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Structural characterization of M(s-*cis*-η^4-C_4H_6)($Me_4C_5SiMe_2NR$) (M = Ti or Zr, R = CMe_3 or CHCMe(1-$C_{10}H_7$)

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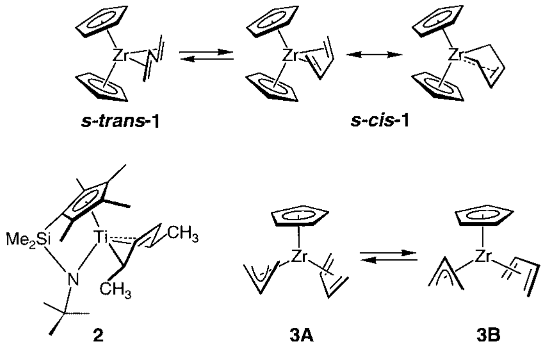
Treatment of M($Me_4C_5SiMe_2NR$)Cl_2 [M = Zr, R = CMe_3 or CHMe(1-$C_{10}H_7$): M = Ti, R = CMe_3] with "butadienemagnesium" gave the respective M(s-*cis*-η^4-C_4H_6)($Me_4C_5SiMe_2NR$) complexes in good yield. In solution, the parent zirconium system Zr(s-*cis*-η^4-C_4H_6)($Me_4C_5SiMe_2NCMe_3$) forms 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 Ti(s-*cis*-η^4-C_4H_6)($Me_4C_5SiMe_2NCMe_3$) case (**A** : **B** = 5 : 95). Complex Zr[s-*cis*-η^4-C_4H_6){$Me_4C_4SiMe_2NCHMe$(1-$C_{10}H_7$)] 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-*cis*-η^4-C_4H_6)(^RCp)$_2$ (M = 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 become of wide interest because of their use in homogeneous Ziegler catalysis,[4] and so have the Zr(η-C_4H_6)(^RCp)$_2$ complexes which served as components for the generation of active single component metallocene Ziegler catalyst systems.[5] The related ($Me_4C_5SiMe_2NR$)-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}(conjugated diene)($Me_4C_5SiMe_2NR$) example so far to the best of our knowledge, namely of the Ti(s-*cis*-*E*,*E*-C_6H_{10})-($Me_4C_5SiMe_2NCMe_3$) complex **2**.[9] We have prepared a series of butadiene complexes of "constrained geometry" frameworks, including the parent complexes M(C_4H_6)($Me_4C_5SiMe_2NCMe_3$) (M = 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.



Scheme 1

Results and discussion

Syntheses and spectroscopic characterization

We have used one of the established synthetic methods for the preparation of the M(C_4H_6)($Me_4C_5SiMe_2NR$) complexes **6**, **8** (M = Zr), and **10** (M = Ti), namely the reaction of the respective M($Me_4C_5SiMe_2NR$)Cl_2 complexes (**5**, **7**, and **9**) with the butadiene dianion equivalent "butadiene-magnesium".[1,3,11,12] Thus, treatment of Zr($Me_4C_5SiMe_2NCMe_3$)Cl_2 **5** with one molar equivalent of the oligomeric butadienemagnesium reagent **4** in toluene gave the (C_4H_6)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 η^4-C_4H_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 Zr(η^3-C_3H_5)(s-*cis*-η^4-C_4H_6)Cp reference system **3A** ("supine" orientation,[13] see Scheme 1 and Table 1). Typically, complex **6A** shows ^{13}C 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 $^1H/^{13}C$ NMR pattern, but markedly different chemical shift values, as expected [δ 111.5, 52.6 (^{13}C), 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

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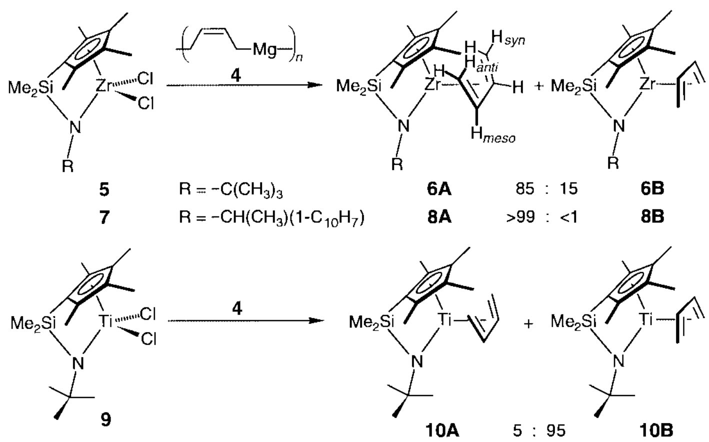

Scheme 2

Table 1 A comparison of selected ^{1}H 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)($Me_4C_5SiMe_2NR$) 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 ^{1}H 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 $[Mg(C_4H_6)(THF)_2]_n$ gave Ti(s-*cis*-η^4-C_4H_6)($Me_4C_5SiMe_2NCMe_3$) **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 ^{1}H 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 Zr(s-*cis*-η^4-C_4H_6)($Me_4C_5SiMe_2NCMe_3$) **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 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 $=CH_2$ 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 $\Delta ZrC = d(Zr–C2) - d(Zr–C1) = 0.159$ 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 (C_4H_6)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; $\Delta CC = d(C1–C2) - d(C2–C2^*) = 0.077$ Å).

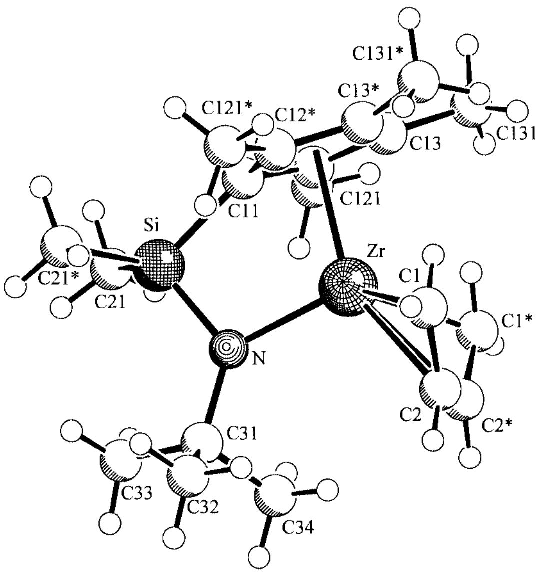

Fig. 1 Molecular structure of complex **6A** in the crystal. Selected bond lengths (Å) and angles (°): Zr–C1 2.300(5), Zr–C2 2.459(5), Zr–N 2.103(5), Zr–C11 2.406(6), Zr–C12 2.469(4), Zr–C13 2.570(4), C11–Si 1.871(7), Si–C21 1.874(5), Si–N 1.731(5), N–C31 1.499(8), C1–C2 1.429(7) and C2–C2* 1.352(11);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

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]
s-*cis*-**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] ΔZrC = *d*(Zr–C2/C3)–*d*(Zr–C1/C4). [b] ΔCC = *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.

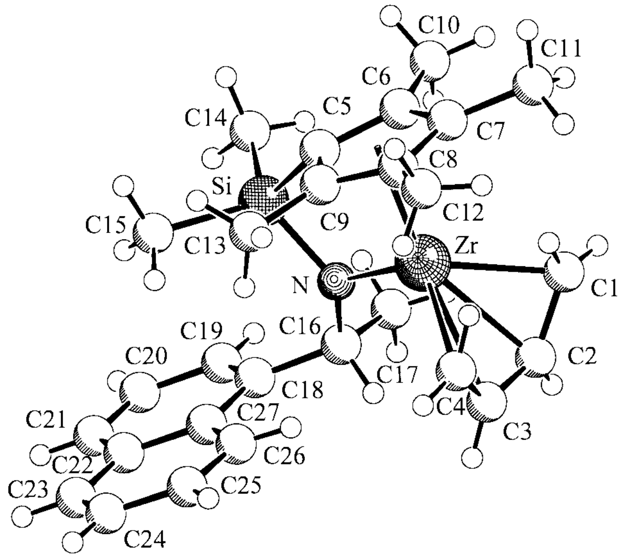

Fig. 2 Molecular structure of complex **8A**. Selected bond lengths (Å) and angles (°): Zr–C1 2.301(3), Zr–C2 2.440(3), Zr–C3 2.437(3), Zr–C4 2.300(3), Zr–N 2.086(2), Zr–C5 2.428(3), Zr–C6 2.462(3), Zr–C7 2.530(3), Zr–C8 2.534(3), Zr–C9 2.475(3), C5–Si 1.876(3), Si–C14 1.865(3), Si–C15 1.868(3), Si–N 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).

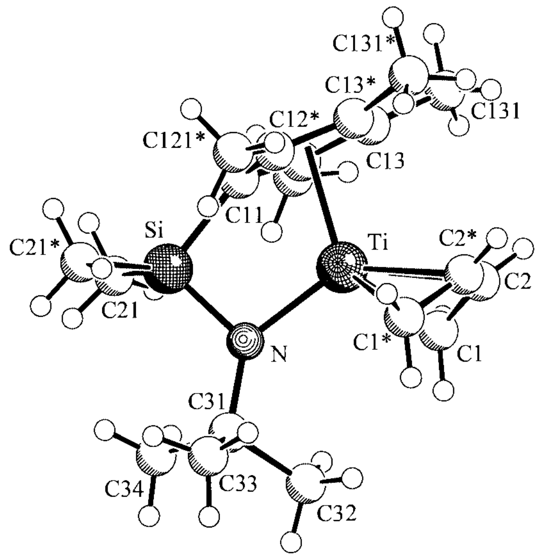

Fig. 3 Molecular structure of the titanium complex **10B**. Selected bond lengths (Å) and angles (°): Ti–C1 2.180(6), Ti–C2 2.260(7), Ti–N 1.983(5), Ti–C11 2.234(6), Ti–C12 2.323(4), Ti–C13 2.472(4), C11–Si 1.860(6), Si–C21 1.880(6), Si–N 1.740(6), N–C31 1.496(7), C1–C2 1.361(11) and C2–C2* 1.40(2); 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 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 ($Me_4C_5SiMe_2NR$) 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 ^{R}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 ^{1}H NMR spectrum of complex **8A** ($Si(CH_3)_2$: 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 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 (C_4H_6)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 ($Me_4C_5SiMe_2NCMe_3$)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 scheme[21] that is responsible for the unusual bonding features of both the (s-*trans*-) and the (s-*cis*-η^4-conjugated diene) $M^{IV}Cp_2$ 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 (C_4H_6)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-C_4H_6) 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 (C_4H_6)($Me_4C_5SiMe_2NR$) metal complexes: general procedure. To a solid mixture of *ca.* 10 mmol of the $M(Me_4C_5SiMe_2NR)Cl_2$ 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-C_4H_6)($Me_4C_5SiMe_2NCMe_3$) 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%. $C_{19}H_{33}NSiZr$ requires C, 57.81; H, 8.43; N, 3.55%). $\tilde{\nu}$/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-$C_5(CH_3)_4$), 1.54 (s, 6 H, β-$C_5(CH_3)_4$), 0.91 (s, 9 H, $C(CH_3)_3$), 0.71 (s, 6 H, $Si(CH_3)_2$) 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-$\mathit{C}_5(CH_3)_4$), 122.9 (CH, butadiene CH), 103.0 (C, *ipso*-$\mathit{C}_5(CH_3)_4$), 56.7 (C, $\mathit{C}(CH_3)_3$), 55.6 (CH_2, butadiene CH_2), 36.3 (CH_3, $C(\mathit{C}H_3)_3$), 15.0 (CH_3, α-$C_5(\mathit{C}H_3)_4$), 11.2 (CH_3, β-$C_5(\mathit{C}H_3)_4$) and 8.1 (CH_3, $Si(CH_3)_2$). Gradient pulsed correlation spectroscopy (GCOSY): δ_C/δ_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): δ_C/δ_H (benzene-d_6, 298 K, 599.9 MHz) 6.02/122.9 (H_{meso}/butadiene CH), 2.94/55.6 (H_{syn}/butadiene CH_2), 2.36/15.0 (α-$C_5(C\mathit{H}_3)_4$/α-$C_5(\mathit{C}H_3)_4$), 1.54/11.2 (β-$C_5(C\mathit{H}_3)_4$/β-$C_5(\mathit{C}H_3)_4$), 0.91/36.3 ($C(C\mathit{H}_3)_3$/$C(\mathit{C}H_3)_3$), 0.71/8.1 ($Si(C\mathit{H}_3)_2$/$Si(\mathit{C}H_3)_2$) and −0.53/55.6 (H_{anti}/butadiene $\mathit{C}H_2$). Gradient pulsed heteronuclear multiple bond correlation (GHMBC): δ_C/δ_H (benzene-d_6, 298 K, 599.9 MHz) 6.02/55.6 (H_{meso}/butadiene $\mathit{C}H_2$), 2.94/122.9 (H_{syn}/butadiene $\mathit{C}H$), 2.36/124.9, 124.4, 103.0 (α-$C_5(C\mathit{H}_3)_4$/α- and β-$\mathit{C}_5(CH_3)_4$, *ipso*-$\mathit{C}_5(CH_3)_4$), 1.54/124.9, 124.4 (β-$C_5(C\mathit{H}_3)_4$/α- and β-$\mathit{C}_5(CH_3)_4$), 0.91/56.7 ($C(C\mathit{H}_3)_3$/$\mathit{C}(CH_3)_3$), 0.71/103.0 ($Si(C\mathit{H}_3)_3$/*ipso*-$\mathit{C}_5(CH_3)_4$) and −0.53/122.9 (H_{anti}/butadiene $\mathit{C}H$).

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-$C_5(CH_3)_4$), 1.33 (s, 6 H, β-$C_5(CH_3)_4$), 1.10 (s, 9 H, $C(CH_3)_3$), 0.76 (s, 6 H, $Si(CH_3)_2$) 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-$\mathit{C}_5(CH_3)_4$), 111.5 (CH, butadiene CH), 98.7 (C, *ipso*-$\mathit{C}_5(CH_3)_4$), 54.9 (C, $\mathit{C}(CH_3)_3$), 52.6 (CH_2, butadiene CH_2), 35.9 (CH_3, $C(\mathit{C}H_3)_3$), 14.9 (CH_3, α-$C_5(\mathit{C}H_3)_4$), 10.8 (CH_3, β-$C_5(\mathit{C}H_3)_4$) and 7.9 (CH_3, $Si(CH_3)_2$). GCOSY: δ_C/δ_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: δ_C/δ_H (benzene-d_6, 298 K, 599.9 MHz) 4.51/111.5 (H_{meso}/butadiene $\mathit{C}H$), 3.17/52.6 (H_{syn}/butadiene $\mathit{C}H_2$), 2.20/14.9 (α-$C_5(C\mathit{H}_3)_4$/α-$C_5(\mathit{C}H_3)_4$), 1.33/10.8 (β-$C_5(C\mathit{H}_3)_4$/β-$C_5(\mathit{C}H_3)_4$), 1.10/35.9 ($C(C\mathit{H}_3)_3$/$C(\mathit{C}H_3)_3$), 0.76/7.9 ($Si(C\mathit{H}_3)_2$/$Si(\mathit{C}H_3)_2$) and 0.61/52.6 (H_{anti}/butadiene $\mathit{C}H_2$). GHMBC: δ_C/δ_H (benzene-d_6, 298 K, 599.9 MHz) 4.51/52.6 (H_{meso}/butadiene $\mathit{C}H_2$), 3.17/111.5 (H_{syn}/butadiene $\mathit{C}H$), 2.20/130.0, 123.0, 98.7 (α-$C_5(C\mathit{H}_3)_4$/α- and β-$\mathit{C}_5(CH_3)_4$, *ipso*-$\mathit{C}_5(CH_3)_4$), 1.33/130.0, 123.0 (β-$C_5(C\mathit{H}_3)_4$/α- and β-$\mathit{C}_5(CH_3)_4$), 1.10/54.9 ($C(C\mathit{H}_3)_3$/$\mathit{C}(CH_3)_3$), 0.76/98.7 ($Si(C\mathit{H}_3)_3$/*ipso*-$\mathit{C}_5(CH_3)_4$) and 0.61/111.5 (H_{anti}/butadiene $\mathit{C}H$).

*Crystal data for compound **6A**.* Single crystals were obtained from toluene at room temperature. Formula $C_{19}H_{33}NSiZr$, $M = 394.77$, $a = 10.338(2)$, $b = 12.819(2)$, $c = 15.032(5)$ Å, $V = 1992.1(8)$ Å^3, $\mu = 6.10$ cm^{-1}, $Z = 4$, orthorhombic, space group *Pnma* (no. 62), $\lambda = 0.71073$ Å, $T = 223$ K, 4218 reflections collected ($-h$, $\pm k$, $-l$), 2112 independent ($R_{int} = 0.060$) and 1300 observed [$I \ge 2\sigma(I)$], $R = 0.040$, $wR2 = 0.096$, *tert*-butyl group disordered (50 : 50%), refined with geometrical constraints.

Zr(s-*cis*-η^4-C_4H_6)[($Me_4C_5SiMe_2NCHMe$)(1-$C_{10}H_7$)] 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, $[\alpha]_{20}^{D} = -8°$ ($c = 0.013$ g ml^{-1}, toluene). Complex **8A** was not obtained analytically pure (*ca.* 2% deviation in *c*), $\tilde{\nu}$/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, $NC\mathit{H}(CH_3)(C_{10}H_7)$), 3.01, 2.82 (m, each 1 H, H_{syn}), 2.34, 2.08, 1.58, 1.55 (s, each 3 H, $C_5(CH_3)_4$), 1.14 (d, $^3J = 6.7$ Hz, 3 H, $NCH(C\mathit{H}_3)(C_{10}H_7)$), 0.48 (s, 3 H, $Si(CH_3)_2$), −0.32, −0.38 (m, each 1 H, H_{anti}) and −0.59 (s, 3 H, $Si(CH_3)_2$). δ_C (benzene d_6, 298 K, 150.8 MHz) 124.6, 122.6 (each CH, butadiene CH), 55.8, 55.1 (each CH_2, butadiene CH_2), 54.5 (CH, $N\mathit{C}H(CH_3)(C_{10}H_7)$), 27.4 ($CH_3$, $NCH(\mathit{C}H_3)(C_{10}H_7)$), 15.2, 14.8, 11.2 (double intensity) (each CH_3, $C_5(\mathit{C}H_3)_4$), 6.3, 3.9 (each CH_3, $Si(CH_3)_2$). Naphthyl and quaternary. $\mathit{C}_5(CH_3)_4$ resonances not assigned GCOSY: δ_C/δ_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 ($NC\mathit{H}(CH_3)(C_{10}H_7)$/$NCH(C\mathit{H}_3)(C_{10}H_7)$), 3.01/5.73, −0.32; 2.82/5.73, −0.38 (each H_{syn}/H_{meso}, H_{anti}), 1.14/5.17 ($NC\mathit{H}(CH_3)(C_{10}H_7)$/$NCH(C\mathit{H}_3)(C_{10}H_7)$), −0.32/5.73, 3.01; and −0.38/5.73, 2.82 (each H_{anti}/H_{meso}, H_{syn}). GHSQC: δ_C/δ_H (benzene-d_6, 298 K, 253 K, 599.9 MHz) 5.73/124.6; 5.73/122.6 (each H_{meso}/butadiene $\mathit{C}H$), 5.17/54.5 ($NC\mathit{H}(CH_3)(C_{10}H_7)$/$N\mathit{C}H(CH_3)(C_{10}H_7)$), 3.01/55.1; 2.82/55.8 (each H_{syn}/butadiene $\mathit{C}H_2$), 2.34/15.2; 2.08/14.8; 1.58/11.2; 1.55/11.2 (each $C_5(C\mathit{H}_3)_4$/$C_5(\mathit{C}H_3)_4$), 1.14/27.4 ($NCH(C\mathit{H}_3)(C_{10}H_7)$/$NCH(\mathit{C}H_3)(C_{10}H_7)$), 0.48/6.3 ($Si(C\mathit{H}_3)_2$/$Si(\mathit{C}H_3)_2$), −0.32/55.1; −0.38/55.8 (each H_{anti}/butadiene $\mathit{C}H_2$) and −0.59/3.9 ($Si(C\mathit{H}_3)_2$/$Si(\mathit{C}H_3)_2$).

*Crystal data for complex **8A**.* Crystals obtained from the preparation described above were suited for structure analysis. Formula $C_{27}H_{35}NSiZr$, $M = 492.87$, $a = 8.567(1)$, $b = 16.693(1)$, $c = 17.164(1)$ Å, $V = 2454.6(4)$ Å^3, $\mu = 5.10$ cm^{-1}, $Z = 4$, orthorhombic, 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-C_4H_6)($Me_4C_5SiMe_2NCMe_3$) 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%. $C_{19}H_{33}NSiTi$ requires C, 64.93; H, 9.46, N, 3.99%). $\tilde{\nu}$/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, $C_5(CH_3)_4$), 1.71 (m, 2 H, H_{anti}), 1.22 (s, 6 H, $C_5(CH_3)_4$), 1.17 (s, 9 H, $C(CH_3)_3$) and 0.76 (s, 6 H, $Si(CH_3)_2$). δ_C (benzene-d_6, 298 K, 150.8 MHz) 130.9, 123.9 (each C, α- and β-$C_5(CH_3)_4$), 111.9 (CH, butadiene CH), 103.6 (C, *ipso*-$C_5(CH_3)_4$), 62.0 (CH_2, butadiene CH_2), 57.4 (C, $C(CH_3)_3$), 35.0 (CH_3, $C(CH_3)_3$), 15.7, 11.3 (each CH_3, $C_5(CH_3)_4$) and 8.2 (CH_3, $Si(CH_3)_2$). GCOSY: δ_C/δ_H (benzene-d_6, 298 K, 599.9 MHz) 4.15/3.01, 1.71 (H_{meso}/H_{syn}, H_{anti}), 3.01/4.15, 1.71 (H_{syn}/H_{meso}, H_{anti}) and 1.71/4.15, 3.01 (H_{anti}/H_{meso}, H_{syn}). GHSQC: δ_C/δ_H (benzene-d_6, 298 K, 599.9 MHz) 4.15/111.9 (H_{meso}/butadiene CH), 3.01/62.0 (H_{syn}/butadiene CH_2), 2.07/15.7 ($C_5(CH_3)_4/C_5(CH_3)_4$), 1.71/62.0 (H_{anti}/butadiene CH_2), 1.22/11.3 ($C_5(CH_3)_4/C_5(CH_3)_4$), 1.17/35.0 ($C(CH_3)_3/C(CH_3)_3$) and 0.76/8.2 ($Si(CH_3)_2/Si(CH_3)_2$). Nuclear Overhauser effect difference spectroscopy (NOE-DIFF): δ_C/δ_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 ($C_5(CH_3)_4$), 1.17 ($C(CH_3)_3$) and 0.76 ($Si(CH_3)_2$); irradiated at δ 1.17 ($C(CH_3)_3$), response at δ 4.15 (H_{meso}), 1.72 (H_{anti}) and 0.76 ($Si(CH_3)_2$). **10A** (minor isomer): only characterized by ^{1}H 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, $C_5(CH_3)_4$), 0.95 (s, 9 H, $C(CH_3)_3$), 0.72 (s, 6 H, $Si(CH_3)_2$) 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 $C_{19}H_{33}NSiTi$, $M = 351.45$, $a = 10.496(4)$, $b = 12.629(2)$, $c = 15.201(2)$ Å, $V = 2015.0(9)$ Å^3, $\mu = 4.82$ 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, MOlEN; 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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