μ-Imido, μ-(η^2,η^2-N,N-Hydrazido) and μ-(η^1-C:η^2-C,N-Isocyanido) Dinuclear (Fulvalene)zirconium Derivatives

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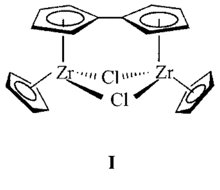
Treatment of the chloro(fulvalene)zirconium(III) compound $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ with an equimolar amount of azobenzene in toluene, under extremely anhydrous conditions, gives the μ-[bis(imido)] derivative $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}NPh)]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**1**). However, when this reaction is carried out under insufficiently dry conditions a mixture of the previously reported μ-oxo complex $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-}O)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ and 1,2-diphenylhydrazine is obtained. When the chloro(fulvalene)zirconium(III) compound reacts with benzo[*c*]cinnoline the μ-(η^2,η^2-N,N-hydrazido) complex $[Zr(\eta^5\text{-}C_5H_5)Cl]_2[\mu\text{-}(NC_6H_4C_6H_4N)][\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**2a**) is obtained, which rearranges to the thermodynamically more stable **2b**. Addition of an equimolar amount of RNC (R = *n*Bu, C_6H_{11}) to a toluene solution of $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ gives $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-}CNR)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ [R = *n*Bu (**3**), C_6H_{11} (**4**)]. Reaction of $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-}CN\mathit{t}Bu)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ with 1 equiv. of $PhCH_2MgCl$ or $(PhCH_2)_2Mg(THF)_2$ afforded the monobenzyl derivatives $[Zr(\eta^5\text{-}C_5H_5)]_2(CH_2Ph)(Cl)(\mu\text{-}CN\mathit{t}Bu)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**5** and **6**). When this reaction was carried out with 2 equiv. or an excess of $PhCH_2MgCl$, a mixture of the monobenzyl and dibenzyl compounds $[Zr(\eta^5\text{-}C_5H_5)]_2(CH_2Ph)(Cl)(\mu\text{-}CN\mathit{t}Bu)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**5**) and $[Zr(\eta^5\text{-}C_5H_5)(CH_2Ph)]_2(\mu\text{-}CN\mathit{t}Bu)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**7**) is obtained. Similar reactions with 1 or 2 equiv. of $(CH_3)_3SiCH_2Li$ afford a mixture of the monoalkyl and dialkyl compounds $[Zr(\eta^5\text{-}C_5H_5)]_2[CH_2Si(CH_3)_3](Cl)(\mu\text{-}CN\mathit{t}Bu)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**8**) and $\{Zr(\eta^5\text{-}C_5H_5)[CH_2Si(CH_3)_3]\}_2(\mu\text{-}CN\mathit{t}Bu)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**9**) compounds. Moreover, methylation of $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-}CN\mathit{n}Bu)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ gives the analytically pure tetramethyl derivative $[Zr(\eta^5\text{-}C_5H_5)(CH_3)]_2(\mu\text{-}CN\mathit{n}Bu)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**10**), whereas $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-}CNC_6H_{11})[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ reacts with MeLi to give a mixture of the monomethyl derivatives $[Zr(\eta^5\text{-}C_5H_5)]_2(CH_3)(Cl)(\mu\text{-}CNC_6H_{11})[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**11** and **12**), as well as the dimethyl compound $[Zr(\eta^5\text{-}C_5H_5)(CH_3)]_2(\mu\text{-}CNC_6H_{11})[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**13**).

Introduction

Complexes with cyclopentadienyl ancillary ligands have dominated the study of early transition metal chemistry. Mono- and dicyclopentadienyltitanium, -zirconium and -hafnium derivatives are considered the most widely studied organometallic transition compounds. The stability, solubility and reactivity of these complexes are dramatically influenced by modifying their cyclopentadienyl ligands.[1]

The presence of two metal centres in homo- and heterodimetallic complexes has generated considerable effort in recent years, with a myriad of studies on their properties as well as cooperative investigations into their reactivity, which were then compared with analogous mononuclear cyclopentadienyl compounds.[2] For such organometallic complexes, particular attention has been devoted to compounds in which two metal centres are coordinated by a fulvalene bridging ligand.[3] The fulvalene group is especially interesting as it tends to form dinuclear complexes with short distances between the two metal centres, which may even have slight metal−metal interactions, as in compound **I**. With this disposition the metal centres are in close proximity, making the possible cooperative effects capable of enhancing or modifying the chemical reactivity. Free rotation of the rings around the C−C bond in the fulvalene plane makes two *cis,trans* conformations (**I**, **II**) of the metal fragments possible. The preferred conformation depends mainly on electronic and steric factors. In this type of ligand each cyclopentadienyl group is substituted through one bond to a second identical group. It makes the metal centre more electron-deficient, reducing secondary reactions such as ring C−H bond activation because of the rigid system that generates the fulvalene.



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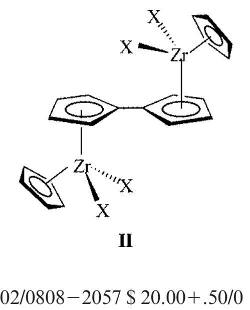

II

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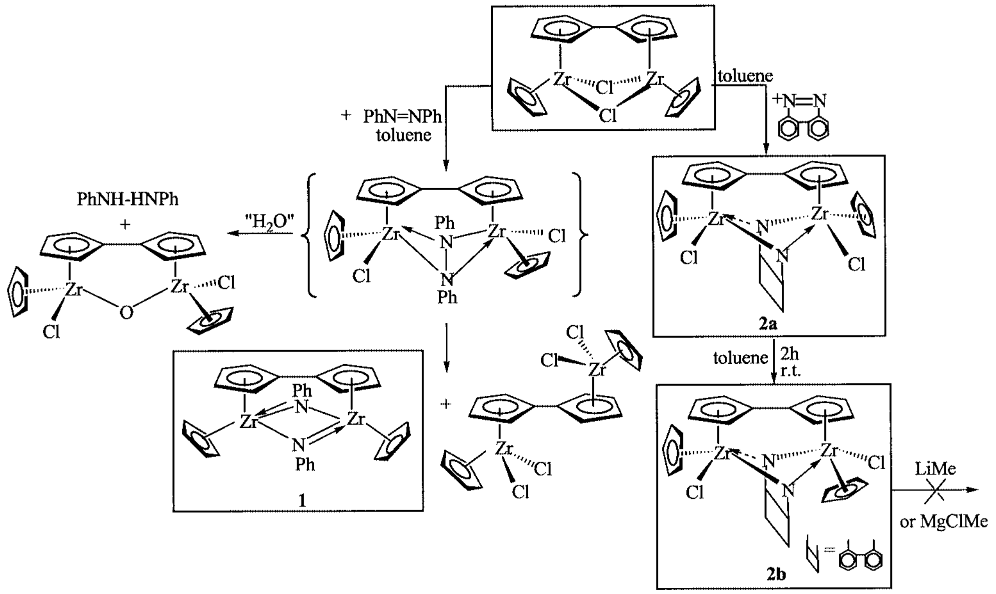


Scheme 1

To enable systematic studies of such compounds we have developed a high-yield route to titanium and zirconium compounds.[4] In recent years, the synthesis and reactivity of dinuclear organotitanium and -zirconium compounds containing the fulvalene ligand have been the focus of our research[5,6] and the study of fundamental chemical reactions with a variety of new fulvalene derivatives has been published.[7] In this paper we report the formation of dinuclear (fulvalene)zirconium complexes where both metal atoms are bridged by an additional μ-imido, μ-(η^2,η^2-N,N-hydrazido) or μ-(η^1-C:η^2-C,N-isocyanido) ligand.

Results and Discussion

μ-Imido, μ-(η^2,η^2-N,N-Hydrazido) Derivatives

Imido complexes of group-4 elements have been synthesized by different routes.[8] According to the described method using the N=N bond cleavage of an azobenzene,[9] the known chloro(fulvalene)zirconium(III) compound $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$[4a] reacts with an equimolar amount of PhN=NPh in toluene, under extremely anhydrous conditions, as shown in Scheme 1. The initially deep violet solution first turns dark yellow and then orange with gradual precipitation of a yellow solid. The solid was identified by elemental analysis and IR spectroscopy as the known chloro(fulvalene)zirconium(IV) complex $[Zr(\eta^5\text{-}C_5H_5)Cl_2]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$.[5c] This compound is rather insoluble in the usual organic solvents and can be separated by simple filtration. By removing the solvent in vacuo from the resulting solution, an orange product was obtained in 46% yield, characterized as the μ-[bis(phenylimido)] derivative $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}NPh)]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**1**).

Complex **1** can be considered as arising from an initial interaction of the zirconium(III) compound with the organic reagent to give a hydrazido intermediate species, which evolves through N−N bond breaking and a subsequent intermolecular ligand exchange to yield the final mixture containing **1** and the chloro(fulvalene)zirconium(IV) complex. This latter step may be favoured by the low solubility of $[Zr(\eta^5\text{-}C_5H_5)Cl_2]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$. Attempts to isolate and characterise the hydrazido intermediate species by carrying out the reaction under milder conditions have not been successful. When this reaction is carried out under insufficiently dry conditions, the final product always contained a mixture of the previously reported μ-oxo complex $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-}O)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$[4a] and 1,2-diphenylhydrazine, identified by analytical and NMR spectroscopic characterisation. This is consistent with the reaction pathway shown in Scheme 1, indicating that the proposed hydrazido intermediate species reacts with water, resulting in the immediate hydrolysis of the Zr−N bonds to give a mixture of the oxo zirconium compound and hydrazine. Several studies reveal that III is an unstable oxidation state for zirconium. It rapidly reacts with oxygen through a peroxo intermediate species, which immediately transforms into the final products, probably containing oxozirconium(IV) species.[1,10] Peroxo and hydrazido are isoelectronic and their zirconium-type derivatives are rare. In order to determine whether a stable hydrazido complex could be isolated, we treated the starting chlorozirconium(III) compound with benzo[*c*]cinnoline, an organic molecule similar to azobenzene in which the biphenyl system connecting the nitrogen atoms prevents the N−N bond from breaking due to the additional C−C bond. Equimolar amounts of the two compounds reacted overnight in toluene solution to give the complex $[Zr(\eta^5\text{-}C_5H_5)Cl]_2[\mu\text{-}(\eta^2,\eta^2NC_6H_4C_6H_4N)][\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**2a**), which converted in toluene solution into **2b** within 2 h (see Scheme 1). Compound **2b** remains unaltered under reflux in toluene solution after 5 h. The N−N bond cleavage and intermolecular ligand exchange processes were not observed and the compound was isolated as a yellow microcrystalline solid in 60% yield.

Both compounds are air- and moisture-sensitive and must be manipulated under dry conditions. They are soluble in aromatic and chlorinated solvents and insoluble in alkanes. Formulation of **1** as an imido-bridged dinuclear compound is based on analytical and spectroscopic data and comparisons with similar structurally characterized titanium and zirconium species.[11] We propose that compound **2** is an unusual μ-(η^2,η^2-hydrazido) bridge derivative. Mass spectra confirm the dinuclear nature of these compounds. The presence of the fulvalene ligand must contribute to the formation and stabilization of the μ-(phenylimido) and μ-(η^2,η^2-hydrazido) disposition.

A medium-intensity absorption at 568 cm^{-1} in the IR spectrum of **2** can be assigned to the ν(N−N) stretching mode and implies that on coordination an important reduction in the N−N multiple-bond character has taken place which supports the bonding description given in Scheme 1. The ^{1}H NMR spectrum for complex **1** (C_6D_6 or $CDCl_3$, room temperature) shows one singlet and three resonances assigned to the cyclopentadienyl and the phenyl group protons, respectively. The fulvalene ligand gives two pseudotriplets corresponding to an AA′BB′ spin system. These spectroscopic features agree with the C_{2v} symmetrical arrangement depicted in Scheme 1 for a dimetallic species with the zirconium centres linked by a fulvalene ligand and two bridging phenylimido groups giving a central Ti_2N_2 heterocyclic ring. The ^{1}H NMR spectrum of **2a** (C_6D_6 or $CDCl_3$, room temperature) shows one singlet and four multiplets corresponding to an ABCD spin system assigned to the cyclopentadienyl and fulvalene groups, respectively. The phenyl protons appear as eight signals and are readily assignable (see Exp. Sect.). These spectroscopic data indicate the formation of a dinuclear zirconium species with a chiral ligand arrangement around each equivalent zirconium centre, with the bridging hydrazido ligand centrally disposed and located perpendicular to the $C_{ipso}-C_{ipso}$ bond of the fulvalene unit and the cyclopentadienyl and chloro ligands in a *cis* disposition. This arrangement makes the two phenylhydrazido rings nonequivalent, generating eight resonances for the corresponding protons. When **2a** is maintained in toluene solution at room temperature, a new compound **2b** is formed within 2 h (Scheme 1). Its ^{1}H NMR spectrum shows the same set of resonances for the cyclopentadienyl and the fulvalene protons observed for **2a**, but they are slightly shifted (see Exp. Sect.). However, the phenyl protons appear as four signals (two doublets of doublets and two doublets of triplets with coupling constant values of $^3J_{H-H} = 8$ Hz and $^4J_{H-H} = 0.97$ Hz). Compounds **2a** and **2b** offer identical elemental analyses, IR and mass spectroscopic data. These observations may be explained by an enantiomeric isomerization process, if the ligands bonded to one of the zirconium centres re-coordinate in **2a** to give the thermodynamically more stable **2b**, in which the cyclopentadienyl and chloro ligands adopt a *trans* disposition. While the nature of the structure of **1** and **2** is of interest, all attempts to obtain crystals of crystallographic quality were unsuccessful.

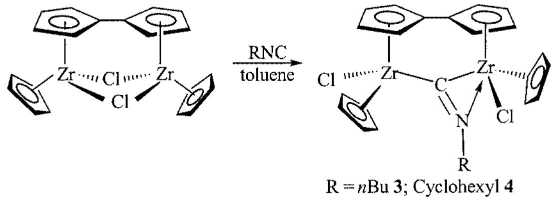
Terminal η^1-hydrazido(2−) coordination $M=N-NR_2$ has been well established for transition metal complexes.[12] There has been some concern about the nature of these species and it has been noted that these compounds appear closer to isodiazene ($M-N=NR_2$) than hydrazido(2−) derivatives.[13] Hydrazido as a bridging dianion ligand is much less common and has been observed in a few transition metal derivatives such as the dinuclear compounds $[W(NPh)Me_3]_2[\mu\text{-}(\eta^1,\eta^1\text{-}NH_2NH_2)][\mu\text{-}(\eta^2,\eta^2\text{-}NHNH)]$[14] and $[Sm(C_5Me_5)]_2[\mu\text{-}(\eta^2,\eta^2\text{-}NRNR)]$ (R = Ph, H).[15]

No reaction was observed when **2b** was treated with MeLi or MeMgCl in THF or toluene under varying conditions; the starting substances were always recovered. The lack of reactivity reflects the stability of this type of compound, with its coordinatively saturated metal centres decreasing its electrophilicity. Compound **1** must be consistent with a formal 18 valence electron species with 4 electrons donated from each μ-imido ligand to the "Zr_2" unit. The hydrazido group in **2** is considered as a 6-electron ligand, thereby also making this compound formally an 18 valence electron species.

μ-(η^1-C:η^2-C,N-Isocyanido) Derivatives

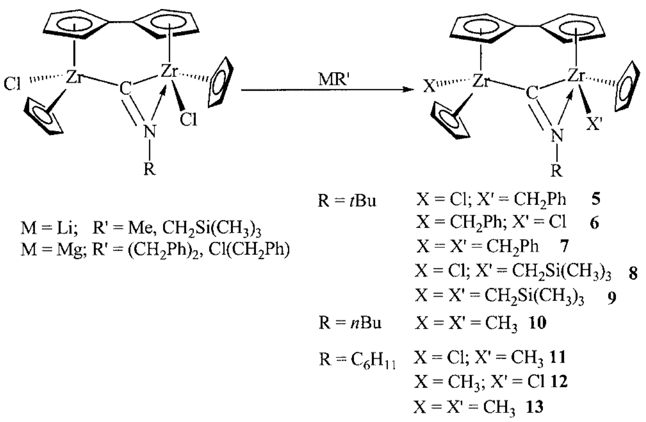
The (fulvalene)bis[chloro(cyclopentadienyl)zirconium] fragment "$(ZrCpCl)_2(C_{10}H_8)$" can provide an excellent support to promote uncommon ligand dispositions. Particularly interesting is the μ-isocyanido bonding mode found in the compounds $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-}CNR)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (R = *t*Bu;[5c,5i] 2,6-$Me_2C_6H_3$ [6a]), which have an unsymmetrical bridging ligand, a μ-(η^1-C:η^2-C,N) 4-electron ligand (σ,π), between their zirconium atoms. We have reported the synthesis of complexes of this type by RNC addition to the dinuclear zirconium(III) derivative $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$. Analogous dicyclopentadienyl compounds have also been described.[16]

Addition of RNC (R = *n*Bu, C_6H_{11}) to a toluene solution of $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (molar ratio 1:1) results in an immediate colour change from violet to bright red. After work up, compounds $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-}CNR)[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ [R = *n*Bu (**3**), C_6H_{11} (**4**)] were isolated in high yield (ca. 80%) (Scheme 2) as red solids, characterized by analytical and spectroscopic methods. Compound **4** was obtained as a partial toluene solvate, indicated by elemental analysis and ^{1}H NMR spectroscopy. These compounds are air- and moisture-sensitive and must be manipulated under dry conditions. They are soluble in benzene, toluene and chloroform but insoluble in alkanes. Characteristic absorptions at $\tilde{\nu}$ = 1656 [1650(sh)] and 1637 cm^{-1} due to ν(C=N) vibrations are observed in the IR spectra of **3** and **4**, similar to those found for other compounds of this type.[5i,6a,7c] The ^{1}H NMR spectra in $CDCl_3$ at room temperature show the expected two ABCD spin systems for the fulvalene protons and two signals for the cyclopentadienyl rings, consistent with a dinuclear species with two zirconium atoms each in a different coordination environment. Characteristic resonances for the cyclohexyl and *n*-butyl groups are also observed. The spectrum of **3** also shows an AB spin system for the diastereotopic "N−CH$_2$" protons. Similar spectroscopic features were observed in the ^{13}C NMR spectra. The resonance for the isocyanide carbon atom (CN−) is observed at δ = 295.0 ppm in compound **3** but not observed for **4**.



Scheme 2

Alkylation of [Zr(η^5-C$_5$H$_5$)Cl]$_2$(μ-CNR)[μ-(η^5,η^5-C$_{10}$H$_8$)] (R = *t*Bu,[5i] *n*Bu, C$_6$H$_{11}$) with R′M [R′ = Me, CH$_2$Si(CH$_3$)$_3$, M = Li; R′ = (PhCH$_2$)$_2$, (PhCH$_2$)Cl, M = Mg] was also studied (Scheme 3). [Zr(η^5-C$_5$H$_5$)Cl]$_2$(μ-CN*t*Bu)[μ-(η^5,η^5-C$_{10}$H$_8$)] reacts with 1 equiv. of PhCH$_2$MgCl or (PhCH$_2$)$_2$Mg(THF)$_2$ to afford an orange yellow oil. Its ^{1}H NMR spectrum in C$_6$D$_6$ indicated a mixture containing the two isomers of the monobenzyl derivatives [Zr(η^5-C$_5$H$_5$)]$_2$(CH$_2$Ph)(Cl)(μ-CN*t*Bu)[μ-(η^5,η^5-C$_{10}$H$_8$)] (**5** and **6**) in a 1:3 molar ratio. When the reaction was carried out with 2 equiv. or an excess of PhCH$_2$MgCl, a mixture of the monobenzyl compound **5** and the dibenzyl complex [Zr(η^5-C$_5$H$_5$)(CH$_2$Ph)]$_2$(μ-CN*t*Bu)[μ-(η^5,η^5-C$_{10}$H$_8$)] (**7**) (30%:70%) was obtained. In an attempt to isolate a pure monoalkyl complex, the bulkier (CH$_3$)$_3$SiCH$_2$Li was used as an alkylating reagent, but the final results were similar to those found with the benzyl and the previously reported methyl reagents.[7c] The starting dichloro compound reacted with 1 or 2 equiv. of (CH$_3$)$_3$SiCH$_2$Li in toluene at room temperature for 16 h to give a mixture of the monoalkyl complex [Zr(η^5-C$_5$H$_5$)]$_2$[CH$_2$Si(CH$_3$)$_3$](Cl)(μ-CN*t*Bu)[μ-(η^5,η^5-C$_{10}$H$_8$)] (**8**) and the dialkyl compound [Zr(η^5-C$_5$H$_5$)]$_2$[CH$_2$Si(CH$_3$)$_3$]$_2$(μ-CN*t*Bu)[μ-(η^5,η^5-C$_{10}$H$_8$)] (**9**). Moreover, when [Zr(η^5-C$_5$H$_5$)Cl]$_2$(μ-CN*n*Bu)[μ-(η^5,η^5-C$_{10}$H$_8$)] was treated in toluene with 2 equiv. of MeLi, the dimethyl complex [Zr(η^5-C$_5$H$_5$)(CH$_3$)]$_2$(μ-CN*n*Bu)[μ-(η^5,η^5-C$_{10}$H$_8$)] (**10**) was isolated as an analytically pure substance, unlike the mixture of the monomethyl and dimethyl compounds obtained in the methylation of [Zr(η^5-C$_5$H$_5$)Cl]$_2$(μ-CN*t*Bu)[μ-(η^5,η^5-C$_{10}$H$_8$)].[7c] Reaction of [Zr(η^5-C$_5$H$_5$)Cl]$_2$(μ-CNC$_6$H$_{11}$)[μ-(η^5,η^5-C$_{10}$H$_8$)] with MeLi in a molar ratio of 1:2 gave the dimethyl compound [Zr(η^5-C$_5$H$_5$)(CH$_3$)]$_2$(μ-CNC$_6$H$_{11}$)[μ-(η^5,η^5-C$_{10}$H$_8$)] (**13**), which was always obtained with small amounts of the monomethyl derivatives [Zr(η^5-C$_5$H$_5$)]$_2$(CH$_3$)(Cl)(μ-CNC$_6$H$_{11}$)[μ-(η^5,η^5-C$_{10}$H$_8$)] (**11** and **12**). Attempts to separate this mixture by repeated recrystallization were unsuccessful.

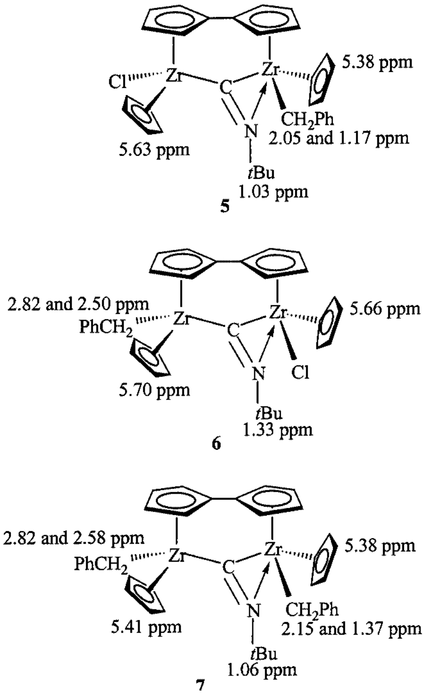


Scheme 3

Compounds **5−13** are moisture-sensitive but thermally stable in the solid state, allowing them to be stored under inert conditions for weeks. They are soluble in aromatic hydrocarbons, THF, dichloromethane and chloroform, but insoluble in diethyl ether and alkanes. The pairs of compounds obtained, **5/6**, **5/7** and **8/9**, and the compounds **11−13**, show the same solubility in all common solvents and therefore could not be separated. Consequently, they have been characterized by NMR spectroscopy but satisfactory elemental analyses were not obtained; **10** can be obtained as a pure compound and has been analytically and spectroscopically identified.

The ^{1}H NMR spectra of complexes **5−13** in C$_6$D$_6$ at room temperature show two ABCD spin systems (eight signals) for the fulvalene ligand and two signals for the cyclopentadienyl ring protons. The expected resonances for the protons of the isocyanide alkyl substituents are observed. The spectra of **5−9** show one singlet for the *tert*-butyl protons. Four signals are assigned to the *n*-butyl protons in **10** with the "NCH$_2$−" methylene groups as diastereotopic protons and four signals are assigned to the cyclohexyl protons in **13**. These spectroscopic data indicate the formation of dinuclear zirconium compounds with the metal atoms in nonequivalent coordination environments.

The "CH$_2$Ph" methylene group protons appear as AB spin systems with two doublets for **5** and **6** (δ = 2.05, 1.17 ppm and δ = 2.82, 2.50 ppm, respectively) and four doublets for **7** (δ = 2.82, 2.58, 2.15, 1.37 ppm) suggesting the presence of CH$_2$ diastereotopic groups. Two of the chemical shifts of the methylene groups in **7** (δ = 2.15 and 1.37 ppm) compare well with the signals for the same protons in **5** (δ = 2.05 and 1.17 ppm), while the other two methylene groups in **7** (δ = 2.82 and 2.58 ppm) compare with the corresponding signals in **6** (δ = 2.82 and 2.50 ppm). These spectroscopic features suggest that the CH$_2$ groups in each pair of compounds occupy very similar chemical environments and must be bonded to the same type of zirconium atom. The presence of the bridging isocyanido group can exert an important influence in the reactivity of these fulvalene derivatives. The η^2-side-on coordination of the isocyanido bridge[5i] to one of the zirconium atoms involves donation of the nitrogen atom's free electron pair to the metal centre to give an 18-electron valence shell. The increase of the electronic density at this zirconium centre must cause shielding of the NMR signals for all of the directly bonded ligands.[7c] These observations allow the structures of **5** and **6** to be distinguished (Scheme 4).



Scheme 4

Similar spectroscopic behaviour has been observed in the ^{1}H NMR spectrum (C_6D_6, room temperature) for the diastereotopic "CH_2SiMe_3" methylene group protons for compounds **8** and **9** (one and two AB spin systems respectively; see Exp. Sect.). Two markedly different chemical shifts are found for the methyl protons in the dimethyl derivatives **10** ($\delta = 0.29$ and -0.37 ppm) and **13** ($\delta = 0.29$ and -0.32 ppm).

These experimental results highlighted differences in the reactivity of the two Zr−Cl bonds present in the starting $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-CNR})[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ compounds and allow us to conclude that the ease of alkylation of the chloride ion bonded to the tetracoordinated zirconium atom is greater than the alkylation of the chloride ion bonded to the pentacoordinated zirconium atom. This proposal is consistent with the results obtained in the methylation reactions of the dichloro compound $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-CN}t\text{Bu})[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$.[7c]

Conclusion

This report shows that dinuclear zirconium(IV) complexes, containing one fulvalene and one additional group (imido, η^2,η^2-N,N-hydrazido or η^1-C:η^2-C,N-isocyanido) as bridging ligands, can be synthesized by adding neutral organic reagents (azobenzene, benzo[*c*]cinnoline, isocyanide) to the easily accessible zirconium(III) derivative $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-Cl})]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$. Alkylation reactions of the chloro(fulvalene)isocyanido complexes show important differences in the reactivity of both chloride ions present in the $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-CNR})[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ compounds.

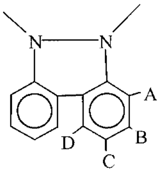
Experimental Section

General Remarks: All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox model HE-63. The solvents were purified by distillation under argon before use, by employing the appropriate drying/deoxygenating agent. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. Azobenzene, benzo[*c*]cinnoline, *n*-butyl isocyanide, cyclohexyl isocyanide, BzMgCl and MeLi (Aldrich) were purchased from commercial sources and used without further purification. $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-Cl})]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$,[4a] $[Zr(\eta^5\text{-}C_5H_5)Cl]_2(\mu\text{-CN}t\text{Bu})[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$,[5i] $(CH_3)_3SiCH_2Li$[17] and $Bz_2Mg(THF)_2$ [18] were prepared by known procedures. C,H, N microanalyses were performed with a Perkin−Elmer 240B and/or a Heraeus CHN-O-Rapid microanalyzer. IR spectra were recorded with a Perkin−Elmer Spectrum 2000 spectrophotometer by using KBr pellets; only selected IR data are reported. NMR spectra, measured at 25 °C, were recorded with a Varian Unity 300 (^{1}H at 300 MHz and ^{13}C at 75 MHz) and a 500 Plus (^{1}H at 300 MHz and ^{13}C at 125 MHz) spectrometer and chemical shifts are referenced to residual proton and carbon signals of the solvent.

$[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-NPh})]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (1): 1.7 g (9.7 mmol) of PhN=NPh was added at room temperature to a solution of 5 g (9.7 mmol) of $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-Cl})]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ in toluene (100 mL). The reaction mixture was heated under reflux (80 °C) and stirred for 12 h. The deep violet solution first turned dark yellow and then changed into a suspension of a yellow solid in an orange solution. After cooling, the yellow solid was separated by filtration and identified as $[Zr(\eta^5\text{-}C_5H_5)Cl_2]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ by IR spectroscopy and elemental analysis (1.8 g, 63% yield). The resulting solution was concentrated to 10 mL and cooled to −30 °C overnight to give compound **1** as a yellow-orange microcrystalline solid. The compound was recrystallised from toluene/hexane (1.4 g, 46% yield). ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 6.04$, 5.65 (AA′BB′ spin system, 4 + 4 H, $J = 2.7$ Hz, $C_{10}H_8$), 5.97 (s, 10 H, C_5H_5), 7.18 (t, 4 H, Ph), 6.77 (t, 2 H, Ph), 6.04 (d, 4 H, Ph) ppm. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 6.21$ (s, 10 H, C_5H_5), 6.19, 6.05 (AA′BB′ spin system, 4 + 4 H, $J = 2.7$ Hz, $C_{10}H_8$), 7.07 (t, 4 H, Ph), 6.59 (t, 2 H, Ph), 5.95 (d, 4 H, Ph) ppm. $C_{32}H_{28}N_2Zr_2$ (623.06): calcd. C 61.69, H 4.50, N 4.50; found C 61.34, H 4.55, N 3.75.

$[Zr(\eta^5\text{-}C_5H_5)Cl]_2[\mu\text{-}(\eta^2,\eta^2\text{-}NC_6H_4C_6H_4N)][\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ (2): 1.2 g (6.8 mmol) of benzo[*c*]cinnoline was added at room temperature to a solution of 3.5 g (6.8 mmol) of $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-Cl})]_2[\mu\text{-}(\eta^5,\eta^5\text{-}C_{10}H_8)]$ in toluene (100 mL). The reaction mixture was heated under reflux and stirred for 12 h. The deep violet solution slowly turned orange-yellow. After cooling and filtration, the resulting solution was concentrated to 10 mL and cooled to −30 °C overnight to give compound **2** as a yellow microcrystalline solid. The compound was recrystallised from toluene/hexane (2.8 g, 60% yield). **2a:** IR (KBr): $\tilde{\nu} = 568$ cm^{-1} [ν(N−N)]. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 6.93$, 5.92, 5.82, 5.54 (ABCD spin system, 4 × 2 H, $C_{10}H_8$), 5.58 (s, 10 H, C_5H_5), 8.18 (dd, 1 H, Ph), 7.25 (dd, 1 H, Ph), 7.17 (dd, 1 H, Ph), 7.13 (t, 1 H, Ph), 7.04 (t, 1 H, Ph), 6.70

(dd, 1 H, Ph), 6.69 (t, 1 H, Ph), 6.67 (t, 1 H, Ph) ppm. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.83, 6.65, 6.33, 5.83 (ABCD spin system, 4 × 2 H, $C_{10}H_8$), 5.71 (s, 10 H, C_5H_5), 7.68 (dd, 1 H, Ph), 7.59 (dd, 1 H, Ph), 7.46 (dd, 1 H, Ph), 7.27 (t, 1 H, Ph), 7.17 (t, 1 H, Ph), 7.08 (dd, 1 H, Ph), 6.91 (t, 1 H, Ph), 6.82 (t, 1 H, Ph) ppm. **2b:** IR (KBr): ṽ = 568 cm^{-1} [ν(N−N)]. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 7.43, 6.97, 5.54, 5.17 (ABCD spin system, 4 × 2 H, $C_{10}H_8$), 5.51 (s, 10 H, C_5H_5), 7.61 [dd, $^{3}J_{H\text{-}H}$ = 8, $^{4}J_{H\text{-}H}$ = 0.97 Hz, 2 H, Ph(A)], 7.19 [dd, $^{3}J_{H\text{-}H}$ = 8, $^{4}J_{H\text{-}H}$ = 0.97 Hz, 2 H, Ph(D)], 7.11 [dt, $^{3}J_{H\text{-}H}$ = 8, $^{4}J_{H\text{-}H}$ = 0.97 Hz, 2 H, Ph(B)], 6.68 (dt, $^{3}J_{H\text{-}H}$ = 8, $^{4}J_{H\text{-}H}$ = 0.97 Hz, 2 H, Ph(C) ppm; the numbering assignment is shown in Scheme 5. ^{13}C NMR (125 MHz, C_6D_6, 25 °C). δ = 122.9, 121.0, 113.3, 110.4 ($C_{10}H_8$), 115.3 (C_5H_5), 101.2 (C_{ipso}, $C_{10}H_8$), 135.7, 131.6, 129.1 ppm, and signals collapsed by the C_6D_6 resonances. $C_{32}H_{26}Cl_2N_2Zr_2$ (691.95): calcd. C 55.54, H 3.79, N 4.05; found C 56.06, H 3.96, N 3.63.



Scheme 5

[Zr(η^5-C_5H_5)Cl]$_2$(μ-CN*n*Bu)[μ-(η^5,η^5-$C_{10}H_8$)] (3): A solution of [Zr(η^5-C_5H_5)(μ-Cl)]$_2$[μ-(η^5,η^5-$C_{10}H_8$)] (1.00 g, 1.94 mmol) in 75 mL of toluene was treated at room temperature with *n*-butyl isocyanide (0.20 mL, 2.00 mmol). The violet solution turned red within an hour. After filtration, the solvent was completely removed in vacuo and the resulting red solid washed with *n*-hexane. After recrystallization from toluene/hexane, a sample of **3** suitable for analysis was obtained (1.04 g, 90%). IR (KBr): ṽ = 1656 [1650 (sh)] cm^{-1} [ν(C=N)]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.18, 5.82 (s, 2 × 5 H, C_5H_5), 6.41, 6.40, 6.28, 6.00, 5.63, 5.40, 4.83, 4.78 (two ABCD spin systems, 8 × 1 H, $C_{10}H_8$), 3.88, 3.35 (AB spin system, 2 × 1 H, $N{-}CH_2{-}[CH_2]_2{-}CH_3$), 1.85 (m, 2 H, $N{-}CH_2{-}CH_2{-}CH_2{-}CH_3$), 1.46 (m, 2 H, $N{-}CH_2{-}CH_2{-}CH_2{-}CH_3$), 1.03 (t, 3 H, $N{-}CH_2{-}CH_2{-}CH_2{-}CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 295.0 (*C*N*n*Bu), 133.2, 120.4 [C_{ipso}, $C_{10}H_8$], 122.3, 117.1, 105.4, 102.7, 101.8, 101.4, 100.1, 95.6 ($C_{10}H_8$), 109.76, 108.62 (C_5H_5), 57.7, 31.7, 20.8, 14.0 (CN*nBu*) ppm. $C_{25}H_{27}Cl_2NZr_2$ (594.87): calcd. C 50.48, H 4.57, N 2.35; found C 50.01, H 4.67, N 2.15.

[Zr(η^5-C_5H_5)Cl]$_2$(μ-CNC_6H_{11})[μ-(η^5,η^5-$C_{10}H_8$)] (4): According to the procedure described for **3**, 1.93 g (3.75 mmol) of [Zr(η^5-C_5H_5)(μ-Cl)]$_2$[μ-(η^5,η^5-$C_{10}H_8$)] and 0.48 mL (3.77 mmol) of cyclohexyl isocyanide were allowed to react in 150 mL of toluene to give **4** (2.25 g, 97%) as a partial toluene solvate, indicated by elemental analysis and ^{1}H NMR spectroscopy. IR (KBr): ṽ = 1637 cm^{-1} [ν(C=N)]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.18, 5.81 (s, 2 × 5 H, C_5H_5), 6.41, 6.37, 6.28, 5.98, 5.64, 5.42, 4.96, 4.82 (two ABCD spin systems, 8 × 1 H, $C_{10}H_8$), 3.85, 1.86, 1.29 (C_6H_{11}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 119.9, 113.5 (C_{ipso}, $C_{10}H_8$), 123.4, 117.5, 104.8, 102.5, 101.8, 101.1, 100.8, 95.7 ($C_{10}H_8$), 109.8, 109.0 (C_5H_5), 67.5, 32.8, 32.3, 25.2 [CN(C_6H_{11})] ppm. $C_{27}H_{29}Cl_2NZr_2 \cdot 1/2$toluene (666.98): calcd. C 54.88, H 4.95, N 2.10; found C 54.74, H 5.01, N 2.06.

[Zr(η^5-C_5H_5)]$_2$(CH_2Ph)(Cl)(μ-CN*t*Bu)[μ-(η^5,η^5-$C_{10}H_8$)] (5 and 6): 1.23 mL of a 2 M solution of BzMgCl in THF (2.45 mmol) was added to a solution of [Zr(η^5-C_5H_5)Cl]$_2$(μ-CN*t*Bu)[μ-(η^5,η^5-$C_{10}H_8$)] (1.46 g, 2.45 mmol) in toluene (50 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 18 h with formation of an $MgCl_2$ precipitate. After filtration, the solvent was removed and an orange yellow solid was obtained which was washed with diethyl ether and hexane. Recrystallization from toluene/hexane gave an orange yellow microcrystalline solid. **5** and **6** have the same composition and therefore they must have an identical elemental analysis. However, the isolated final solid consisted mainly of **5** and **6**, but it contained a small amount of unidentified impurities that could not be removed, and satisfactory elemental analysis was not obtained. Spectroscopic data showed the presence of **5** (25%) and **6** (75%). **6:** ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 7.40−6.98 (m, 5 H, CH_2*Ph*), 5.70, 5.66 (s, 2 × 5 H, C_5H_5), 6.50, 6.36, 5.76, 5.65, 5.05, 4.46, 4.41, 4.40 (two ABCD spin systems, 8 × 1 H, $C_{10}H_8$), 2.82, 2.50 (AB spin system, 2 × 1 H, CH_2Ph), 1.03 (s, 9 H, *t*BuNC) ppm. **5:** ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 7.40−6.98 (m, 5 H, CH_2*Ph*), 5.63, 5.38 (s, 2 × 5 H, C_5H_5), 5.57, 5.55, 5.45, 5.27, 5.06, 4.86, 4.60, 4.48 (two ABCD spin systems, 8 × 1 H, $C_{10}H_8$), 2.05, 1.17 (AB spin system, 2 × 1 H, CH_2Ph), 1.33 (s, 9 H, *t*BuNC) ppm.

[Zr(η^5-C_5H_5)]$_2$(CH_2Ph)(Cl)(μ-CN*t*Bu)[μ-(η^5,η^5-$C_{10}H_8$)] (5) and [Zr(η^5-C_5H_5)(CH_2Ph)]$_2$(μ-CN*t*Bu)[μ-(η^5,η^5-$C_{10}H_8$)] (7): According to the same procedure described for the preparation of **5** + **6**, using 2.46 mL of a 2 M solution of BzMgCl in THF (4.90 mmol) and 1.46 g (2.45 mmol) of [Zr(η^5-C_5H_5)Cl]$_2$(μ-CN*t*Bu)[μ-(η^5,η^5-$C_{10}H_8$)] a mixture of **5** (30%) + **7** (70%) was obtained and spectroscopically characterized. **5** and **7** have the same solubility in all common solvents. They could not be separated and satisfactory elemental analyses were not obtained. **7:** ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 7.40−6.98 (m, 5 H, CH_2*Ph*), 5.41, 5.38 (s, 2 × 5 H, C_5H_5), 6.60, 6.50, 5.29, 5.14, 4.99, 4.48, 4.46, 4.40 (two ABCD spin systems, 8 × 1 H, $C_{10}H_8$), 2.82, 2.58, 2.15, 1.37 (two AB spin systems, 4 × 1 H, CH_2Ph), 1.06 (s, 9 H, *t*BuNC) ppm.

[Zr(η^5-C_5H_5)]$_2$[$CH_2Si(CH_3)_3$](Cl)(μ-CN*t*Bu)[μ-(η^5,η^5-$C_{10}H_8$)] (8) and [Zr(η^5-C_5H_5)]$_2$[$CH_2Si(CH_3)_3$]$_2$(μ-CN*t*Bu)[μ-(η^5,η^5-$C_{10}H_8$)] (9): 0.09 g (1.0 mmol) of $(CH_3)_3SiCH_2Li$ was added to a solution of [Zr(η^5-C_5H_5)Cl]$_2$(μ-CN*t*Bu)[μ-(η^5,η^5-$C_{10}H_8$)] (0.6 g, 1.0 mmol) in toluene (50 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 16 h with the formation of an LiCl precipitate. After filtration, the solvent was removed and a red solid was obtained which was washed with diethyl ether and hexane. Recrystallization from toluene/hexane gave an orange microcrystalline solid identified as a mixture of **8** + **9** (molar ratio 2:1) with the presence of a small amount of the starting zirconium compound. When 0.19 g (2.0 mmol) of $(CH_3)_3SiCH_2Li$ was used to react with 0.6 g (1.0 mmol) of [Zr(η^5-C_5H_5)Cl]$_2$(μ-CN*t*Bu)[μ-(η^5,η^5-$C_{10}H_8$)] a mixture of **8** + **9** (molar ratio 1:3) with no traces of the starting zirconium compound was obtained. **8** and **9** have the same solubility in all common solvents. They could not be separated and satisfactory elemental analyses were not obtained. Spectroscopic data showed the presence of **8** (25%) + **9** (75%). **8:** ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 5.64, 5.62 (s, 2 × 5 H, C_5H_5), 6.58, 6.26, 5.72, 5.50, 5.40, 5.39, 4.86, 4.70 (two ABCD spin systems, 8 × 1 H, $C_{10}H_8$), 1.37 (s, 9 H, CN*t*Bu), 0.20 (s, 9 H, Si*Me$_3$*), −0.19, −0.40 (AB spin system, CH_2SiMe$_3$) ppm. **9:** ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 5.65, 5.47 (s, 2 × 5 H, C_5H_5), 6.38, 6.32, 5.60, 5.44, 5.20, 4.58, 4.55, 4.40 (two ABCD spin systems, 8 × 1 H, $C_{10}H_8$), 1.08 (s, 9 H, CN*t*Bu), 0.42, 0.29 (s, 9 × 2 H, Si*Me$_3$*), 0.33, 0.11, −0.05, −0.37 (two AB spin systems, CH_2SiMe$_3$) ppm.

[Zr(η^5-C_5H_5)(CH_3)]$_2$(μ-CN*n*Bu)[μ-(η^5,η^5-$C_{10}H_8$)] (10): 1.12 mL of a 1.50 M solution of LiMe in diethyl ether (1.70 mmol) was added at −78 °C to a solution of [Zr(η^5-C_5H_5)Cl]$_2$(μ-CN*n*Bu)[μ-(η^5,η^5-

$C_{10}H_8$)] (0.50 g, 0.84 mmol) in toluene (50 mL). The reaction mixture was stirred for 30 min and warmed to room temperature. After filtration, the solvent was removed and an orange-yellow solid was obtained. Recrystallization from toluene/hexane gave **10** as a microcrystalline solid (0.21 g, 46%). IR (KBr): $\tilde{\nu}$ = 1660 [1620 (sh)] cm^{-1} [ν(C=N)]. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ = 5.58, 5.44 (s, 2 × 5 H, C_5H_5), 5.97, 5.94, 5.36, 5.33, 5.13, 4.57, 4.42, 4.12 (two ABCD spin systems, 8 × 1 H, $C_{10}H_8$), 3.41, 2.89 (AB spin system, $N-CH_2-[CH_2]_2-CH_3$), 1.57 (m, $N-CH_2-CH_2-CH_2-CH_3$), 1.23 (m, $N-CH_2-CH_2-CH_2-CH_3$), 0.89 (t, $N-CH_2-CH_2-CH_2-CH_3$), 0.29, −0.37 (s, $Zr-CH_3$) ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 116.2, 111.9 (C_{ipso}, $C_{10}H_8$), 116.6, 110.0, 101.8, 101.0, 99.9, 97.6, 96.7, 92.8 ($C_{10}H_8$), 105.7, 105.6 (C_5H_5), 57.9, 32.3, 21.0, 14.2 (CN*nBu*), 13.4, 9.5 ($Zr-CH_3$) ppm. $C_{27}H_{33}NZr_2$ (554.04): calcd. C 58.54, H 5.96, N 2.53; found C 58.11, H 6.12, N 2.29.

[Zr(η^5-C_5H_5)]$_2$(CH_3)(Cl)(μ-CNC_6H_{11})[μ-(η^5,η^5-$C_{10}H_8$)] (11 + 12) and [Zr(η^5-C_5H_5)(CH_3)]$_2$(μ-CNC_6H_{11})[μ-(η^5,η^5-$C_{10}H_8$)] (13): 1.0 mL of a 1.50 M solution of MeLi in diethyl ether (1.5 mmol) was added to a solution of [Zr(η^5-C_5H_5)Cl]$_2$(μ-CNC_6H_{10})[μ-(η^5,η^5-$C_{10}H_8$)] (0.5 g, 0.75 mmol) in toluene (50 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 16 h with formation of an LiCl precipitate. After filtration, the solvent was removed and a red solid was obtained which was washed with hexane. Recrystallization from toluene/hexane gave a red solid identified by NMR spectroscopy as a mixture of **11** + **12** + **13** (molar ratio 1:1:4). They could not be separated and satisfactory elemental analyses were not obtained. **13:** ^1H NMR (500 MHz, C_6D_6, 25 °C): δ = 5.60, 5.43 (s, 2 × 5 H, C_5H_5), 5.96, 5.94, 5.36, 5.32, 5.15, 4.60, 4.58, 4.19 (two ABCD spin systems, 8 × 1 H, $C_{10}H_8$), 3.60 (m, 1 H, *ipso*-C_6H_{11}), 2.00−1.00 (C_6H_{11}), 0.29, −0.32 (s, $Zr-CH_3$) ppm.^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 115.9, 111.7 (C_{ipso}, $C_{10}H_8$), 117.4, 110.4, 101.7, 100.8, 99.2, 98.0, 97.7, 92.9 ($C_{10}H_8$), 106.0, 105.6 (C_5H_5), 65.8, 33.8, 33.1, 25.8 (C_6H_{11}), 14.4, 9.8 ($Zr-CH_3$) ppm.

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