ansa-Titanocene and -Zirconocene η^2-Alkyne Complexes – Synthesis, Spectral Characteristics, and X-ray Crystal Structure

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The reduction of the complex $[(\eta^5\text{-}C_5H_4)\text{-}ansa\text{-}(\eta^5\text{-}C_5H_4)]TiCl_2$ with magnesium in the presence of $Me_3SiC_2SiMe_3$ in THF at room temperature gives the *ansa*-titanocene alkyne complex $[(\eta^5\text{-}C_5H_4)\text{-}ansa\text{-}(\eta^5\text{-}C_5H_4)]Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (*ansa* = $Me_2Si{-}O{-}SiMe_2$, **1**). The similar pyridine-stabilized zirconium complexes could be obtained by analogous reactions and addition of pyridine: $[(\eta^5\text{-}C_5H_4)\text{-}ansa\text{-}(\eta^5\text{-}C_5H_4)]Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (*ansa* = $Me_2Si{-}O{-}SiMe_2$, L = pyridine: **2**; *ansa* = $SiMe_2$, L = pyridine: **3**). All complexes were characterized by spectroscopic methods. An X-ray structure determination of complex **3** was conducted, and the data were compared to those of the complexes *rac*-(EBHI)Zr(L)(η^2-$Me_3SiC_2SiMe_3$) [L = (*S*)-(–)-nicotine: **6**, EBHI = ethylenebis(tetrahydroindenyl)] and $Cp_2Zr(py)(Me_3SiC_2SiMe_3)$.

Alkyne complexes of group-4 metallocenes can be used synthetically for many purposes[1a–h]. Recently, we obtained such titanocene complexes of silylalkynes without additional ligands, e.g. $Cp_2Ti(\eta^2\text{-}PhC_2SiMe_3)$[2] and also zirconocene complexes with additional ligands like $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (L = thf[4a], pyridine[4b]). In this series the complexes of bis(trimethylsilyl)acetylene are excellent preparative sources for the generation of "Cp_2M" under smooth conditions in reactions with alkynes[3], butadiynes[5a,5b,5c], or acetylenedicarboxylates[5d].

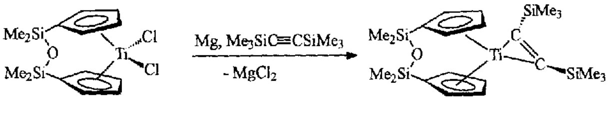
A large number of chiral group-4 *ansa*-metallocene complexes which are important in stereoselective synthesis via organometallic compounds were synthesized[6a]. These complexes were used as catalysts for many enantioselective reactions[6a,b], frequently in the polymerization of olefins to highly isotactic polymers[6c]. Among them stable alkyne complexes without additional ligands $[(\eta^5\text{-}C_5H_4)\text{-}ansa\text{-}(\eta^5\text{-}C_5H_4)]M(\eta^2\text{-alkyne})$ or with stabilizing ligands $[(\eta^5\text{-}C_5H_4)\text{-}ansa\text{-}(\eta^5\text{-}C_5H_4)]M(L)(\eta^2\text{-alkyne})$ have been unknown so far as starting materials in these reactions.

Recently we described the first zirconocene alkyne complex *rac*-(EBHI)Zr(η^2-$Me_3SiC_2SiMe_3$) [EBHI = ethylenebis(tetrahydroindenyl)] without additional ligands[11].

In this paper we report on the synthesis, spectral characteristics, and X-ray structural determination of the *ansa*-metallocene alkyne complexes $[(\eta^5\text{-}C_5H_4)\text{-}ansa\text{-}(\eta^5\text{-}C_5H_4)]Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (*ansa* = $Me_2Si{-}O{-}SiMe_2$: **1**) and $[(\eta^5\text{-}C_5H_4)\text{-}ansa\text{-}(\eta^5\text{-}C_5H_4)]Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (*ansa* = $Me_2Si{-}O{-}SiMe_2$, L = py: **2**; *ansa* = $SiMe_2$, L = py: **3**) as well as the complexes *rac*-(EBHI)Zr(L)(η^2-$Me_3SiC_2SiMe_3$) [L = py: **5**; (*S*)-(–)-nicotine: **6**].

Bis(trimethylsilyl)acetylene imparts the ability to generate under mild conditions the *ansa* systems $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)M]$ (M = Ti, Zr), $[(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5H_4)Zr]$, and [*rac*-(EBHI)Zr] for synthetical purposes as mentioned above for the unbridged complexes.

The reduction of $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)]TiCl_2$[7] with magnesium in the presence of $Me_3SiC_2SiMe_3$ in thf at room temperature (eq. 1) gives the yellow titanocene alkyne complex without additional ligands $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)]Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) in 40% yield.



(1)

1

The absorption at 1687 cm^{-1} in the IR spectrum and the signals of the acetylenic carbon atoms at $\delta = 242.0$ in the ^{13}C-NMR spectrum of complex **1** are typical for such alkyne complexes[3] and prove once again the description as a titanacyclopropene structure[1f]. The reduction of the zirconium complex $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)]ZrCl_2$[8] with magnesium in the presence of $Me_3SiC_2SiMe_3$ in tetrahydrofuran at room temperature does not yield analogous to titanium an *ansa*-zirconocene alkyne complex without additional ligands, but the thf-containing complex $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)]Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$, which easily eliminates thf and is too unstable for the isolation of pure samples. Only NMR measurements show undoubtless a structure analogous to the unbridged

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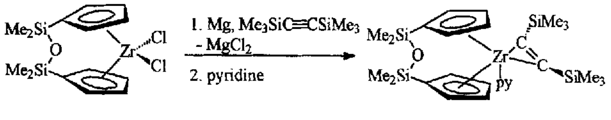
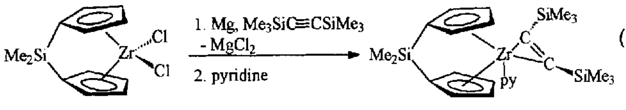
well-known complex $Cp_2Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$[4a]. Replacement of thf by pyridine (eq. 2) gives red-brown crystals of the isolable complex $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)]Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**).



(2)

2

The reduction of the silylene-bridged zirconocene dichloride complex $[(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5H_4)]ZrCl_2$[9] with magnesium in the presence of $Me_3SiC_2SiMe_3$ under analogous conditions did not afford a zirconocene alkyne complex without additional ligands, but the thf-containing complex $[(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5H_4)]Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$, which is only stable in tetrahydrofuran solution as shown by NMR investigations. In the solid state the complex eliminates thf and decomposes. The subsequent replacement of thf by pyridine (eq. 3) gave red-brown crystals of the more stable complex $[(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5H_4)]Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**3**) in 51% yield.



(3)

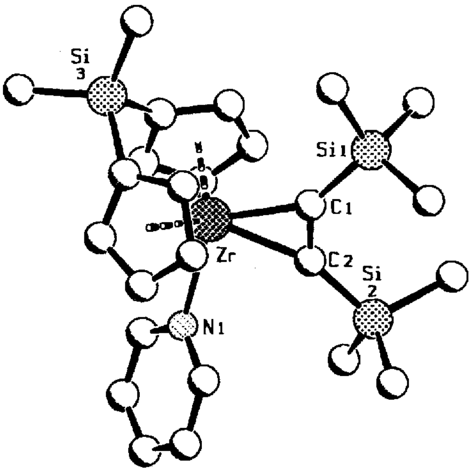
3

The ^1H- and ^{13}C-NMR spectra of the complexes **2** and **3** with additional ligands (as well as the later in this work described complexes *rac*-**5** and *rac*-**6**) exhibit partly broadened resonance lines. They were shown to be temperature-dependent. These compounds form fluxional molecules, not unexpectedly, since this was found and discussed in detail for the unbridged analogues $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$, L = thf or pyridine[4a,b].

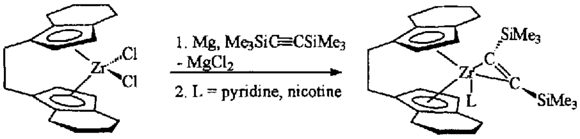
The solid-state structure of **3** is shown in Figure 1. Compared to the unbridged example the silylene bridge exerts no marked influence on the structural details of the bonding (Table 1). The Cp′−M−Cp′ ($Cp_{centroid}-M-Cp_{centroid}$) angles that have been observed for **3** [125.9(1)°] and the non-bridged example $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**7**) [127.5(1)°] differs only slightly from those of the corresponding zirconocene dichlorides $[(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5H_4)]ZrCl^2$ (125.4°) and Cp_2ZrCl_2 (129.1°)[10].

Interestingly, the reduction of ethylenebis(tetrahydroindenyl)]zirconium dichloride *rac*-(EBHI)$ZrCl_2$ with magnesium in the presence of $Me_3SiC_2SiMe_3$ in tetrahydrofuran gives, as already described, the first zirconocene alkyne complex without additional ligands *rac*-(EBHI)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**)[11]. No thf is complexed, and the obtained complex is stable in the solid state up to 137 °C. Complex **4** reacts with equimolar amounts of stronger donor ligands to afford *rac*-(EBHI)$Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ [L = pyridine: **5**[11]; (*S*)-(−)-nicotine: **6**[11]] (eq. 4).

Figure 1. Molecular structure of **3**; selected bond lengths [Å] and angles [°]: C(1)−C(2) 1.297(6), C(1)−Si(1) 1.858(4), C(2)−Si(2) 1.846(4), C(1)−Zr 2.223(4), C(2)−Zr 2.258(4), N(1)−Zr 2.449(3); C(1)−Zr−C(2) 33.65(14), Zr−C(1)−C(2) 74.7(3), Zr−C(2)−C(1) 71.7(3), Si(1)−C(1)−C(2) 137.9(3), Si(2)−C(2)−(1) 136.3, C(4)−Si(3)−C(8) 96.4, C(1)−Zr−N(1) 117.0(1), C(2)−Zr−N(1) 83.6(1)



rac-(EBHI)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ **4** $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ **7**



(4)

rac-**5** L = pyridine
rac-**6** L = (s)-(-)- nicotine

For the complex *rac*-**6** a kinetic resolution of the obtained mixture of diastereomers (*R,R,S*)-**6** and (*S,S,S*)-**6** by recrystallization was not successful because both forms crystallize in one crystal.

The solid-state structure of *rac*-**6** is shown in Figure 2. In comparison to the silylene bridge, the ethylene bridge together with the tetrahydroindenyl systems give less space for coordination of additional ligands (Table 1). The stability of the complex *rac*-(EBHI)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ in contrast to the thf-containing complexes $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)]Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and $[(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5H_4)]Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$, which decompose after elimination of thf, is explained by this effect. The analogous complexes **2**, **3**, and *rac*-**5** with the flat pyridine as ligand are stable for both types of *ansa* ligands.

In the obtained *ansa*-titanocene and -zirconocene η^2-alkyne complexes the special quality of the bis(trimethylsilyl)acetylene as the complexed alkyne is stabilizing the complexes. Our investigations show the different sterical demands of the two *ansa* systems $(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)$ and $(\eta^5\text{-}C_5H_4)(SiMe_2(\eta^5\text{-}C_5H_4)$ on one side and the

Figure 2. Molecular structure of *rac*-**6**; selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.34(2), C(1)–Si(1) 1.85(1), C(2)–Si(2) 1.83(1), C(1)–Zr(1) 2.22(1), C(2)–Zr(1) 2.27(1), Zr(1)–N(1) 2.380(9); C(1)–Zr(1)–C(2) 34.8(4), Zr(1)–C(1)–C(2) 74.5(6), Zr(1)–C(2)–C(1) 70.7(6), Si(1)–C(1)–C(2) 133.3(8), Si(2)–C(2)–C(1) 142.1(8), C(1)–Zr(1)–N(1) 111.3(3), C(2)–Zr(1)–N(1) 79.6(3)

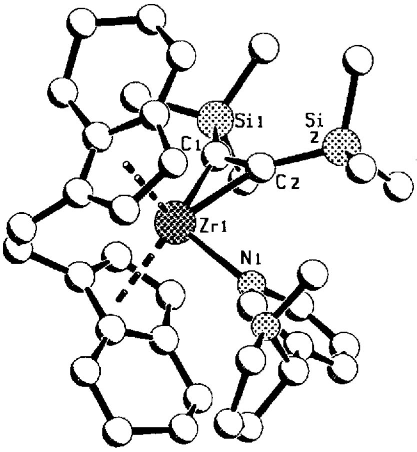


Table 1. Comparison of structural data of the bridged zirconium η^2-alkyne complexes with additional ligand **3**, *rac*-**6**, and $Cp_2Zr(py)(\eta^2-Me_3SiC_2SiMe_3)$ (**7**)

Complex	**3**	*rac*-**6**	**7**[4b]
Distances [Å]			
Zr–N	2.449(3)	2.380(9)	2.437(2)
Zr–C(1)	2.223(4)	2.22(1)	2.216(2)
Zr–C(2)	2.258(4)	2.27(1)	2.242(2)
C(1)–C(2)	1.297(6)	1.34(1)	1.312(3)
Angles [°]			
C(1)–Zr–C(2)	33.7(1)	34.8(4)	34.22(9)
Zr–C(1)–C(2)	74.7(3)	74.5(6)	74.0(1)
Zr–C(2)–C(1)	71.7(3)	70.7(6)	71.8(1)
Si(1)–C(1)–C(2)	137.9(3)	133.3(8)	138.7(2)
Si(2)–C(2)–C(1)	136.3(3)	142.1(8)	135.2(2)
Cp´(1)–Zr–Cp (2)[a]	125.9(1)	116.7(1)	127.5(1)

[a] Cp′(1)–Zr–Cp′(2) angle is for $Cp_{centroid}$–Zr–$Cp_{centroid}$.

sterically more demanding ethylene(bistetrahydroindenyl) ligand on the other side. Consequences of these effects of bridging groups and Cp substituents on the stability of the additional ligand-free and -containing alkyne complexes as well as on their chemo-, regio-, and stereoselective reactions in contrast to the unbridged examples are under investigation.

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Experimental

All operations were carried out under argon with standard Schlenk techniques. Solvents were freshly distilled from sodium tetraethylaluminate under argon prior to use. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled and stored under argon. – NMR: Bruker ARX 400. – IR: Nicolet Magna 550 (Nujol mulls using KBr plates). – MS: AMD 402. – Melting points: sealed capillaries, Büchi 535 apparatus.

X-ray Crystallographic Study[12]: Crystal data are presented in the experimental part of the corresponding compounds. Diffraction data were collected on a Stoe-IPDS diffractometer using Mo-K_α radiation. The structures were solved by direct methods (SHELXS-86)[13] and refined by full-matrix least-square techniques against F^2 (SHELXL-93)[14]; structural representation: (Schakal-92; E. Keller, University of Freiburg).

Preparation of $[(\eta^2\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)]Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**): To a solution of 0.3 g of $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)]TiCl_2$ (0.79 mmol) in 20 ml of tetrahydrofuran 0.0192 g (0.79 mmol) of Mg pieces and 0.178 ml (0.79 mmol) of bis(trimethylsilyl)acetylene were added. The solution was heated to 50 °C, and the color changed from red to brown. The reaction mixture was stirred for 3 h at room temp., the solvent was removed and the residue taken up in *n*-hexane. After filtration of the solution small yellow crystals precipitated. The crystals were isolated by filtration washed with *n*-hexane and dried in vacuo to give 0.15 g (40%) of **1**, m.p. 184–185 °C. – ^{1}H NMR ([D$_8$]THF): δ = –0.34 (18 H, SiMe$_3$), –0.03 (12 H, SiMe$_2$), 6.70, 7.80 (4 H each, C$_5$H$_4$). – ^{13}C NMR ([D$_8$]THF): δ = 0.7 (SiMe$_2$), 0.8 (SiMe$_3$), 121.7, 127.2 [CH(C$_5$H$_4$)], 123.4 [C(C$_5$H$_4$)], 242.0 (C, alkyne). – ^{29}Si NMR ([D$_8$]THF): δ = –4.3 (SiMe$_2$), –14.0 (SiMe$_3$). – IR (nujol mull): $\tilde{\nu}$ = 1253, 1244 cm^{-1} [δ_s(CH$_3$–Si)], 1023 (νSi–O–Si), 1687 [ν(C=C)$_{coord.}$]. – MS (70 eV), *m/z*: 308 [M$^+$ – alkyne], 170 [alkyne$^+$], 262 [(C$_5$H$_4$SiMe$_2$)$_2$O$^+$]. – $C_{22}H_{39}OSi_4Ti$ (479.8): calcd. C 55.08, H 8.19; found C 54.63, H 8.07.

Preparation of $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)]Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**): To a solution of 0.95 g (2.25 mmol) of $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)]ZrCl_2$ in 25 ml of tetrahydrofuran 0.0546 g (2.25 mmol) of Mg pieces and 0.515 ml (2.25 mmol) of bis(trimethylsilyl)acetylene were added. The color turned to violet, and the solution was stirred for 3 h room temp. Than 0.18 ml of pyridine was added, the solvent removed and replaced by *n*-hexane. The red-brown solution was filtered. During cooling the filtrate to –30 °C red-brown crystals (0.8 g, 59%) precipated, m.p. 133–134 °C. – ^{1}H-NMR (C$_6$D$_6$, 345 K): δ = 0.26 (12 H SiMe$_2$), 0.27 (18 H SiMe$_3$), 5.85, 5.96 (4 H each C$_5$H$_4$), 6.60 (2 H pyridine), 6.94 (1 H pyridine), 9.06 (2 H pyridine); ([D$_8$]toluene, 230 K) 0.17, 0.53 (9 H each SiMe$_3$), 0.12, 0.32 (6 H each SiMe$_2$), 5.26, 5.41, 5.80, 6.19 (2 H each C$_5$H$_4$), 6.24 (2 H pyridine), 6.60 (1 H pyridine), 8.98 (2 H pyridine). – ^{13}C NMR (C$_6$D$_6$, 345 K): δ = 1.4 (SiMe$_2$), 2.5 (SiMe$_3$), 107.6 [C(C$_5$H$_4$)], 112.7, 115.5 [CH(C$_5$H$_4$)], 212.5 [C(alkyne)]; ([D$_8$]toluene, 230 K): 0.7, 1.9 (SiMe$_2$), 2.6, 2.6 (SiMe$_3$), 102.5 [C(C$_5$H$_4$)], 108.7, 110.8, 111.8, 122.8 [CH(C$_5$H$_4$)], 122.3, 137.3, 154.9 (pyridine), 193.9, 217.2 [C(alkyne)]. – IR (Nujol mull): $\tilde{\nu}$ = 1250, 1242 cm^{-1} [δ_s(CH$_3$–Si)], 1035 (νSi–O–Si), 1597, 1587 [ν(C=C)$_{coord.}$]. – MS (70 eV), *m/z*: 521 [M$^+$ – py], 351 [(C$_5$H$_4$SiMe$_2$)$_2$OZr$^+$], 262 [C$_5$H$_4$SiMe$_2$)$_2$O$^+$], 170 [alkyne$^+$]. – $C_{27}H_{43}NOSi_4Zr$ (601.2): calcd. C 53.94, H 7.21, N 2.33; found C 53.60, H 7.27, N 2.45.

Preparation of $[(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5H_4)]Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**3**): To a solution of 0.43 g (1.23 mmol) of $[(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5H_4)]ZrCl_2$ in 20 ml of tetrahydrofuran 0.03 g (1.23 mmol) of Mg pieces and 0.278 ml (1.23 mmol) of bis(trimethylsilyl)acetylene were added. The solution was heated at 50 °C until the color changed to violet. Further preparation as described for 3. Red-brown crystals: 0.33 g (51%), m.p. 120–121 °C. – ^{1}H NMR ([D$_8$]toluene, 225 K): δ = 0.04, 0.53 (9 H each SiMe$_3$), 0.38, 0.48 (6 H each SiMe$_2$), 5.01, 5.41, 5.59, 6.31 (2 H each C$_5$H$_4$), 6.23 (2 H pyridine), 6.66 (1 H pyridine), 8.61 (2 H pyridine), [(D$_8$]toluene, 378 K): 0.14 (18 H SiMe$_3$), 0.38 (12 H SiMe$_2$), 5.59, 5.46 (4 H each C$_5$H$_4$), 6.57 (2 H pyridine), 6.96 (1 H pyridine), 8.71 (2 H pyridine). – ^{13}C NMR ([D$_8$]toluene, 225 K): δ = 2.4, 2.5 (SiMe$_3$), –4.5, –5.4 (SiMe$_2$), 97.8, 102.8, 104.7 [C(C$_5$H$_4$)], 117.1, 118.2 [CH(C$_5$H$_4$)], 122.8, 136.5, 153.5 (pyridine), 193.0, 218.5 [C(alkyne)], ([D$_8$]toluene, 378 K): 2.6 (SiMe$_3$), –4.6 (SiMe$_2$), 102.0, 117.6, 106.6

(C_5H_4), 123.2, 136.3, 153.1 (pyridine), 207.0 [C(alkyne)]. – IR (Nujol mull): $\tilde{\nu}$ = 1261, 1238 cm^{-1} [$\delta_s(CH_3{-}Si)$], 1579, 1597 [$\nu(C{=}C)_{coord.}$]. – MS (70 eV), *m/z*: 447 [M^+ – pyridine], 277 [$Cp_2SiMe_2Zr^+$], 188 [$(C_5H_4)_2SiMe_2^+$], 170 [alkyne$^+$]. – $C_{25}H_{37}NSi_3Zr$ (527.05): calcd. C 56.97, H 7.08, N 2.66; found C 56.57, H 7.12, N 2.79.

Crystal Data for **3**: Suitable crystals were obtained from a hexane solution. Crystal dimensions 0.4 × 0.2 × 0.1; a = 8.163(1), b = 10.745(1), c = 16.842(2) Å, α = 80.74(1), β = 86.10(1), γ = 73.16(1)°, V = 1395.1(3) Å^3, space group P-1, Z = 2, mol. mass 527.05, d(calcd.) = 1.255 g/cm^3, λ = 0.71069 Å, measured reflections 8166, independent reflections 4206, observed reflections 3460, refined parameters 272, R = 0.046 and wR_2 = 0.113 (all data)[12].

For the Preparation of **5** see ref.[11].

Preparation of rac-(EBHI)Zr(L)(η^2-$Me_3SiC_2SiMe_3$) L = (S)-(–)-Nicotine (**6**): To a solution of 0.32 g (0.61 mmol) of *rac*-(EBHI)Zr(η^2-$Me_3SiC_2SiMe_3$)[11] in 10 ml of *n*-hexane 0.098 ml of (*S*)-(–)-nicotine was added. After removal of the solvent a dark oily residue was obtained which was crystallized from *n*-hexane to afford violet crystals, m.p. 91–94°C. – IR (nujol mull): $\tilde{\nu}$ = 1560 cm^{-1} [$\nu(C{=}C)_{cood.}$]. – ^1H NMR (C_6D_6): δ = 8.60 (1H), 8.32 (1H), 7.40 (1H), 6.63 (1H), 5.28 (br, 4H, CH=CH), 2.98, 2.75, 2.49, 2.20 (14H), H, 2.02 (3H, NCH_3), 1.85, 1.68, 1.43, 1.25 (12H) H, 0.37 (br, 18H, $SiMe_3$). – $C_{38}H_{56}N_2Si_2Zr$ (688.3): calcd. C 66.31, H 8.20, N 4.07; found C 65.0, H 8.30, N 3.95.

*Crystal Data for (R,R,S)-**6** and (S,S,S)-**6** · 0.5 Hexane* (suitable crystals from hexane solution): Crystal dimensions 0.4 × 0.2 × 0.1; a = 9.463(10), b = 13.245(2), c = 17.053(2) Å, α = 104.102(9), β = 99.521(9), γ = 95.152(4)°, V = 2025.4(4) Å^3, space group $P\bar{1}$, Z = 2, mol. mass 1418.53, d(calcd.) 1.163 g/cm^3, λ = 0.71069 Å, measured reflections 11507, independent reflections 11507, observed reflections 9509, refined parameters 797, R = 0.047 and wR_2 = 0.128 (all data)[12].

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[12] Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-391017 and -391018 the names of the authors, and the journal citation.

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