

Structural characterization of $M(s\text{-}cis\text{-}\eta^4\text{-C}_4\text{H}_6)(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NR})$ ($M = \text{Ti}$ or Zr , $R = \text{CMe}_3$ or $\text{CHCMe}(1\text{-C}_{10}\text{H}_7)$)

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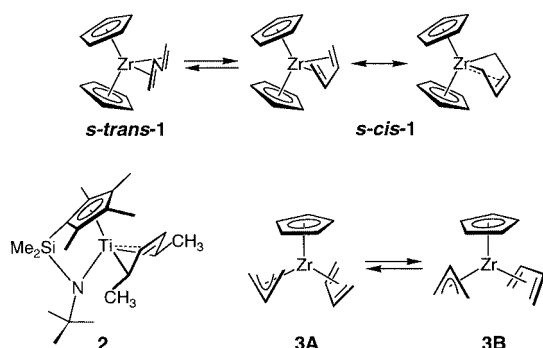
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Treatment of $M(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NR})\text{Cl}_2$ [$M = \text{Zr}$, $R = \text{CMe}_3$ or $\text{CHMe}(1\text{-C}_{10}\text{H}_7)$; $M = \text{Ti}$, $R = \text{CMe}_3$] with “butadienemagnesium” gave the respective $M(s\text{-}cis\text{-}\eta^4\text{-C}_4\text{H}_6)(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NR})$ complexes in good yield. In solution, the parent zirconium system $\text{Zr}(s\text{-}cis\text{-}\eta^4\text{-C}_4\text{H}_6)(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NCMe}_3)$ forms a 85 : 15 equilibrium mixture of the supine (**A**) and prone (**B**) isomers, whereas the isomer which has the *s-cis*-butadiene ligand oriented with its open side toward the amido group (prone) is favored in the $\text{Ti}(s\text{-}cis\text{-}\eta^4\text{-C}_4\text{H}_6)(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NCMe}_3)$ case (**A** : **B** = 5 : 95). Complex $\text{Zr}[s\text{-}cis\text{-}\eta^4\text{-C}_4\text{H}_6]\{\text{Me}_4\text{C}_4\text{SiMe}_2\text{NCHMe}(1\text{-C}_{10}\text{H}_7)\}$ was obtained as a single isomer (supine orientation **A** favored). The favored isomers were in each case characterized by single crystal X-ray structure analyses. The zirconium complexes contain a central metallacyclic σ^2, π -type (*s-cis*- η^4 -butadiene) metal framework, whereas the titanium structure is more like that expected for a conventional π -butadiene metal complex.

Introduction

The Group 4 metallocenes were the first frameworks at which the unusual *s-trans*- η^4 co-ordination of a 1,3-butadiene ligand was established.¹ The corresponding $M^{IV}(s\text{-}cis\text{-}\eta^4\text{-C}_4\text{H}_6)(^R\text{Cp})_2$ ($M = \text{Zr}$ or Hf) isomers also show unusual structural features: they exhibit metallacyclic σ^2, π -type structures (e.g. *s-cis*-**1**, see Scheme 1).^{2,3} The chemistry of the Group 4 metallocenes has



Scheme 1

become of wide interest because of their use in homogeneous Ziegler catalysis,⁴ and so have the $\text{Zr}(\eta\text{-C}_4\text{H}_6)(^R\text{Cp})_2$ complexes which served as components for the generation of active single component metallocene Ziegler catalyst systems.⁵ The related $(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NR})\text{-Ti-}$ and -Zr- derived complexes have found extensive use in the chemistry of the related “constrained geometry” Ziegler catalysts,^{6–8} which includes their η -butadiene complexes.^{9,10} In contrast to the (butadiene) Group 4 metallocenes, whose structural features are well established by crystal structure determinations and detailed spectroscopic investigations of a large number of examples, only one detailed molecular structure analysis in the solid state has been reported of a $M^{IV}(\text{conjugated diene})(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NR})$ example so far to the best of our knowledge, namely of the $\text{Ti}(s\text{-}cis\text{-}E,E\text{-C}_6\text{H}_{10})\text{-}$

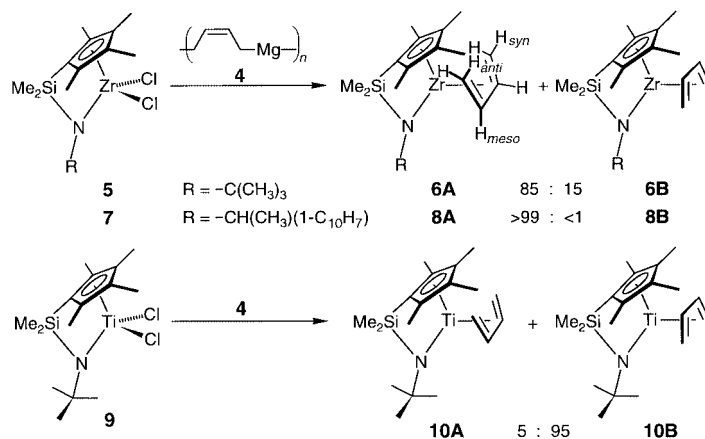
$(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NCMe}_3)$ complex **2**.⁹ We have prepared a series of butadiene complexes of “constrained geometry” frameworks, including the parent complexes $M(\text{C}_4\text{H}_6)(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NCMe}_3)$ ($M = \text{Ti}$ or Zr) and characterized their structures, and that of a related chiral system, by X-ray diffraction in the crystal and NMR spectroscopy in solution. The results of this study are described.

Results and discussion

Syntheses and spectroscopic characterization

We have used one of the established synthetic methods for the preparation of the $M(\text{C}_4\text{H}_6)(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NR})$ complexes **6**, **8** ($M = \text{Zr}$), and **10** ($M = \text{Ti}$), namely the reaction of the respective $M(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NR})\text{Cl}_2$ complexes (**5**, **7**, and **9**) with the butadiene dianion equivalent “butadiene-magnesium”.^{1,3,11,12} Thus, treatment of $\text{Zr}(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NCMe}_3)\text{Cl}_2$ **5** with one molar equivalent of the oligomeric butadienemagnesium reagent **4** in toluene gave the $(\text{C}_4\text{H}_6)\text{zirconium}$ complex **6** in 86% yield (Scheme 2). The NMR spectra (in benzene-*d*₆ at 298 K) showed the presence of two isomers in a 85 : 15 ratio. Both have the butadiene ligand η^4 co-ordinated to zirconium, and both show an *s-cis* arrangement of the $\eta^4\text{-C}_4\text{H}_6$ moiety. From the NMR data and the result of a crystal structure analysis (see below) we assign the major isomer the structure **6A**, in which the U-shaped butadiene ligand is arranged with its “open” side toward the substituted cyclopentadienyl ligand, similarly as in the related $\text{Zr}(\eta^3\text{-C}_3\text{H}_5)(s\text{-}cis\text{-}\eta^4\text{-C}_4\text{H}_6)\text{Cp}$ reference system **3A** (“supine” orientation,¹³ see Scheme 1 and Table 1). Typically, complex **6A** shows ¹³C NMR signals of the butadiene framework at δ 122.9 (C2, C3) and 55.6 (C1, C4) and a ¹H NMR set of signals at δ 6.02 (2-H, 3-H, i.e. “H_{meso}”), 2.94 (H_{syn}), and –0.53 (H_{anti}).¹⁴ The minor isomer **6B** shows an analogous ¹H/¹³C NMR pattern, but markedly different chemical shift values, as expected [δ 111.5, 52.6 (¹³C), 4.51, 3.17, +0.61 (¹H)].

Analogous treatment of the zirconium dichloride **7**, that has a chiral 1-(1-naphthyl)ethyl substituent bonded to the nitrogen



Scheme 2

Table 1 A comparison of selected ^1H and ^{13}C NMR data of the *s-cis*- η^4 -butadiene Group 4 metal complexes **3**, **6**, **8**, and **10**^a

Complex	M	H_{meso}	H_{syn}	H_{anti}	CH	CH_2
3A ^b	Zr	5.34	2.15	-0.67	112.5	45.8
3B ^b	Zr	5.12	3.62	-1.57	99.9	48.4
6A	Zr	6.02	2.94	-0.53	122.9	55.6
6B	Zr	4.51	3.17	0.61	111.5	52.6
10A	Ti	6.33	2.84	0.04	^c	^c
10B	Ti	4.15	3.01	1.71	111.9	62.0
8A	Zr	5.73 ^d	3.01	-0.32	124.6	55.8
			2.82	-0.38	122.6	55.1

^a See Schemes 1 and 2 for molecular formula; spectra in benzene- d_6 at 298 K, unless stated otherwise, chemical shifts of the butadiene NMR signals, δ scale. ^b In toluene- d_8 at 220 K, from ref. 20. ^c Signals of the minor isomer not observed. ^d H_{meso} and H'_{meso} resonances not resolved.

center,¹⁵ with “butadienemagnesium” gave a single Zr(*s-cis*- η^4 - C_4H_6)($\text{Me}_4\text{C}_5\text{SiMe}_2\text{NR}$) product **8** that was isolated as a crystalline solid in close to 70% yield. Inspection of its NMR spectra revealed that it is of the same structural type as the major **6A** isomer described above (see Table 1). However, the presence of the chirality center at the amido nitrogen atom has led to a diastereotopic differentiation of the two vinyl subgroups of the *s-cis*- η^4 -butadiene ligand in complex **8A**. Consequently, a set of four ^{13}C NMR C_4H_6 signals are observed (δ 124.6, 122.6, 55.8 and 55.1), and the ^1H NMR signals of the “left and right” side of the butadiene ligand are clearly differentiated from each other (see Table 1).

Treatment of complex **9** with $[\text{Mg}(\text{C}_4\text{H}_6)(\text{THF})_2]_n$ gave $\text{Ti}(\text{s-cis-}\eta^4\text{-C}_4\text{H}_6)(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NCMe}_3)$ **10**. It was isolated as a mixture of the two stereoisomers **10A** and **10B** in a ratio of 5:95 in a combined yield of ca. 80% after recrystallization from pentane. Both isomers clearly contain a *s-cis*-oriented η^4 -butadiene ligand according to their NMR spectra (see Table 1). An NOE NMR experiment was inconclusive to decide between the two structural alternatives. From a comparison of the ^1H NMR data we tentatively assign the major isomer (**10B**) the structure in which the *s-cis*-butadiene ligand is oriented with its open side toward the amido ligand sector (“prone-orientation”, see Table 1, and also Fig. 3).

Crystal structure analyses

The three new complexes **6A**, **8A**, and **10B** were characterized by X-ray diffraction. Single crystals of $\text{Zr}(\text{s-cis-}\eta^4\text{-C}_4\text{H}_6)(\text{Me}_4\text{C}_5\text{SiMe}_2\text{NCMe}_3)$ **6A** were obtained from toluene solution at room temperature. The complex is C_s symmetric in the crystal (with a disordered *tert*-butyl group at the amido nitrogen atom) (Fig. 1). The Zr–N bond length is 2.103(5) Å. The Zr–N–Si bond angle amounts to 104.6(2)°. The Si–Cp vector (Si–C11 1.871(7) Å) is bent slightly from the general Cp plane in the

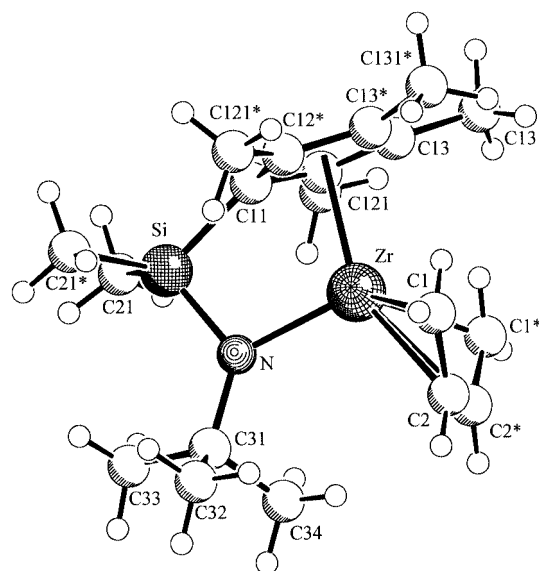


Fig. 1 Molecular structure of complex **6A** in the crystal. Selected bond lengths (Å) and angles (°): Zr–C1 2.300(5), Zr–C2 2.459(5), Zr–N 2.103(5), Zr–C11 2.406(6), Zr–C12 2.469(4), Zr–C13 2.570(4), C11–Si 1.871(7), Si–C21 1.874(5), Si–N 1.731(5), N–C31 1.499(8), C1–C2 1.429(7) and C2–C2* 1.352(11); Zr–C1–C2 78.7(3), Zr–C11–Si 89.8(2), C11–Si–N 94.2(3), Si–N–Zr 104.6(2) and C1–C2–C2* 125.9(4).

direction toward zirconium. The Cp(centroid)–Zr–N angle is found at 101.8°, which is markedly smaller than the typical Cp(centroid)–Zr–Cp(centroid) angles observed in the related Group 4 bent metallocene chemistry.¹⁶ Thus, the Zr–cyclopentadienyl carbon distances in **6A** are in rather broad range between 2.406(6) (Zr–C11), 2.469(4) (Zr–C12/C12*) and 2.570(4) Å (Zr–C13/C13*). The butadiene ligand attains the *s-cis* conformation. It is η^4 co-ordinated to zirconium, oriented with its $=\text{CH}_2$ groups pointing toward the Me_4C_5 ring (“supine” orientation), as was proposed for the major isomer of the system **6** in solution (see above). The co-ordination of the conjugated diene ligand to the central metal atom is quite unsymmetric: complex **6A** features short Zr–C1/C1* bond lengths (2.300(5) Å) that are in the typical zirconium to carbon σ -bond range, and much longer (2.459(5) Å) Zr–C2/C2* distances between the internal butadiene carbon atoms and the metal center $\Delta\text{ZrC} = d(\text{Zr–C2}) - d(\text{Zr–C1}) = 0.159$ Å. This large ΔZrC difference is typical of a σ^2, π -type structured (diene)M complex that exhibits a pronounced metallacyclic structural component, as is often found for early metal conjugated diene complexes.^{17,18} As expected, the C–C bond lengths inside the $(\text{C}_4\text{H}_6)\text{Zr}$ framework of **6A** are quite different: the central C2–C2* bond is short at 1.352(11) Å, while the adjacent C1–C2 bonds are much longer (1.429(7) Å; $\Delta\text{CC} = d(\text{C1–C2}) - d(\text{C2–C2*}) = 0.077$ Å).

Table 2 A comparison of characteristic bond lengths (in Å) of the (*s-cis*- η^4 -butadiene)M unit in a variety of Group 4 metal complexes

Complex	M	M–C1/C4	M–C2/C3	C1–C2	C2–C3	ΔZrC^a	ΔCC^b
<i>s-cis</i> - 1 ^c	Zr	2.332(5)	2.492(6)	1.391(9)	1.365(9)	0.160	0.026
3a ^d	Zr	2.360(5)	2.463(5)	1.384(7)	1.358(8)	0.103	0.026
6A	Zr	2.300(5)	2.459(5)	1.429(7)	1.352(11)	0.159	0.077
8A	Zr	2.301(3)	2.440(3)	1.443(5)	1.376(5)	0.139	0.067
		2.300(3)	2.437(3)	1.431(5)		0.137	0.055
10B	Ti	2.180(6)	2.260(7)	1.361(11)	1.40(2)	0.080	–0.039
2 ^e	Ti	2.183(6)	2.293(6)	1.397(9)	1.404(9)	0.110	–0.007

^a $\Delta ZrC = d(Zr-C2/C3) - d(Zr-C1/C4)$. ^b $\Delta CC = d(C1-C2) - d(C2-C3)$. ^c From ref. 19. ^d From ref. 20. ^e From ref. 9. Averaged values; the two sides of the conjugated diene ligand in **2** are not symmetry-equivalent in the crystal.

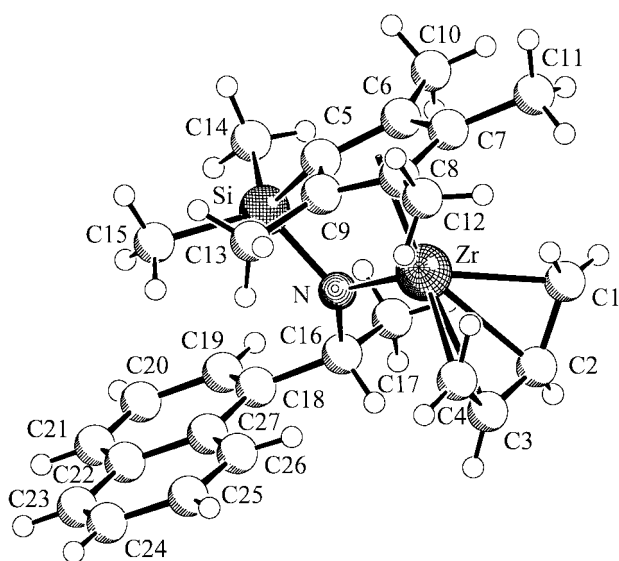


Fig. 2 Molecular structure of complex **8A**. Selected bond lengths (Å) and angles (°): Zr–C1 2.301(3), Zr–C2 2.440(3), Zr–C3 2.437(3), Zr–C4 2.300(3), Zr–N 2.086(2), Zr–C5 2.428(3), Zr–C6 2.462(3), Zr–C7 2.530(3), Zr–C8 2.534(3), Zr–C9 2.475(3), C5–Si 1.876(3), Si–C14 1.865(3), Si–C15 1.868(3), Si–N 1.731(2), N–C16 1.477(4), C1–C2 1.443(5), C2–C3 1.376(5) and C3–C4 1.431(5); Zr–C1–C2 77.6(2), Zr–C4–C3 77.8(2), Zr–C5–Si 89.2(1), C5–Si–N 94.1(1), Si–N–Zr 105.5(1), C1–C2–C3 124.7(3) and C2–C3–C4 125.4(3).

The chiral complex **8A** exhibits an analogous molecular structure (Fig. 2). Again, the isomer observed in the crystal is that which opens the *s-cis*- η^4 -butadiene ligand toward the substituted Cp* ring. In this case the presence of the chirality center C16 adjacent to nitrogen makes the remaining halves of the (Me₄C₅SiMe₂NR) ligand system structurally diastereotopic. Consequently, slightly differing Zr–C1 and Zr–C4 as well as Zr–C2 and Zr–C3 bond lengths are found for complex **8A** (see Table 2). This diastereotopic differentiation extends into the butadiene C–C bond lengths (C1–C2 1.443(5), C3–C4 1.431(5), C2–C3 1.376(5) Å) and also to the co-ordination of the Si-substituted Cp* ligand (Zr–C5 2.428(3); Zr–C6 2.462(3)/Zr–C9 2.475(3); Zr–C7 2.530(3)/Zr–C8 2.534(3) Å). It can be seen from the projection depicted in Fig. 2 that the large 1-naphthyl substituent at the chirality center C16 favors a conformational arrangement which orientates it almost parallel to the plane of the Cp* ring. In solution such a naphthyl orientation should make the methyl groups at the bridging silicon atom of the ligand framework spectroscopically very different. This effect is actually observed in the ¹H NMR spectrum of complex **8A** (Si(CH₃)₂: δ +0.48 (s, 3 H), –0.59 (s, 3 H); see for a comparison **6A** [δ +0.71 (s, 6 H)] and **6B** [δ +0.76 (s, 6 H)]).

Single crystals of the deeply colored titanium complex **10B** were obtained from pentane at –20 °C. The butadiene ligand is *s-cis*- η^4 co-ordinated to titanium (Fig. 3). In contrast to the zirconium systems (**6A**, **8A**, see above) “prone” orientation of

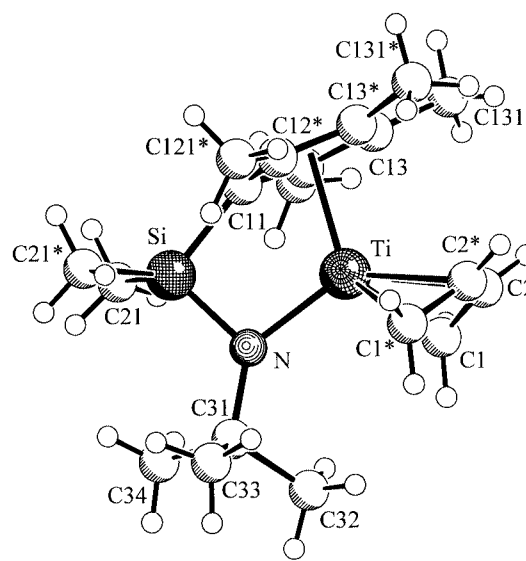


Fig. 3 Molecular structure of the titanium complex **10B**. Selected bond lengths (Å) and angles (°): Ti–C1 2.180(6), Ti–C2 2.260(7), Ti–N 1.983(5), Ti–C11 2.234(6), Ti–C12 2.323(4), Ti–C13 2.472(4), C11–Si 1.860(6), Si–C21 1.880(6), Si–N 1.740(6), N–C31 1.496(7), C1–C2 1.361(11) and C2–C2* 1.40(2); Ti–C1–C2 75.4(5), Ti–C11–Si 88.3(2), C11–Si–N 94.1(3), Si–N–Ti 100.5(2) and C1–C2–C2* 124.9(5).

the η -butadiene ligand is observed in **10B**. The Ti–C1 bond (2.180(6) Å) is only slightly shorter than the Ti–C2 linkage (2.260(7) Å) and the butadiene C–C bond lengths order is reversed (C1–C2: 1.361(11) Å, C2–C2*: 1.40(2) Å), which renders the structure of complex **10B** more related to a conventional π -butadiene metal system as compared to its zirconium congeners **6** and **8**. Related structural features were principally also observed in the previously reported complex **2**, but the differences from the zirconium complexes (**6A**, **8A**) become even more pronounced with the parent (butadiene)-titanium compound **10B**. The (C₄H₆)Ti envelope structure in **10B** is slightly less folded (angle Ti–C1–C2 in **10B**: 75.4(5)°) than in the zirconium complexes **6A** and **8A** (**6A** 78.7(3)°, **8A** 77.6(2)°). The remaining (Me₄C₅SiMe₂NCMe₃)Ti framework is similar to that of the related zirconium complexes **6A** and **8A** (**10B**, angle Si–N–Ti 100.5(2)°; **6A**, angle Si–N–Zr 104.6(2)°).

The Group 4 metallocenes exhibit a unique MO scheme²¹ that is responsible for the unusual bonding features of both the (*s-trans*-) and the (*s-cis*- η^4 -conjugated diene) M^{IV}Cp₂ systems, the latter in the case of zirconium and hafnium being characterized by a pronounced metallacyclic σ^2, π -type bonding geometry. The silylene-bridged Cp-amido Group 4 metal frameworks have a markedly different molecular orbital arrangement,²² nevertheless their *s-cis*- η^4 -butadiene complexes show pronounced similarities in their typical bonding features with the (C₄H₆)M moieties of the respective bent metallocene systems (aside from the fact that the *s-trans*- η^4 -diene isomers have not been observed so far for the Cp-amido half-sandwich systems).

This is illustrated by comparing the respective structural parameters of the series of (*s-cis*- η^4 -C₄H₆) Group 4 metal complexes compiled in Table 2. These observed structural analogies emphasize the chemical similarities between the Group 4 bent metallocenes and the respective Cp-amido complexes as has been noted in their related behavior as components of active homogeneous Ziegler catalysts.^{6–8}

Experimental

All reactions were carried out under argon using Schlenk-type glassware or in a glove-box. Solvents, including deuteriated solvents used for the spectroscopic characterization, were dried and distilled under argon prior to use. For additional general information, including a list of spectrometers and equipment used for the physical characterization of the complexes, see *e.g.* ref. 5; for a description of the specific NMR experiments used, see ref. 23. The butadienemagnesium reagent **4**^{3,11} and the starting materials **5**, **7**, and **9** were prepared analogously to published procedures.^{6,7,15}

Preparations

Group 4 metal (C₄H₆)(Me₄C₅SiMe₂NR) metal complexes: general procedure. To a solid mixture of *ca.* 10 mmol of the M(Me₄C₅SiMe₂NR)Cl₂ starting material with 1.1 molar equivalents of **4** was added slowly *ca.* 100 mL of toluene at -78°C . The mixture was allowed to warm to room temperature with stirring during 6 h and then stirred for 6 h at ambient temperature. The precipitated magnesium chloride was removed by filtration and washed twice with toluene (20 mL). The combined organic solutions were concentrated *in vacuo* until crystallization of the product set in. The solid was redissolved by warming the mixture to 45°C for *ca.* 30 min then crystallized or precipitated at -20°C . It was collected by filtration, washed with pentane (10 mL) and dried *in vacuo*. Concentration of the mother-liquor *in vacuo* and repetition of the crystallization process furnished additional clean product fractions.

Zr(*s-cis*- η^4 -C₄H₆)(Me₄C₅SiMe₂NCMe₃) **6.** Reaction of 5.77 g (14.0 mmol) of complex **5** with 3.46 g (15.5 mmol) of **4** as described above gave 4.74 g (86%) of the **6A/6B** (85:15) mixture of isomers as a red crystalline solid, mp 177°C (Found: C, 57.32; H, 8.43; N, 3.64%. C₁₉H₃₃NSiZr requires C, 57.81; H, 8.43; N, 3.55%). $\tilde{\nu}/\text{cm}^{-1}$ (KBr) 2974, 1460, 1384, 1364, 1322, 1247, 1199, 1020 and 836.

Isomer **6A**: δ_{H} (benzene-*d*₆, 298 K, 600 MHz) 6.02 (m, 2 H, H_{meso}), 2.94 (m, 2 H, H_{syn}), 2.36 (s, 6 H, α -C₅(CH₃)₄), 1.54 (s, 6 H, β -C₅(CH₃)₄), 0.91 (s, 9 H, C(CH₃)₃), 0.71 (s, 6 H, Si(CH₃)₂) and -0.53 (m, 2 H, H_{anti}). δ_{C} (benzene-*d*₆, 298 K, 150.8 MHz) 124.9, 124.4 (each C, α - and β -C₅(CH₃)₄), 122.9 (CH, butadiene CH), 103.0 (C, *ipso*-C₅(CH₃)₄), 56.7 (C, C(CH₃)₃), 55.6 (CH₂, butadiene CH₂), 36.3 (CH₃, C(CH₃)₃), 15.0 (CH₃, α -C₅(CH₃)₄), 11.2 (CH₃, β -C₅(CH₃)₄) and 8.1 (CH₃, Si(CH₃)₂). Gradient pulsed correlation spectroscopy (GCOSY): $\delta_{\text{C}}/\delta_{\text{H}}$ (benzene-*d*₆, 298 K, 599.9 MHz) 6.02/2.94, -0.53 (H_{meso}/H_{syn}, H_{anti}), 2.94/6.02, -0.53 (H_{syn}/H_{meso}, H_{anti}) and -0.53 /6.02, 2.94 (H_{anti}/H_{meso}, H_{syn}). Gradient pulsed heteronuclear single quantum coherence (GHSQC): $\delta_{\text{C}}/\delta_{\text{H}}$ (benzene-*d*₆, 298 K, 599.9 MHz) 6.02/122.9 (H_{meso}/butadiene CH), 2.94/55.6 (H_{syn}/butadiene CH₂), 2.36/15.0 (α -C₅(CH₃)₄/ α -C₅(CH₃)₄), 1.54/11.2 (β -C₅(CH₃)₄/ β -C₅(CH₃)₄), 0.91/36.3 (C(CH₃)₃/C(CH₃)₃), 0.71/8.1 (Si(CH₃)₂/Si(CH₃)₂) and -0.53 /55.6 (H_{anti}/butadiene CH₂). Gradient pulsed heteronuclear multiple bond correlation (GHMBC): $\delta_{\text{C}}/\delta_{\text{H}}$ (benzene-*d*₆, 298 K, 599.9 MHz) 6.02/55.6 (H_{meso}/butadiene CH₂), 2.94/122.9 (H_{syn}/butadiene CH), 2.36/124.9, 124.4, 103.0 (α -C₅(CH₃)₄/ α - and β -C₅(CH₃)₄, *ipso*-C₅(CH₃)₄), 1.54/124.9, 124.4 (β -C₅(CH₃)₄/ α - and β -C₅(CH₃)₄), 0.91/56.7 (C(CH₃)₃/C(CH₃)₃), 0.71/103.0 (Si(CH₃)₃/*ipso*-C₅(CH₃)₄) and -0.53 /122.9 (H_{anti}/butadiene CH).

Minor isomer **6B**: δ_{H} (benzene-*d*₆, 298 K, 599.9 MHz) 4.51 (m, 2 H, H_{meso}), 3.17 (m, 2 H, H_{syn}), 2.20 (s, 6 H, α -C₅(CH₃)₄), 1.33 (s, 6 H, β -C₅(CH₃)₄), 1.10 (s, 9 H, C(CH₃)₃), 0.76 (s, 6 H, Si(CH₃)₂) and 0.61 (m, 2 H, H_{anti}). δ_{C} (benzene-*d*₆, 298 K, 150.8 MHz) 130.0, 123.0 (each C, α - and β -C₅(CH₃)₄), 111.5 (CH, butadiene CH), 98.7 (C, *ipso*-C₅(CH₃)₄), 54.9 (C, C(CH₃)₃), 52.6 (CH₂, butadiene CH₂), 35.9 (CH₃, C(CH₃)₃), 14.9 (CH₃, α -C₅(CH₃)₄), 10.8 (CH₃, β -C₅(CH₃)₄) and 7.9 (CH₃, Si(CH₃)₂). GCOSY: $\delta_{\text{C}}/\delta_{\text{H}}$ (benzene-*d*₆, 298 K, 599.9 MHz) 4.51/3.17, 0.61 (H_{meso}/H_{syn}, H_{anti}), 3.17/4.51, 0.61 (H_{syn}/H_{meso}, H_{anti}) and 0.61/4.51, 3.17 (H_{anti}/H_{meso}, H_{syn}). GHSQC: $\delta_{\text{C}}/\delta_{\text{H}}$ (benzene-*d*₆, 298 K, 599.9 MHz) 4.51/111.5 (H_{meso}/butadiene CH), 3.17/52.6 (H_{syn}/butadiene CH₂), 2.20/14.9 (α -C₅(CH₃)₄/ α -C₅(CH₃)₄), 1.33/10.8 (β -C₅(CH₃)₄/ β -C₅(CH₃)₄), 1.10/35.9 (C(CH₃)₃/C(CH₃)₃), 0.76/7.9 (Si(CH₃)₂/Si(CH₃)₂) and 0.61/52.6 (H_{anti}/butadiene CH₂). GHMBC: $\delta_{\text{C}}/\delta_{\text{H}}$ (benzene-*d*₆, 298 K, 599.9 MHz) 4.51/52.6 (H_{meso}/butadiene CH₂), 3.17/111.5 (H_{syn}/butadiene CH), 2.20/130.0, 123.0, 98.7 (α -C₅(CH₃)₄/ α - and β -C₅(CH₃)₄, *ipso*-C₅(CH₃)₄), 1.33/130.0, 123.0 (β -C₅(CH₃)₄/ α - and β -C₅(CH₃)₄), 1.10/54.9 (C(CH₃)₃/C(CH₃)₃), 0.76/98.7 (Si(CH₃)₃/*ipso*-C₅(CH₃)₄) and 0.61/111.5 (H_{anti}/butadiene CH).

Crystal data for compound 6A. Single crystals were obtained from toluene at room temperature. Formula C₁₉H₃₃NSiZr, *M* = 394.77, *a* = 10.338(2), *b* = 12.819(2), *c* = 15.032(5) Å, *V* = 1992.1(8) Å³, μ = 6.10 cm^{−1}, *Z* = 4, orthorhombic, space group *Pnma* (no. 62), λ = 0.71073 Å, *T* = 223 K, 4218 reflections collected ($-h$, $\pm k$, $-l$), 2112 independent (*R*_{int} = 0.060) and 1300 observed [*I* ≥ 2σ(*I*)], *R* = 0.040, *wR*2 = 0.096, *tert*-butyl group disordered (50:50%), refined with geometrical constraints.

Zr(*s-cis*- η^4 -C₄H₆)(Me₄C₅SiMe₂NCHMe)(1-C₁₀H₇) **8.** Treatment of 550 mg (1.08 mmol) of complex **7** (*R* enantiomer) with 264 mg (1.19 mmol) of **4** analogously as described above yielded 362 mg (68%) of complex **8A** as an orange-red solid, mp 129°C , [α]_D²⁰ = -8° (*c* = 0.013 g ml^{−1}, toluene). Complex **8A** was not obtained analytically pure (*ca.* 2% deviation in *c*), $\tilde{\nu}/\text{cm}^{-1}$ (KBr) 3060, 2955, 1502, 1457, 1254, 1247, 1095, 960, 832, 812, 805 and 786. δ_{H} (benzene-*d*₆, 298 K, 600 MHz) 7.53 (m), 7.50 (d, 3J = 8.4), 7.45 (d, 3J = 7.9) (each 1 H, naphthyl H), 7.19, 7.13 (m, each 2 H, naphthyl H), 5.73 (m, 2 H, H_{meso}), 5.17 (q, 3J = 6.7, 1 H, NCH(CH₃)(C₁₀H₇)), 3.01, 2.82 (m, each 1 H, H_{syn}), 2.34, 2.08, 1.58, 1.55 (s, each 3 H, C₅(CH₃)₄), 1.14 (d, 3J = 6.7 Hz, 3 H, NCH(CH₃)(C₁₀H₇)), 0.48 (s, 3 H, Si(CH₃)₂), -0.32 , -0.38 (m, each 1 H, H_{anti}) and -0.59 (s, 3 H, Si(CH₃)₂). δ_{C} (benzene-*d*₆, 298 K, 150.8 MHz) 124.6, 122.6 (each CH, butadiene CH), 55.8, 55.1 (each CH₂, butadiene CH₂), 54.5 (CH, NCH(CH₃)(C₁₀H₇)), 27.4 (CH₃, NCH(CH₃)(C₁₀H₇)), 15.2, 14.8, 11.2 (double intensity) (each CH₃, C₅(CH₃)₄), 6.3, 3.9 (each CH₃, Si(CH₃)₂). Naphthyl and quaternary. C₅(CH₃)₄ resonances not assigned GCOSY: $\delta_{\text{C}}/\delta_{\text{H}}$ (benzene-*d*₆, 298 K, 599.9 MHz) 7.53/7.19; 7.50/7.19; 7.45/7.13; 7.19/7.53, 7.50; 7.13/7.45 (each naphthyl H/naphthyl H), 5.73/3.01, 2.82, -0.32 , -0.38 (H_{meso}/H_{syn}, H_{anti}), 5.17/1.14 (NCH(CH₃)(C₁₀H₇)/NCH(CH₃)(C₁₀H₇)), 3.01/5.73, -0.32 ; 2.82/5.73, -0.38 (each H_{syn}/H_{meso}, H_{anti}), 1.14/5.17 (NCH(CH₃)(C₁₀H₇)/NCH(CH₃)(C₁₀H₇)), -0.32 /5.73, 3.01; and -0.38 /5.73, 2.82 (each H_{anti}/H_{meso}, H_{syn}). GHSQC: $\delta_{\text{C}}/\delta_{\text{H}}$ (benzene-*d*₆, 298 K, 253 K, 599.9 MHz) 5.73/124.6; 5.73/122.6 (each H_{meso}/butadiene CH), 5.17/54.5 (NCH(CH₃)(C₁₀H₇)/NCH(CH₃)(C₁₀H₇)), 3.01/55.1; 2.82/55.8 (each H_{syn}/butadiene CH₂), 2.34/15.2; 2.08/14.8; 1.58/11.2; 1.55/11.2 (each C₅(CH₃)₄/C₅(CH₃)₄), 1.14/27.4 (NCH(CH₃)(C₁₀H₇)/NCH(CH₃)(C₁₀H₇)), 0.48/6.3 (Si(CH₃)₂/Si(CH₃)₂), -0.32 /55.1; -0.38 /55.8 (each H_{anti}/butadiene CH₂) and -0.59 /3.9 (Si(CH₃)₂/Si(CH₃)₂).

Crystal data for complex 8A. Crystals obtained from the preparation described above were suited for structure analysis. Formula C₂₇H₃₅NSiZr, *M* = 492.87, *a* = 8.567(1), *b* = 16.693(1), *c* = 17.164(1) Å, *V* = 2454.6(4) Å³, μ = 5.10 cm^{−1}, *Z* = 4, ortho-

rhombic, space group $P2_12_12_1$ (no. 19), $\lambda = 0.71073$ Å, $T = 223$ K, 2833 reflections collected ($-h, -k, +l$), 2833 independent and 2615 observed [$I > 2\sigma(I)$], $R = 0.022$, $wR2 = 0.060$, Flack $-0.05(4)$.

Ti(s-cis- η^4 -C₆H₆)(Me₄C₅SiMe₂NCMe₃) 10. Treatment of 800 mg (2.17 mmol) of complex **9** with 531 mg (2.39 mmol) of **4** analogously as described above, followed by recrystallization from pentane, gave two product fractions of **10** in a combined yield of 620 mg (81%) as a 5:95 mixture of the supine and prone isomers **10A** and **10B**, mp 123 °C (Found: C, 64.56; H, 10.02; N, 3.92%. C₁₉H₃₃NSiTi requires C, 64.93; H, 9.46, N, 3.99%). $\tilde{\nu}/\text{cm}^{-1}$ (KBr) 2963, 1376, 1359, 1334, 1247, 1226, 1028, 923, 834, 775 and 744. **10B** (major isomer): δ_{H} (benzene- d_6 , 298 K, 600 MHz) 4.15 (m, 2 H, H_{meso}), 3.01 (m, 2 H, H_{syn}), 2.07 (s, 6 H, C₅(CH₃)₄), 1.71 (m, 2 H, H_{anti}), 1.22 (s, 6 H, C₅(CH₃)₄), 1.17 (s, 9 H, C(CH₃)₃) and 0.76 (s, 6 H, Si(CH₃)₂). δ_{C} (benzene- d_6 , 298 K, 150.8 MHz) 130.9, 123.9 (each C, α - and β -C₅(CH₃)₄), 111.9 (CH, butadiene CH), 103.6 (C, *ipso*-C₅(CH₃)₄), 62.0 (CH₂, butadiene CH₂), 57.4 (C, C(CH₃)₃), 35.0 (CH₃, C(CH₃)₃), 15.7, 11.3 (each CH₃, C₅(CH₃)₄) and 8.2 (CH₃, Si(CH₃)₂). GCOSY: $\delta_{\text{C}}/\delta_{\text{H}}$ (benzene- d_6 , 298 K, 599.9 MHz) 4.15/3.01, 1.71 ($H_{\text{meso}}/H_{\text{syn}}$, H_{anti}), 3.01/4.15, 1.71 ($H_{\text{syn}}/H_{\text{meso}}$, H_{anti}) and 1.71/4.15, 3.01 ($H_{\text{anti}}/H_{\text{meso}}$, H_{syn}). GHSQC: $\delta_{\text{C}}/\delta_{\text{H}}$ (benzene- d_6 , 298 K, 599.9 MHz) 4.15/111.9 (H_{meso} /butadiene CH), 3.01/62.0 (H_{syn} /butadiene CH₂), 2.07/15.7 (C₅(CH₃)₄/C₅(CH₃)₄), 1.71/62.0 (H_{anti} /butadiene CH₂), 1.22/11.3 (C₅(CH₃)₄/C₅(CH₃)₄), 1.17/35.0 (C(CH₃)₃/C(CH₃)₃) and 0.76/8.2 (Si(CH₃)₂/Si(CH₃)₂). Nuclear Overhauser effect difference spectroscopy (NOE-DIFF): $\delta_{\text{C}}/\delta_{\text{H}}$ (benzene- d_6 , 298 K, 599.9 MHz) irradiated at δ 4.15 (H_{meso}), response at δ 3.01 (H_{syn}), 1.71 (H_{anti}), 1.22 (C₅(CH₃)₄), 1.17 (C(CH₃)₃) and 0.76 (Si(CH₃)₂); irradiated at δ 1.17 (C(CH₃)₃), response at δ 4.15 (H_{meso}), 1.72 (H_{anti}) and 0.76 (Si(CH₃)₂). **10A** (minor isomer): only characterized by ¹H NMR because of the low equilibrium concentration. δ_{H} (benzene- d_6 , 298 K, 599.9 MHz) 6.33 (m, 2 H, H_{meso}), 2.84 (m, 2 H, H_{syn}), 2.25, 1.45 (s, each 6 H, C₅(CH₃)₄), 0.95 (s, 9 H, C(CH₃)₃), 0.72 (s, 6 H, Si(CH₃)₂) and 0.04 (m, 2 H, H_{anti}).

Crystal data for complex 10B. Crystals obtained from the preparation described above were suited for structure analysis. Formula C₁₉H₃₃NSiTi, $M = 351.45$, $a = 10.496(4)$, $b = 12.629(2)$, $c = 15.201(2)$ Å, $V = 2015.0(9)$ Å³, $\mu = 4.82$ cm⁻¹, $Z = 4$, orthorhombic, space group $Pnma$ (no. 62), $\lambda = 0.71073$ Å, $T = 223$ K, 2127 reflections collected ($-h, +k, +l$), 2127 independent and 1310 observed [$I \geq 2\sigma(I)$], $R = 0.064$, $wR2 = 0.194$, *tert*-butyl group disordered (50:50%).

Data sets were collected with Enraf-Nonius CAD4 or MACH3 diffractometers, equipped with a rotating anode generator Nonius FR591. Programs used:²⁴ data collection, EXPRESS; data reduction, MOIEN; structure solution, SHELXS 97; structure refinement, SHELXL 97; graphics (with unsystematic numbering schemes), SCHAKAL.

CCDC reference number 186/1942.

See <http://www.rsc.org/suppdata/dt/b0/b000570n/> for crystallographic files in .cif format.

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References

- G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich and C. Krüger, *J. Am. Chem. Soc.*, 1980, **102**, 6344.
- Reviews: H. Yasuda, K. Tatsumi and A. Nakamura, *Acc. Chem. Res.*, 1985, **18**, 120; G. Erker, C. Krüger and G. Müller, *Adv. Organomet. Chem.*, 1985, **24**, 1; H. Yasuda and A. Nakamura,

- Angew. Chem.*, 1987, **99**, 745; *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 723.
- G. Erker, J. Wicher, K. Engel and C. Krüger, *Chem. Ber.*, 1982, **115**, 3300; G. Erker, K. Engel, C. Krüger and A.-P. Chiang, *Chem. Ber.*, 1982, **115**, 3311; H. Yasuda, Y. Kajihara, K. Mashima, K. Nagasuna, K. Lee and A. Nakamura, *Organometallics*, 1982, **1**, 388; Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, K. Nagasuna, H. Yasuda and A. Nakamura, *J. Chem. Soc., Chem. Commun.*, 1982, 191; T. Okamoto, N. Kanehisa, A. Nakamura, H. Yasuda, Y. Kai and N. Kasai, *J. Am. Chem. Soc.*, 1988, **110**, 5008; see also: H. C. Strauch, G. Erker and R. Fröhlich, *Organometallics*, 1998, **17**, 5746 and references cited therein.
 - Reviews: H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, 1980, **18**, 99; R. F. Jordan, *Adv. Organomet. Chem.*, 1991, **32**, 325; T. J. Marks, *Acc. Chem. Res.*, 1992, **25**, 57; M. Aulbach and F. Küber, *Chem. Unserer Zeit*, 1994, **28**, 197; H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. Waymouth, *Angew. Chem.*, 1995, **107**, 1255; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143; M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255.
 - B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich and S. Kotila, *Angew. Chem.*, 1995, **107**, 1867; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1755; B. Temme, J. Karl and G. Erker, *Chem. Eur. J.*, 1996, **2**, 919; J. Karl, G. Erker and R. Fröhlich, *J. Am. Chem. Soc.*, 1997, **119**, 11165; G. J. Pindado, M. Thornton-Pett, M. Bowkamp, A. Meetsma, B. Hessen and M. Bochmann, *Angew. Chem.*, 1997, **109**, 2457; *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2358; J. Karl, G. Erker and R. Fröhlich, *J. Organomet. Chem.*, 1997, **535**, 59; J. Karl and G. Erker, *Chem. Ber./Recueil*, 1997, **130**, 1261; J. Karl, M. Dahlmann, G. Erker and K. Bergander, *J. Am. Chem. Soc.*, 1998, **120**, 5643; M. Dahlmann, G. Erker, M. Nissinen and R. Fröhlich, *J. Am. Chem. Soc.*, 1999, **121**, 2820.
 - (a) P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1994, **116**, 4623; W. E. Piers, P. J. Shapiro, E. E. Bunel and J. E. Bercaw, *Synlett*, 1990, **2**, 74; E. E. Bunel, B. J. Burger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1988, **110**, 976; P. J. Shapiro, E. E. Bunel, W. P. Schaefer and J. E. Bercaw, *Organometallics*, 1990, **9**, 867; (b) J. C. Stevens, F. J. Timmers, D. R. Wilson, G. F. Schmidt, P. N. Nickias, R. K. Rosen, G. W. Knight and S. Lai, *Eur. Pat. Appl.*, EP 416815-A2, 1991 (Dow Chemical Co.); J. M. Canich, *Eur. Pat. Appl.*, EP 420436-A1, 1991 (Exxon Chemical Co.); J. M. Canich, G. G. Hlatky and H. W. Turner, *PCT Appl.*, WO 92-00333, 1992.
 - Review: A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587.
 - For C₁-bridged analogues see e.g.: L. Duda, G. Erker, R. Fröhlich and F. Zippel, *Eur. J. Inorg. Chem.*, 1998, 1153; A. Bertuleit, M. Koenemann, L. Duda, G. Erker and R. Fröhlich, *Top. Catal.*, 1999, **7**, 37.
 - D. D. Devore, F. J. Timmers, D. L. Hasha, R. K. Rosen, T. J. Marks, P. A. Deck and C. L. Stern, *Organometallics*, 1995, **14**, 3132.
 - M. Dahlmann, Doctoral Dissertation, Universität Münster, 1999.
 - H. E. Ramsden, *US Pat.*, 3388179, 1968; Y. Nakano, K. Natsukawa, H. Yasuda and H. Tani, *Tetrahedron Lett.*, 1972, 2833; K. Fujita, Y. Ohnuma, H. Yasuda and H. Tani, *J. Organomet. Chem.*, 1976, **113**, 201; H. Yasuda, Y. Nakano, K. Natsukawa and H. Tani, *Macromolecules*, 1978, **11**, 586; Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, H. Yasuda and A. Nakamura, *Chem. Lett.*, 1982, 1277. See also: S. Datta, S. S. Wreford, R. P. Beatty and T. J. McNeese, *J. Am. Chem. Soc.*, 1979, **101**, 1053; S. S. Wreford and J. F. Whitney, *Inorg. Chem.*, 1981, **20**, 3918.
 - P. Czisch, G. Erker, H.-G. Korth and R. Sustmann, *Organometallics*, 1984, **3**, 945; R. Beckhaus and K.-H. Thiele, *J. Organomet. Chem.*, 1986, **317**, 23; U. Böhme, K.-H. Thiele and A. Rufinska, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1455.
 - For "prone" and "supine" definition see: H. Yasuda, K. Tatsumi, T. Okamoto, K. Mashima, K. Lee, A. Nakamura, Y. Kai, N. Kanehisa and N. Kasai, *J. Am. Chem. Soc.*, 1985, **107**, 2410.
 - For H_{meso} , H_{syn} , H_{anti} definition see: E. G. Hoffmann, R. Kallweit, G. Schroth, K. Seevogel, W. Stempfle and G. Wilke, *J. Organomet. Chem.*, 1975, **97**, 183.
 - The complex $\text{Zr}[\eta^5\text{Me}_4\text{C}_5\text{SiMe}_2\text{NCHMe}(\text{1-C}_{10}\text{H}_7)]\text{Cl}_2$ **7** was synthesized for the first time following the general route described in ref. 6(b) using 1-naphthylethylamine as reagent to form the amido ligand.
 - D. J. Cardin, M. F. Lappert and C. L. Raston, in *Chemistry of Organo-Zirconium and -Hafnium Compounds*, Wiley, New York, 1986; *Comprehensive Organometallic Chemistry*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 4.
 - G. Erker, K. Engel, C. Krüger and G. Müller, *Organometallics*, 1984, **3**, 128; C. Krüger, G. Müller, G. Erker, U. Dorf and K. Engel, *Organometallics*, 1985, **4**, 215; G. Erker, T. Mühlenbernd, R. Benn,

- A. Rufinska, Y.-H. Tsay and C. Krüger, *Angew. Chem.*, 1985, **97**, 336; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 321.
- 18 For related mono-Cp or Cp-free butadiene Group 4 metal complexes see e.g.: Zr, B. Hessen and J. H. Teuben, *J. Organomet. Chem.*, 1988, **358**, 135; Y. Wielstra, A. Meetsma and S. Gambarotta, *Organometallics*, 1989, **8**, 258; Y. Wielstra, S. Gambarotta and A. L. Spek, *Organometallics*, 1990, **9**, 572; M. D. Fryzuk, T. S. Haddad and S. J. Rettig, *Organometallics*, 1989, **8**, 1723; G. M. Diamond, M. L. H. Green, N. M. Walker, J. A. K. Howard and S. A. Mason, *J. Chem. Soc., Dalton Trans.*, 1992, 2641; L. Giannini, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem.*, 1994, **106**, 2279; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2204; A. Caselli, L. Giannini, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 1997, **16**, 5457; Ti, M. Mena, P. Royo, R. Serrano, M. A. Pellinghelli and A. Tiripicchio, *Organometallics*, 1988, **7**, 258; *Organometallics*, 1989, **8**, 476; H. Yamamoto, H. Yasuda, K. Tatsumi, K. Lee, A. Nakamura, J. Chen, Y. Kai and N. Kasai, *Organometallics*, 1989, **8**, 105; F. G. N. Cloke and A. McCamley, *J. Chem. Soc., Chem. Commun.*, 1991, 1470; G. J. Balaich, J. E. Hill, S. A. Waratuke, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1995, **14**, 656; M. D. Spencer, S. R. Wilson and G. S. Girolami, *Organometallics*, 1997, **16**, 3055.
- 19 T. Bürgi, H. Berke, D. Wingbermühle, C. Psiorz, R. Noe, T. Fox, M. Knickmeier, M. Berlekamp, R. Fröhlich and G. Erker, *J. Organomet. Chem.*, 1995, **497**, 149.
- 20 G. Erker, K. Berg, C. Krüger, G. Müller, K. Angermund, R. Benn and G. Schroth, *Angew. Chem.*, 1984, **96**, 445; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 455.
- 21 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729; J. C. Green, *Chem. Soc. Rev.*, 1998, **27**, 263.
- 22 T. K. Woo, P. M. Margl, J. C. W. Lohrenz, P. E. Blöchl and T. Ziegler, *J. Am. Chem. Soc.*, 1996, **118**, 13021; T. K. Woo, L. Fan and T. Ziegler, *Organometallics*, 1994, **13**, 2252; L. Fan, D. Harrison, T. K. Woo and T. Ziegler, *Organometallics*, 1995, **14**, 2018; T. K. Woo, P. M. Margl, T. Ziegler and P. E. Blöchl, *Organometallics*, 1997, **16**, 3454.
- 23 S. Braun, H.-O. Kalinowski and S. Berger, in *150 and More Basic NMR Experiments*, VCH, Weinheim, 1998 and references cited therein.
- 24 EXPRESS, Nonius B.V., Delft, 1994; MOLEN, K. Fair, Enraf Nonius B.V., Delft, 1990; SHELXS 97, G. M. Sheldrick, *Acta Crystallogr.*, 1990, **46**, 467; SHELXL 97, Universität Göttingen, 1997, SCHAKAL, E. Keller, Universität Freiburg, 1997.