44,45] complemented with a set of d polarisation shells on C and Si atoms. The

Table 3. Summary of crystallographic data and structure refinement results for zincocenes **1–6**, **8–10** and for compound **C**.

	1	**2**	**3**[10]	**4**[10]	**5**
formula	$C_{32}H_{52}Si_4Zn_2$	$C_{18}H_{26}Zn$	$C_{26}H_{42}Zn$	$C_{30}H_{54}Si_2Zn$	$C_{24}H_{42}Si_2Zn$
M_r	679.84	307.76	419.97	536.28	452.13
crystal size [mm³]	$0.20 \times 0.17 \times 0.10$	$0.24 \times 0.08 \times 0.08$	$0.40 \times 0.40 \times 0.40$	$0.30 \times 0.16 \times 0.16$	$0.30 \times 0.20 \times 0.10$
crystal system	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
space group	$Pbca$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a [Å]	21.8924(11)	10.5114(10)	8.7494(5)	8.8811(8)	9.0211(7)
b [Å]	8.5200(5)	9.4461(8)	16.8068(10)	9.0111(8)	34.925(3)
c [Å]	38.551(2)	16.0839(17)	8.7537(5)	10.5436(9)	8.8173(7)
α [°]	90	90	90	69.755(2)	90
β [°]	90	101.034(4)	113.1450(10)	78.177(2)	112.114(2)
γ [°]	90	90	90	77.920(2)	90
V [Å³]	7190.7(7)	482.17(1)	1183.62(12)	766.02(12)	2573.6(4)
Z	8	4	2	1	4
ρ_{calcd} [M gm⁻³]	1.256	1.304	1.178	1.163	1.167
μ [mm⁻¹]	1.486	1.552	1.045	0.895	1.054
$F(000)$	2880	656	456	292	976
θ_{max} [°]	26.4	30.6	26.4	26.4	28.4
T [K]	100	100	296	296	173
reflns collected	117748	15109	6337	4118	9516
reflns used	7383	4746	2365	2870	5401
parameters	355	186	134	163	258
$R_1(F)$[a]	0.067	0.054	0.046	0.042	0.041
$wR_2(F^2)$[b] (all data)	0.217	0.142	0.128	0.117	0.106
S[c] (all data)	1.062	1.025	1.089	1.076	0.971

	6	**8**	**9**	**10**	**C**
formula	$C_{22}H_{36}SiZn$	$C_{27}H_{35}NZn$	$C_{33}H_{51}NSi_2Zn$	$C_{29}H_{39}NZn$	$C_{22}H_{36}O_3SiZn$
M_r	393.97	438.93	583.30	466.98	441.97
crystal size [mm³]	$0.37 \times 0.27 \times 0.22$	$0.28 \times 0.26 \times 0.18$	$0.04 \times 0.02 \times 0.02$	$0.20 \times 0.10 \times 0.10$	$0.35 \times 0.27 \times 0.21$
crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [Å]	9.2189(2)	9.9180(11)	9.9268(4)	8.4780(6)	8.4191(7)
b [Å]	27.7187(6)	15.2485(17)	11.8932(5)	18.2105(13)	11.3237(9)
c [Å]	17.2493(3)	16.3811(17)	14.8911(6)	16.7621(12)	12.6510(9)
α [°]	90	90	76.1630(10)	90	84.152(2)
β [°]	91.5900(10)	106.846(4)	80.9800(10)	95.753(2)	76.436(2)
γ [°]	90	90	80.0590(10)	90	89.830(2)
V [Å³]	4406.12(16)	2371.1(4)	1669.11(12)	2574.8(3)	1166.07(16)
Z	8	4	2	4	2
ρ_{calcd} [M gm⁻³]	1.188	1.230	1.161	2574.8(3)	1.259
μ [mm⁻¹]	1.170	1.048	0.828	0.969	1.122
$F(000)$	1696	936	628	1000	472
θ_{max} [°]	30.5	30.5	31.2	28.3	30.6
T [K]	100	100	173	173	100
reflns collected	73694	55632	11874	9034	26732
reflns used	13371	7246	8821	4496	6983
parameters	433	264	350	292	252
$R_1(F)$[a]	0.034	0.028	0.046	0.044	0.024
$wR_2(F^2)$[b] (all data)	0.082	0.079	0.119	0.098	0.063
S[c] (all data)	1.054	1.074	0.910	0.857	1.033

[a] $R_1(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ for the observed reflections $[F^2 > 2\sigma(F^2)]$. [b] $wR_2(F^2) = \{\Sigma[w(F_o^2 - F_c^2)2]/\Sigma w(F_o^2)2\}^{1/2}$. [c] $S = \{\Sigma[w(F_o^2 - F_c^2)2]/(n-p)\}^{1/2}$; ($n =$ number of reflections, $p =$ number of parameters).

optimised geometries were characterised as energy minima either by a nonexistence of imaginary frequencies (NImag = 0) or by very low vibrational frequencies (< 15 cm⁻¹, see Table 1) in the diagonalisation of the analytically computed Hessian (vibrational frequency calculations). The presence of this very low vibrational frequencies that do not lead to productive transition-state optimisation has been reported in other cases,[46] and it seems to be associated to numerical errors in the DFT integration grid. They could be eliminated by much more expensive calculation with a better grid. All DFT calculations were performed with the Gaussian-98 package.[47] For the DFT/MM calculations, the IMOMM[48] approach was used. The DFT region was in all cases defined by $[Zn(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_4SiH_3)]$, and the rest of the atoms constituted the MM region. The

DFT description was the same applied in the pure DFT calculations. The MM description consisted of the MM3 force field,[49] with van der Waals parameters for Zn taken from the UFF force field.[50] IMOMM calculations were performed with a program built from modified versions of two standard programs: Gaussian 98 for the quantum mechanics part and MM3(92) for the molecular mechanics part.[51]

Synthesis of $C_5Me_4(SiMe_3)_2$: ClSiMe₃ (0.6 mL, 5 mmol) was added to a suspension of LiC₅Me₄SiMe₃[52a] (970 mg, 4.8 mmol) in THF (50 mL). After the mixture was stirred for 5 h at room temperature, the solvent was removed under vacuum and the yellowish oil was extracted with hexane (70 mL), yielding the compound as a yellow oil. Yield: 984 mg (75%); elemental analysis calcd (%): C 67.6, H 11.3; found: C 67.7, H

11.0; [1H] NMR (500 MHz, C_6D_6, 25°): δ = 0.01 (s, 18H; SiMe_3), 1.83 (s, 12H; Me), 1.97 ppm (s, 12H; Me); [13C-{1H}] NMR (125 MHz, C_6D_6, 25°C): δ = −0.3 (SiMe_3), 11.1 (C-Me), 15.2 (C-Me), 55.6 (C-SiMe$_3$), 133.9 (C-Me), 136.8 ppm (C-Me).

Synthesis of [Zn(C$_5$H$_4$SiMe$_3$)$_2$] (1):[12a] LiC$_5$H$_4$SiMe$_3$ (1.00 g, 6.93 mmol) and ZnCl$_2$ (0.47 g, 3.47 mmol) were dissolved in THF (30 mL) and stirred at room temperature for 12 h. After evaporation of the solvent, the residue was extracted with pentane (2×20 mL). The yellow solution was concentrated and left at −20°C until crystals suitable for X-ray analysis were obtained. Yield: 0.60 g (51%); [1H] NMR (500 MHz, C_6D_6, 25°C): δ = 0.05 (s, 18H; SiMe_3), 6.26 (s, 4H; CH), 6.6131 ppm (s, 4H; CH); [13C-{1H}] NMR (125 MHz, C_6D_6, 25°C): δ = −0.2 (SiMe_3), 87.2 (C-Si), 117.5 (CH), 117.7 ppm (CH).

Synthesis of [Zn(C$_5$Me$_4$H)$_2$] (2): Octamethylmagnesocene[16] (1.57 g, 11.51 mmol) and ZnCl$_2$ (3.07 g, 11.51 mmol) were dissolved in of a 1:1 mixture of diethyl ether and toluene (80 mL) in a 250 mL thick-walled glass ampoule equipped with Teflon screw cap (Young valve). The reaction mixture was heated at 115°C under vacuum for 48 h. After evaporation of solvents the residue was extracted with hexane (2×30 mL) and crystallised from the same solvent. Yield: 2.13 g (60%); elemental analysis calcd (%): C 70.3, H 8.5; found: C 69.7, H 8.6; [1H] NMR (300 MHz, C_6D_6, 25°C): δ = 1.84 (s, 6H; C-Me), 1.95 (s, 6H; C-Me), 4.31 ppm (s, 1H; CH); [13C-{1H}] NMR (75 MHz, C_6D_6, 25°C): δ = 10.4 (C-Me), 12.6 (C-Me), 73.7 (CH), 118.7 (C-Me), 120.8 ppm (C-Me).

Synthesis of [Zn(C$_5$Me$_4$tBu)$_2$] (3), [Zn(C$_5$Me$_4$SiMe$_2$tBu)$_2$] (4) and [Zn(C$_5$Me$_4$SiMe$_3$)$_2$] (5): These compounds were prepared by reaction of ZnCl$_2$ and MCp′ in THF, at room temperature, for a period of about 3 h (M = K, Cp′ = C$_5$Me$_4$tBu for **3**;[53] M = Li, Cp′ = C$_5$Me$_4$SiMe$_2$tBu for **4**;[54] M = K, Cp′ = C$_5$Me$_4$SiMe$_3$ for **5**;[52b]). After removal of the volatiles in vacuo the residue was dissolved in hexane and the solutions filtered. Partial evaporation of the solvent and cooling at −20°C afforded crystals of the corresponding zincocenes in good isolated yields (ca. 70–80%). Analytical and spectroscopic data for these compounds are listed below.

[Zn(C$_5$Me$_4$tBu)$_2$] (3): Yield: 78%; elemental analysis calcd (%): C 74.40, H 10.11; found: C 74.4, H 10.3; [1H] NMR (400 MHz, C_6D_6, 25°C): δ = 1.51 (s, 9H; C-tBu), 1.94 (s, 6H; C-Me), 2.10 (s, 6H; C-Me); [13C-{1H}] NMR (100 MHz, C_6D_6, 25°C): δ = 11.3 (C-Me), 15.5 (C-Me), 32.8 (C-Me$_3$), 67.8 (C-Me$_3$), 100.2 (C-tBu), 118.0 (C-Me), 120.8 ppm (C-Me).

[Zn(C$_5$Me$_4$SiMe$_2$tBu)$_2$] (4): Yield: 70%; elemental analysis calcd (%): C 67.23, H 10.07; found: C 67.3, H 9.9; [1H] NMR (300 MHz, C_6D_6, 25°C): δ = 0.14 (s, 6H; SiMe$_2$tBu), 0.79 (s, 9H; SiMe$_2$tBu), 1.99 (s, 6H; C-Me), 2.11 ppm (s, 6H; C-Me); [13C-{1H}] NMR (75 MHz, C_6D_6, 25°C): δ = −0.9 (SiMe$_2$Bu), 11.1 (C-Me), 14.3 (C-Me), 20.7 (C-Me$_3$), 26.9 (C-Me$_3$), 76.7 (C-Si), 122.8 (C-Me), 125.1 ppm (C-Me).

[Zn(C$_5$Me$_4$SiMe$_3$)$_2$] (5): Yield: 80%; elemental analysis calcd (%): C 63.69, H 9.29; found: C 62.9, H 9.1; [1H] NMR (500 MHz, C_6D_6, 25°C): δ = 0.14 (s, 9H; C-SiMe$_3$), 1.96 (s, 6H; C-Me), 2.04 ppm (s, 6H; C-Me); [13C-{1H}] NMR (125 MHz, C_6D_6, 25°C): δ = 1.3 (C-SiMe$_3$), 10.8 (C-Me), 14.0 (C-Me), 77.7 (C-SiMe$_3$), 122.6 (C-Me), 125.0 ppm (C-Me).

Synthesis of [Zn(C$_5$Me$_5$)(C$_5$Me$_4$SiMe$_3$)] (6) and [Zn(C$_5$Me$_5$)(C$_5$H$_4$SiMe$_3$)] (7): The mixed-ring zincocenes **6** and **7** were prepared by conproportionation of [Zn(C$_5$Me$_5$)$_2$] and the corresponding [ZnCp′$_2$] at 60°C for 24 h, with THF as the reaction solvent. For **6**, [Zn(C$_5$Me$_5$)$_2$] (2.9 g, 8.6 mmol) and **5** (3.9, 8.6 mmol) were used to give the desired compound (3.5 g, ca. 50% isolated yield). The compound proved difficult to crystallise, but suitable crystals were obtained from 1,4-dioxane. In the case of **7**, [Zn(C$_5$Me$_5$)$_2$] (0.67 g, 2 mmol) and **1** (0.68 g, 2 mmol) were used to give a yellow oil after removal of the solvent under vacuum. Washing the oil with pentane at −50°C afforded 0.9 g (66% yield) of **7**.

[Zn(C$_5$Me$_5$)(C$_5$Me$_4$SiMe$_3$)] (6): Elemental analysis calcd (%): C 67.07, H 9.21; found: C 68.0, H 9.4; [1H] NMR (500 MHz, C_6D_6, 25°C): δ = 0.06 (s, 9H; SiMe$_3$), 1.90 (s, 15H; CH$_3$-Cp*), 1.96 (s, 6H; CH$_3$-Cp), 2.03 ppm (s, 6H; CH$_3$-Cp); [13C{1H}] NMR (125 MHz, C_6D_6, 25°C): δ = 0.8 (SiMe$_3$), 9.5 (CH$_3$-Cp′), 11.3 (CH$_3$-Cp′), 15.2 (CH$_3$-Cp*), 51.4 (C$_{ipso}$), 107.4 (C$_5$Me$_5$), 130.3 (C$_q$-(C$_5$Me$_4$SiMe$_3$)), 130.4 ppm (C$_q$-(C$_5$Me$_4$SiMe$_3$)).

[Zn(C$_5$Me$_5$)(C$_5$H$_4$SiMe$_3$)] (7): [1H] NMR (500 MHz, C_6D_6, 25°C): δ = 0.02 (s, 9H; SiMe$_3$), 1.83 (s, 15H; CH$_3$-Cp*), 6.44 (s, 2H; CH), 6.87 ppm (s,

2H; CH); [13C{1H}] NMR (125 MHz, C_6D_6, 25°C): δ = −0.2 (SiMe$_3$), 9.9 (CH$_3$-Cp*), 69.7 (CSiMe$_3$), 108.1 (C$_5$Me$_5$), 111.6 (CH), 123.0 ppm (CH).

Synthesis of iminoacyls [Zn(η^5-C$_5$Me$_4$R)(η^1-C(C$_5$Me$_4$R)NXyl)], (8 and 9): The C$_5$Me$_5$ derivative **10** has been reported.[20] Compounds **8** (R = H) and **9** (R = SiMe$_3$) were generated by the reaction of equimolar amounts of **2** and **5** (0.5–0.7 mmol), respectively, with CNXyl in hexane, at room temperature for a period of 4–5 h. Iminoacyls **8** and **9** were crystallised in pentane or hexane and isolated in about 90% yield.

[Zn(η^5-C$_5$Me$_4$H)(η^1-C(C$_5$Me$_4$H)NXyl)] (8): Yield: 95%; elemental analysis calcd (%): C 73.9, H 8.0, N 3.2; found: C 73.5, H 8.0, N 3.2; IR (nujol): $\tilde{v}$ = 1585 cm^{-1} (C=N); [1H] NMR (300 MHz, C_6D_6, 25°C): δ = 1.62 (s, 6H; C-Me), 1.72 (s, 6H; C-Me), 1.82 (s, 6H; C-Me), 1.90 (s, 6H; C-Me), 1.99 (s, 6H; C-Me), 3.54 (s, 1H; CH), 5.12 (s, 1H; CH) 6.80 (t, 1H; H_p), 7.03 (d, 2H; H_m); [13C{1H}] NMR (75 MHz, C_6D_6, 25°C): δ = 9.7 (η^5-Me$_\alpha$), 11.5 (Me$_\alpha$), 12.1 (η^5-Me$_\beta$), 13.6 (Me$_\beta$), 19.3 (Me-CNXyl), 73.6 (CH), 96.7 (η^5-CH), 128.7 (CH$_m$), 123.5 (C$_q$-Me), 128.0 (CH$_p$), 156.2 (C$_q$-N), 202.2 ppm (C=N).

[Zn(η^5-C$_5$Me$_4$SiMe$_3$)(η^1-C(C$_5$Me$_4$SiMe$_3$)NXyl)] (9): Yield 85%; elemental analysis calcd (%): C 67.99, H 8.75, N 2.40; found: C 67.7, H 8.7, N 2.6; IR (nujol): $\tilde{v}$ = 1580 cm^{-1} (C=N); [1H] NMR (400 MHz, C_6D_6, 25°C): δ = 0.22 (s, 9H; SiMe$_3$), 0.23 (s, 9H; SiMe$_3$), 1.69 (s, 6H; C-Me), 1.73 (s, 6H; C-Me), 1.84 (s, 6H; C-Me), 1.91 (s, 6H; C-Me), 2.12 (s, 6H; C-Me), 6.48 (t, 1H; H_p), 7.00 ppm (d, 2H; H_m); [13C-{1H}] NMR (100 MHz, C_6D_6, 25°C): δ = −1.9 (SiMe$_3$), 2.1 (SiMe$_3$), 9.9 (C-Me), 11.5 (C-Me) 12.4 (C-Me), 14.2 (C-Me), 19.5 (C-Me), 75.9 (C-SiMe$_3$), 96.4 (C-SiMe$_3$), 115.5 (C-Me), 117.6 (C-Me), 122.7 (C-H), 126.1 (C-Me), 128.7 (C-H), 134.6 (C-Me), 139.1 (C-Me), 156.1 (C-N), 201.2 ppm (C=N).

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