Reactivity of vinyl and alkynyl zirconium complexes with the di-ansa-[1,1',2,2'-bis(dimethylsilanediyl) dicyclopentadienyl] ligand

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Abstract

Vinylation of the chloro–ethyl and dichloro zirconium complexes \([\text{Zr}(\text{CpSi}_2\text{Cp})\text{Cl}_X]\) (\(X = \text{Et}, \text{Cl}\)) with one or two equivalents of \(\text{Mg(CH}_2\text{CH}_2\text{Cl)}\) gave the new zirconacyclopentane \([\text{Zr}(\text{CpSi}_2\text{Cp})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{H})\)] and \((\eta^4\text{-butadiene)})zirconium \([\text{Zr}(\text{CpSi}_2\text{Cp})(\eta^4\text{-butadiene})]\) complexes, respectively. Addition of a toluene solution of \(\text{PhC}_2\text{CPh}\) to the zirconacyclopentane compound afforded the zirconacyclopentadiene derivative \([\text{Zr}(\text{CpSi}_2\text{Cp})\text{CPh}_2\text{CPh}_2\text{CPh}_2\text{CPh}_2\text{H})]\). Reaction of the chloro–ethyl zirconium complex with \(\text{LiC}_2\text{CPh}\) afforded the alkynyl compound \([\text{Zr}(\text{CpSi}_2\text{Cp})\text{EtCPh})\) which reacted with \(\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\) to give the insertion product \([\text{Zr}(\text{CpSi}_2\text{Cp})(\eta^2\text{-C}(\text{Et})\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{H})]\). Reactions of the chloro–ethyl \([\text{Zr}(\text{CpSi}_2\text{Cp})\text{EtCl})\) and alkynyl-ethyl \([\text{Zr}(\text{CpSi}_2\text{Cp})\text{EtCPh})\) complexes with the Lewis acid \(\text{B(C}_6\text{F}_5)\text{Cl)}\) yielding various cationic species have been monitored by \(^1\text{H}-\text{NMR} \) spectroscopy. The new complexes reported and their intermediates have been identified by IR and \(^1\text{H}-\text{and} \(^{13}\text{C}-\text{NMR} \) spectroscopy. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Alkenyl; Alkynyl; Alkylzirconacycles

1. Introduction

Bridged dicyclopentadienyl Group 4 metal complexes are particularly interesting systems, used extensively as active and stereoselective catalysts for olefin polymerization processes [1]. Their activity is increased [2] when silyl-substituted rings are used, and for this reason many studies on the synthesis and reactivity of ansa metallocenes of Group 4 metals with one [3] or two [4] dimethylsilyl bridges have been reported in recent years. Most of the studies concerning applications in olefin polymerization have focused on alkyl derivatives without \(\beta\)-hydrogen-containing alkyl groups, because of their higher stability. We recently reported [5] the synthesis and structure of \(\beta\)-hydrogen containing alkyl dicyclopentadienyl zirconium complexes and some aspects of their reactivity.

Dicyclopentadienyl–zirconacyclopentane compounds have been prepared by reaction of different alkenes with \(\text{C}_2\text{Zr}(\text{alkene})\) generated in situ [6] and by alkylation of \(\text{C}_2\text{ZrCl}_2\) with 1,4-dilithiobutane and \(\text{BrMg(CH}_2\text{H}_2\text{MgBr)}\). These reactive compounds readily undergo reductive decoupling reactions by \(\text{C}_2\text{ZrCl}_2\) with \(\text{PhC}_2\text{CPh}\) affording \(\text{C}_2\text{Zr}(\text{PhC}_2\text{CPh})\text{L}\) and react with different alkenes and alkynes to give new zirconacyclopentene, -pentene and -pentadiene complexes [6] which have been studied particularly as stereoselective reagents for many catalytic [6,8] and stoichiometric carbon–carbon bond-forming reactions [9].

Vinyl derivatives are interesting and reactive species which provide new synthetic pathways to many related compounds. Divinyl species may rearrange to form zirconacyclopent-1-enes through \(\beta\)-hydrogen elimination [10] and give butadiene derivatives [11,12] by \(\text{C} = \text{C}\) coupling. The structure of such butadiene compounds has been extensively explored and their behaviour as \(\eta^4\text{-diene or} \sigma^2\pi\text{-zirconacyclopent-2-ene} \) species with a
significant $\pi$-bonding contribution from the central C–C double bond has been discussed [13,14]. Because of its known higher stability, we chose the bis(dimethylsilanediyl)dicyclopentadienyl (CpSi$_2$Cp) ligand to study the behaviour of various mixed dialkyl zirconium complexes, to attempt to isolate or characterize intermediates formed during their thermal decomposition by NMR spectroscopy, and to characterize cationic species generated from their reactions with strong Lewis acids, such as B(C$_6$F$_5$)$_3$.

2. Results and discussion

2.1. Reactions with Mg(CH=CH$_2$)Cl

We reported [5] the isolation and thermal transformation of the $\beta$-hydrogen containing zirconium diethyl [Zr(CpSi$_2$Cp)Et$_2$] derivative of the di-ansa-dicyclopentadienyl [1,1',2,2'-SiMe$_2$($\eta^5$-C$_5$H$_3$)$_2$][CpSi$_2$Cp] ligand. This transformation proceeds via activation of the carbon bonded $\beta$-hydrogen with elimination of ethane to give the ethylene bridged zirconium complex [Zr(CpSi$_2$Cp)Et]$_2$(m-CH$_2$CH$_2$). Hydrogen elimination from sp$^2$ carbon centres is less favourable and therefore the use of mixed ethyl and alkenyl compounds opens new reaction pathways. When a THF solution of the chloro–ethyl complex [Zr(CpSi$_2$Cp)ClEt] reacted with Mg(CH=CH$_2$)Cl the expected mixed alkyl–alkenyl complex was not observed even at 78°C, and the zirconacyclopentane derivative [Zr(CpSi$_2$Cp){$\eta^2$-(CH$_2$)$_4$}] (1) was immediately and quantitatively formed (see Scheme 1).

Complex 1 was isolated as an extremely air and moisture sensitive yellow solid. The $^1$H-NMR spectrum of 1 showed two multiplets for the $\alpha$- and $\beta$-CH$_2$ groups and one ABB spin system for two equivalent C$_5$H$_3$ rings resulting from a fast interconversion of the zirconacyclopentane. The $^{13}$C-NMR spectrum showed two triplets at $\delta$ 34.8 ($^1$J$_{C,H}$ = 124.1 Hz) and $\delta$ 23.0 ($^1$J$_{C,H}$ = 125.5 Hz) typical for the sp$^3$-carbons of the zirconacyclic system and consistent with this formulation.

When the $^1$H- and $^{13}$C-NMR spectra of 1 were recorded in wet C$_6$D$_6$ the oxo-butyl complex [Zr(CpSi$_2$Cp)Bu]$_2$(µ-O), formed by hydrolytic opening of the zirconacycle, was observed. However this compound could not be isolated because the reaction at a preparative level gave an unresolvable mixture of reaction products.

The di-olefin character of complex 1 (see Scheme 1) was demonstrated from its reaction in toluene with PhC=CPh, which displaces the olefin to give the more stable zirconacyclopentadiene derivative [Zr(Cp$_2$Si$_2$Cp)$_2${(µ-CH$_2$CH$_2$)$_4$}] (2). The formation of the zirconacyclopentene [Zr(Cp$_2$Si$_2$Cp)$_2${(µ-CH$_2$CPh)CH$_2$)] intermediate was observed by $^1$H-NMR spectroscopy as a minor component in a sample of the solution taken after refluxing for 2 h. Complex 2 was isolated, after refluxing for 15 h, as a crystalline yellow solid and characterized by elemental analysis and NMR spectroscopy (see Section 4).

1 NMR spectra of the major component observed when solutions of 1 were recorded in wet C$_6$D$_6$. $^1$H-NMR (C$_6$D$_6$, 300 MHz, $\delta$ ppm): $\delta$ 6.78 (m, 4H, C$_5$H$_3$), 6.51 (m, 4H, C$_5$H$_3$), 6.09 (m, 4H, C$_5$H$_3$), 1.82, 1.16, 1.20, 0.89 (4m, 9H, Bu), 0.76 (s, 6H, SiMe$_2$), 0.60 (s, 6H, SiMe$_2$), 0.52 (s, 6H, SiMe$_2$), 0.27 (s, 6H, SiMe$_2$). $^{13}$C-NMR (C$_6$D$_6$, 75 MHz, $\delta$ ppm): 132.0 (C$_5$H$_3$), 129.8 (C$_5$H$_3$), 120.4 (C$_5$H$_3$, C$_{mom}$), 111.7 (C$_5$H$_3$, C$_{mom}$), 109.8 (C$_5$H$_3$), 42.0 (C$_5$, Bu), 37.6 (C$_5$, Bu), 30.9 (C$_5$, Bu), 14.4 (C$_5$, Bu), 2.7 (SiMe$_2$), 2.4 (SiMe$_2$), −2.7 (SiMe$_2$), −4.7 (SiMe$_2$).

Scheme 1.
The reaction of [Zr(CpSi₂Cp)Cl₂] [4b] with two equivalents of Mg(CH=CH₂)Cl in a sealed tube was monitored by ¹H-NMR spectroscopy in THF-d₈. No reaction was observed at −78°C but the divinyl complex [Zr(CpSi₂Cp)(CH=CH₂)₂] was quantitatively formed after 5 min at −50°C, as evidenced by the ¹H-NMR spectrum of this solution which showed two singlets for the exo and endo silicon–methyl groups, the expected ABB" spin system for the cyclopentadienyl ring protons, and an ABX spin system for both equivalent vinyl groups (²Jtrans = 21.2, ³Jcis = 15.4 and ²J = 2.6 Hz). The ¹³C{¹H} spectrum showed the Cα signal at δ 184.7 (see Section 4). This divinyl complex was further transformed when the solution was heated to −10°C and after 30 min at room temperature (r.t.) gave the (η⁴-butadiene) zirconium complex [Zr(CpSi₂Cp){η⁴-(butadiene)}] (3) in 30% yield, together with a mixture of unidentified products. This is the transformation expected for reductive elimination [12], although the presence of other reaction products reveals that this is not a selective reaction. The r.t. ¹H-NMR spectrum of complex 3 shows inequivalent cyclopentadienyl rings due to a high energy barrier for the transformation shown in Scheme 2 and three multiplets for the 1,4-η2-2-butene ligand, one of them clearly shifted to high field (δ ~ 0.80) corresponding to the butadiene Hα protons. This behaviour is consistent with the pronounced σ₂,π-metallacyclopentene character reported for related compounds. The high inversion barrier has been related to the stronger bonding of the butadiene internal carbon atoms for metallocenes which have narrow Cp–M–Cp angles (ca. 119°, average from six Zr(CpSi₂Cp) structures) [14]. This formulation is consistent with the ¹³C-NMR spectrum, which shows six resonances for the ring carbons, two resonances for the Cα and Cβ of the butene ligand and two resonances for the silicon–methyl groups.

2.2. Reaction with LiC=CPH

Reaction of the chloro–ethyl complex [Zr(CpSi₂Cp)EtCl] with one equivalent of LiC=CPH in THF afforded the mixed alkyl–alkynyl complex [Zr(CpSi₂Cp)Et(C=CPH)] (4), which was isolated as a crystalline yellow solid in 60% yield after recrystallization from pentane. β-Hydrogen elimination was not observed in a THF solution at r.t. and complex 4 was stable for short periods under these conditions. The ν(C=C) IR absorption at 2078 cm⁻¹ and characteristic resonances in its ¹H-NMR spectrum confirmed the presence of phenylalkynyl and ethyl ligands located in the equatorial plane, making the four silicon–methyl groups inequivalent, whereas an ABC spin system was observed for two equivalent cyclopentadienyl rings. This formulation is also consistent with the ¹³C-NMR data (see Section 4).

Complex 4 reacted in toluene with one equivalent of CN(2,6-Me₂C₆H₃) which selectively inserted into the zirconium–ethyl bond to give the iminoacyl complex [Zr(CpSi₂Cp)(C=CPH){η²-C(Et)=N(2,6-Me₂C₆H₃)}] (5) (Scheme 3), isolated as a white solid in 90% yield. The IR ν(C=C) and ν(C=N) absorptions were observed at

![Scheme 2](image)

![Scheme 3](image)
The presence of 1/2 equivalent excess of B(C₆F₅)₃. Thus, the use of the zirconium-bound ethyl group was confirmed by the observation of an A₂B₃ spin system in the ¹H spectrum (δ 1.09 t, 3H, J = 7.5 Hz) and two signals at δ 16.2 and δ 61.5 in the ¹³C-NMR spectrum.

When the temperature was raised to −10°C for 30 min the ¹H- and ¹³C-NMR spectra of the resulting solution showed three proton and five carbon resonances corresponding to one ABC spin system due to four equivalent C₅H₅ rings, and four proton and carbon singlets for the silicon-bound methyl groups of a dinuclear cation which does not contain ethyl groups. This behaviour is consistent with the presence of [Zr(CpSi₂Cp)Cl(μ-Cl)]Zr(CpSi₂Cp)Cl⁺ formed by the irreversible reaction of the previous cation with the chlorinated CD₂Cl₂ solvent [17].

This cationic species exhibited reversible dynamic behaviour between −70 and 20°C, consistent with an anti–syn transformation through a transition state formed by three chlorine bridges and characterized by ΔG°(‡263 K) = 13 kcal mol⁻¹ at coalescence temperature (see Scheme 4). Finally a quantitative transformation led to the dichloro complex [Zr(CpSi₂Cp)Cl₂] when the solution was heated to r.t. for 24 h.

A similar study was carried out adding one equivalent of B(C₆F₅)₃ to one equivalent of the ethyl alkynyl complex [Zr(CpSi₂Cp)Et(C₅C₆Ph)] (4) at −78°C in CD₂Cl₂. Formation of the [B(C₆F₅)₃]⁺ borate anion was also observed along with a series of different cationic complexes (Scheme 4). The ¹H-NMR spectrum at −50°C showed one multiplet at δ −1.65 (2H) corresponding to a CH₂–CH₃ bridging group, an ABC spin system for four equivalent C₅H₅ rings and four singlets for the methyl–silicon protons (see Table 1). This is consistent with the presence of the cationic dimer [[Zr(CpSi₂Cp)(C₅C₆Ph)(μ-CH₂CH₃)]⁺. Between −50 and −20°C a mixture of compounds was observed, which after 1 h at −20°C contained two major components which could not be identified. A slow
transformation took place finally when the solution was heated at r.t. for more than 24 h to give the dichloro derivative \([\text{Zr}(\text{CpSi}_2\text{Cp})\text{Cl}_2]\).

3. Conclusions

Easy \(\beta\)-hydrogen elimination from the ethyl group of \([\text{Zr}(\text{CpSi}_2\text{Cp})\text{EtCl}](\text{C}=\text{CPh})\) when it is vinylated is an appropriate method to synthesize the zirconacyclopentane derivative and the related zirconacyclopentadiene from its reaction with phenylacetylene. In contrast, the alkynyl compound \([\text{Zr}(\text{CpSi}_2\text{Cp})\text{Et}(\text{C}=\text{CPh})]\) is thermally stable and can insert isocyanide into its Zr–ethyl bond. Thermal transformation of the divinyl derivative \([\text{Zr}(\text{CpSi}_2\text{Cp})(\text{CH}_2\text{CH}_3)_{2}]\), which can be isolated in solution between \(-50\) and \(-10^\circ\)C, leads to the corresponding \(\eta^4\)-butadiene) zirconium complex \([\text{Zr}(\text{CpSi}_2\text{Cp})\{\eta^4\text{-butadiene}\}]\). Reactions of the chloro–ethyl and alkynyl–ethyl compounds with \(\text{B}(\text{C}_6\text{F}_5)_3\) in sealed NMR tubes allow new dinuclear cationic species to be identified.

4. Experimental

4.1. General

All operations were performed under an inert atmosphere of argon using Schlenk and vacuum-line techniques or a VAC glovebox Model HE-63-P. The following solvents were pre-dried by standing over 4 Å molecular sieves and purified by distillation under argon before use by employing the appropriate drying/de-

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**Scheme 4.**

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oxygenated agents: tetrahydrofuran (sodium/benzophenone), toluene (sodium) and hexane (sodium/potassium alloy). \([\text{Zr}(\text{CpSi}_2\text{Cp})\text{Cl}(\text{CH}_2\text{CH}_3)]\) [5], \([\text{Zr}(\text{CpSi}_2\text{Cp})\text{Cl}_2]\) [4b] and \(\text{B}(\text{C}_6\text{F}_5)_3\) [18] were prepared according to literature procedures. \(\text{Mg}(\text{CH}_2\text{CH}_3)\text{Cl}\) (Aldrich), \(\text{PhC}=\text{CPh}\) (Aldrich), \(\text{HC}=\text{CPh}\) (Aldrich), were purchased from commercial sources and used without further purification. \(^1\text{H}\) and \(^{13}\text{C}\)-NMR spectra were recorded on Unity-300 and Unity 500 Plus spectrometers. \(^1\text{H}\) and \(^{13}\text{C}\) chemical shifts are reported in \(\delta\) units measured with respect to the solvent signals. Mass spectra were recorded on a Hewlett–Packard 5890 spectrometer. Elemental C and H analyses were performed with a Perkin–Elmer 240B microanalyzer.

4.2. \([\text{Zr}\{\eta^5\text{-C}_5\text{H}_5\}\{\text{Si}(\text{CH}_3)\}_{2}]\cdot\{\eta^2\text{-}[\text{CH}_2\text{-}(\text{CH}_2\text{-CH}_2)]\}]\) (1)

A 1 M THF solution of \(\text{Mg}(\text{CH}_2\text{CH}_3)\text{Cl}\) (2.51 ml, 2.51 mmol) was added to a toluene solution (25 ml) of \([\text{Zr}(\text{CpSi}_2\text{Cp})(\text{CH}_2\text{-CH}_3)\text{Cl}]\) (1.00 g, 2.51 mmol) at 0°C. The mixture was stirred for 2 h to give a red solution which after the solvent was removed and the residue extracted into hexane afforded complex 1, as a yellow solid. Yield, 0.79 g, 80%. Anal. Calc. for \(\text{C}_{18}\text{H}_{24}\text{Si}\text{Zr}\): C, 55.46; H, 6.72. Found: C, 54.92; H, 6.40%. \(^1\text{H}\)-NMR (\(\text{C}_6\text{D}_6\), 500 MHz): \(\delta\) 6.64 (d, 4\(\text{H}\), \(\text{C}_5\text{H}_3\)), \(\delta\) 6.60 (t, 2\(\text{H}\), \(\text{C}_5\text{H}_3\)), 1.80 (m, 4\(\text{H}\), \(\text{Zr}\text{-CH}_3\)) 1.10 (m, 4\(\text{H}\), \(\text{Zr}\text{-CH}_3\)) 0.47 (s, 6\(\text{H}\), \(\text{SiMe}_3\)), \(-0.05\) (s, 6\(\text{H}\), \(\text{SiMe}_3\)); \(^{13}\text{C}\)-NMR (\(\text{C}_6\text{D}_6\), 125 MHz): \(\delta\) 128.4 (\(\text{C}_2\text{H}_3\)), 114.9 (\(\text{C}_2\text{H}_3\)), 110.9 (\(\text{C}_2\text{H}_3\)), \(34.8\) (t, \(1\text{J}_{\text{CH}}=124.1\) Hz, \(\text{Zr}\text{-CH}_2\)), \(23.0\) (t, \(1\text{J}_{\text{CH}}=125.5\) Hz, \(\text{CH}_3\text{-CH}_2\)), \(2.0\) (\(\text{SiMe}_3\)), \(-4.1\) (\(\text{SiMe}_3\)).
4.3. [Zr\{\eta^5-C_5H_5\}_2\{Si(CH_3)_2\}_2 Cl]\{\eta^2-(CPh−CPh−CPh−CPh)\} (2)

A THF solution of 1 prepared as described above from Mg(CH=CH)Cl (2.51 ml, 2.51 mmol) and [Zr(CpSi2Cp)CH2Ct] (0.99 mmol) was evaporated and the residue was treated with a toluene solution (30 ml) of PhC=Ph (0.89 g, 5.20 mmol) and then refluxed for 2 h. The 1H-NMR spectrum of this solution showed that the intermediate complex [Zr(CpSi2Cp)\{\eta^2-(CPh−CPh−CPh−CPh)\}] was present as a minor component. 1H-NMR (C6D6, 300 MHz, δ ppm): δ 6.17–8.60 (m, 10H, C5H3), 6.72 (m, 2H, C5H3), 6.64 (m, 2H, C5H3), 1.30 (t, 2H, JCH = 6.6 Hz, −CH2−CH2−), 1.14 (t, 2H, JHH = 6.6 Hz, Zr−CH2−), 0.52 (s, 3H, SiMe2), 0.45 (s, 3H, SiMe2), 0.01 (s, 3H, SiMe2), −0.40 (s, 3H, SiMe2). After refluxing for 15 h the solution was filtered and the solvent was removed under vacuum. The solid residue was washed with hexane (15 ml) to give a yellow solid which was characterized by NMR spectroscopy and elemental analysis as compound 2. Yield 1.03 g, 60%. Anal. Calc. for C31H36Si2Zr; C, 73.09; H, 5.55. Found: C, 73.42; H, 5.68%. Mass spectrum (EI): m/z 689 [M+2 − PhC=Ph, 2], 333 [M+2 − 2PhC=Ph, 64.7], 178 [PhC=Ph, 100]. 1H-NMR (C6D6, 300 MHz, δ ppm): δ 7.10–7.04 (m, 6H, C5H3), 6.96 (t, 2H, C5H3), 6.10–6.04 (m, 8H, C5H3), 6.77–6.74 (m, 4H, C5H3), 6.80 (d, 4H, C5H3), 6.60–6.55 (m, 2H, C5H3), 0.36 (s, 6H, SiMe2). 13C-NMR (C6D6, 75 MHz, δ ppm): δ 193.2 (Zr−CPh), 150.7 (PhC=Ph), 141.9 (C5H3, Cipso), 132.4, 120.3, 126.8, 129.4, 123.1 (C5H3), 135.5 (C5H3, Cipso), 127.9 (C5H3), 116.5 (C5H3), 2.60 (SiMe2), −5.06 (SiMe2).

4.4. Reaction of [Zr\{\eta^5-C_5H_5\}_2\{Si(CH_3)_2\}_2 Cl] with two equivalents of Mg(CH=CH)Cl

4.4.1. NMR tube scale

An NMR tube containing a mixture of the dichlororiziconocene (0.05 g, 0.12 mmol) and a 1 M THF solution of Mg(CH=CH)Cl (0.24 ml) in 0.75 ml of THF-d8 was sealed under vacuum at −78°C. The reaction was monitored by 1H- and 13C-NMR spectroscopy. After 5 min at −50°C all of the starting complex had been transformed into [Zr(CpSi2Cp)(CH2Ct)], which was the only organometallic compound present in the NMR solution (yield ca. 100%). 1H-NMR (THF-d8, −50°C, 500 MHz, δ ppm): δ 7.47 (dd, 2H, JCH = 21.2, 3JCH = 15.4 Hz, Zr−CH2−), 6.43 (d, 4H, J = 2.8 Hz, C5H3), 6.22 (t, 2H, J = 2.8 Hz, C5H3), 5.87 (dd, 2H, JCH = 15.4, 2JCH = 2.6 Hz, −CH2−), 5.35 (dd, 2H, JCH = 21.2, 2JCH = 2.6 Hz, −CH2−), 0.65 (s, 6H, SiMe2), 0.37 (s, 6H, SiMe2). 13C-NMR (THF-d8, −50°C, 125 MHz, δ ppm): δ 184.7 (−CH=), 131.5 (C5H3), 126.8 (−CH2), 113.6 (C5H3), 110.1 (C5H3, Cipso), 2.4 (SiMe2), 4.1 (SiMe2). After 30 min at 20°C, resonances of complex 3 started to appear and after 12 h at r.t. complex 3 was the major component in the solution, together with other unidentified complexes.

4.4.2. Preparative scale

A 1 M THF solution of Mg(CH=CH)Cl (5 ml, 5 mmol) was added to a toluene solution (50 ml) of [Zr(CpSi2Cp)Cl2] (1.00 g, 2.47 mmol) at r.t. and stirred for 12 h to give a red−brown solution. The solution was filtered and the solvent was removed under vacuum to give a red oil. Recrystallization from hexane afforded the zirconacyclo-3-pentene complex [Zr(CpSi2Cp)\{\eta^2-(CH2−CH−CH−CH)\}] (3) as a red solid. Yield 0.29 g, 30%. Anal. Calc. for C41H32Si2Zr: C, 55.75; H, 6.24. Found: C, 55.54; H, 6.31%. 1H-NMR (C6D6, 300 MHz, δ ppm): δ 6.52 (d, 2H, C5H3), 5.25 (d, 2H, C5H3), 5.05 (t, 1H, C5H3), 4.64 (m, 2H, −CH−), 4.14 (t, 1H, C5H3), 3.28 (m, 2H, −CH2−sym), 0.71 (s, 6H, SiMe2), 0.42 (s, 6H, SiMe2), −0.80 (m, 2H, −CH2−anti). 13C-NMR (C6D6, 125 MHz, δ ppm): δ 129.8 (C5H3, Cipso), 126.7 (C5H3, Cipso), 124.1 (C5H3), 112.5 (C5H3), 110.7 (−CH−), 110.1 (C5H3), 102.4 (C5H3), 49.8 (dd, 1JCH = 158.7, 1JCH = 132.0 Hz, −CH2−), 2.2 (SiMe2), −3.1 (SiMe2).

4.5. [Zr\{\eta^5-C_5H_5\}_2\{Si(CH_3)_2\}_2 Cl] (4)

A THF (25 ml) solution of LiC=Ph (0.11 g, 1.00 mmol) was added to a THF solution (25 ml) of [Zr(CpSi2Cp)Cl(C2H5)] (0.40 g, 1.00 mmol) at 0°C. The mixture was stirred for 3 h to give a dark red solution, the solvent was removed in vacuo and the residue was extracted into hexane to give complex 4, which was recrystallized from pentane as yellow crystals. Yield 0.30 g, 64%. Anal. Calc. for C41H32Si2Zr: C, 62.14; H, 6.08. Found: C, 61.87; H, 6.01%. IR (Nujol) 2078 cm−1 [v(C=Zr)]. 1H-NMR (C6D6, 300 MHz, δ ppm): δ 7.53 (m, 2H, C5H3), 7.18 (m, 2H, C5H3), 6.96–7.01 (m, 3H, C5H3), 6.51 (m, 2H, C5H3), 6.32 (m, 2H, C5H3), 1.33 (t, 3H, 3JHH = 8 Hz, −CH2−CH2−), 0.72 (q, 2H, 2JHH = 8 Hz, −CH2−CH2−), 0.54 (s, 3H, SiMe2), 0.51 (s, 3H, SiMe2), 0.50 (s, 3H, SiMe2), 0.12 (s, 3H, SiMe2). 13C-NMR (C6D6, 75 MHz, δ ppm): δ 135.6 (Zr−C=), 131.5 (C5H3), 129.2 (C5H3), 127.1 (C5H3), 126.0 (C5H3), 119.0 (CPh), 113.1 (C5H3), 111.8 (C5H3, Cipso), 109.2 (C5H3, Cipso), 49.5 (t, JCH = 115.5 Hz, CH2−CH2−), 13.1 (q, JCH = 123.2 Hz, CH2−CH2−), 2.42 (SiMe2), 2.40 (SiMe2), −3.72 (SiMe2), −3.62 (SiMe2).

4.6. [Zr\{\eta^5-C_5H_5\}_2\{Si(CH_3)_2\}_2 Cl] (4)

A toluene (25 ml) solution of 2,6-dimethylphenylosyanide (0.25 g, 1.90 mmol) was added to a toluene (25 ml) solution of [Zr(CpSi2Cp)Cl] (4) (0.90 g,
1.90 mmol) at 20°C. The mixture was stirred for 12 h to give a red dark solution. Solvent was removed in vacuo and the residue extracted into hexane to yield complex 5 after evaporation. Yield 1.02 g, 90%. Anal. Calc. for C₃H₇NSi₆Zr: C, 66.61; H, 6.27; N, 2.35. Found: C, 66.42; H, 6.04; N, 2.14%. IR: (Nujol) 2086 [v(C=C)], 1592 cm⁻¹ [v(C=N)]. ¹H-NMR (C₆D₆, 300 MHz, δ ppm): δ 7.50 (m, 2H, C₆H₅), 7.30 (m, 2H, C₆H₅), 7.05 (t, 1H, C₆H₅), 6.94 (m, 3H, Me₂C₆H₃), 6.90 (m, 2H, C₆H₅), 6.59 (m, 2H, C₆H₅), 5.36 (m, 2H, C₆H₅), 2.40 (q, 2H, JCH = 7.5 Hz, CH₂–CH₃), 1.84 (s, 6H, Me₆C₆H₃). ¹³C-NMR (C₆D₆, 75 MHz, δ ppm): δ 241.0 (C₆), 145.0 (Zr–C=), 134.8 (C₆H₅), 131.4 (Ph), 129.4 (Ph), 125.6 (Ph), 125.3 (Ph), 122.1 (C₆H₅), 118.0 (CH), 109.4 (C₆H₅, C₆), 107.8 (C₆H₅), 107.3 (C₆H₅, C₆), 31.7 (t, JCH = 123.8 Hz, CH₂–CH₃), 19.0 (q, JCH = 125.7 Hz, Me₂C₆H₃), 10.1 (q, JCH = 127.5 Hz, CH₂–CH₃), 3.2 (SiMe₂), 3.1 (SiMe₂), −3.50 (SiMe₂), −3.9 (SiMe₂).

4.7. Reaction of [Zr{η⁵-C₅H₅}₂(Si(CH₃)₃)Cl](CH₂Cl₂) with B(C₆F₅)₃

An NMR tube containing a mixture of the zirconium complex (0.05 g, 0.12 mmol) and B(C₆F₅)₃ (0.065 g, 0.12 mmol) in 0.75 ml of CD₂Cl₂ was sealed under vacuum at −78°C and the reaction was monitored by ¹H- and ¹³C-NMR spectroscopy.

4.8. Reaction of [Zr{η⁵-C₅H₅}₂(Si(CH₃)₃)₂Et(C=CPh)] with B(C₆F₅)₃

An NMR tube containing a mixture of complex 4 (0.04 g, 0.08 mmol) and B(C₆F₅)₃ (0.041 g, 0.08 mmol) in 0.75 ml of CD₂Cl₂ was sealed under vacuum at −78°C. The reaction was monitored by ¹H-NMR spectroscopy.

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References