3486 *Organometallics* **1996,** *15,* 3486−3490

Articles

rac-[1,2-Ethylene-1,1′-bis(η^5-tetrahydroindenyl)][η^2-bis(trimethylsilyl)acetylene]zirconium, the First Zirconocene−Alkyne Complex without Additional Ligands: Synthesis, Reactions, and X-ray Crystal Structure

Claudia Lefeber, Wolfgang Baumann, Annegret Tillack, Rhett Kempe,
Helmar Görls,[†] and Uwe Rosenthal*

*Arbeitsgruppe "Komplexkatalyse" of the Max-Planck-Gesellschaft at the University of Rostock,
Buchbinderstrasse 5-6, D-18055 Rostock, Germany*

Received January 18, 1996[⊗]

The reduction of *rac*-(EBTHI)$ZrCl_2$ [EBTHI = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)] with equimolar amounts of magnesium in the presence of $Me_3SiC_2SiMe_3$ in THF at room temperature gave the first zirconocene−alkyne complex containing no additional ligands, *rac*-(EBTHI)Zr(η^2-$Me_3SiC_2SiMe_3$), **2**. With pyridine and (*S*)-(−)-nicotine complex **2** gave the ligand-containing complexes *rac*-(EBTHI)Zr(L)(η^2-$Me_3SiC_2SiMe_3$) (L = pyridine, **3**; L = (*S*)-(−)-nicotine, **4**). In the reaction of **2** with acetone the insertion product *rac*-(EBTHI)-($ZrOCMe_2C(SiMe_3)$=C($SiMe_3$)), **5**, was formed. Complex **2** reacted with 2 equiv of PhN=CHPh with substitution of the alkyne to form *rac*-(EBTHI)ZrNPhCHPhCHPhNPh, **6**. Compounds **2** and **6** were characterized by an X-ray structure analysis.

Introduction

Group 4 bent metallocene complexes are important organometallic compounds which are used frequently as reagents and catalysts.[1a−e] Especially the chiral *ansa*-metallocene systems, originally developed by Brintzinger,[1f] are excellent catalysts or reagents for stereoselective reactions.[1g]

Among the well characterized group 4 metallocene−acetylene complexes only the titanocene complexes, e.g., Cp^*_2M(η^2-acetylene) or Cp_2M(η^2-acetylene), do not contain additional ligands.[2] Analogous complexes of zirconocene are less well-known. The complex Cp^*_2Zr(η^2-PhC_2Ph) has been mentioned briefly[3a] and discussed[1b,3b] but was not characterized in detail by spectroscopic or structural methods.[3c]

Recently, we described the first structures of titanocene−silylalkyne complexes such as Cp_2Ti(η^2-PhC_2SiMe_3)[4a] and Cp_2Ti(η^2-${}^tBuC_2SiMe_3$).[4b] A complete series of complexes $(C_5H_{5-n}Me_n)_2Ti$(η^2-$Me_3SiC_2SiMe_3$) (n = 0−5)[4c] was reported later by Mach and his co-workers.[4c] In the case of zirconocene only the complexes Cp_2Zr(L)(η^2-$Me_3SiC_2SiMe_3$) (L = THF,[5a] py[5b]), which contain an additional stabilizing ligand, were obtained under analogous conditions.

Metallocene−bis(trimethylsilyl)acetylene complexes that contain a silylalkyne which is reluctant to undergo coupling reactions are useful precursors for the metallocenes "Cp_2Ti" and "Cp_2Zr" under mild conditions.[1e] They show a rich chemistry, including some unexpected and novel reactions, with different substrates, e.g., with carbonyl compounds, acetylenedicarboxylates, aldimines, ketimines, azoles, diynes, and Si−H compounds.[1e] Extension of the well-established chemo- and regioselectivity of these reactions to diastereo- and enantioselectivity would require the use of chiral complexes with, e.g., Brintzinger's *ansa* ligands,[1f] instead of the simple η^5-cyclopentadienyl complexes.

We report here the complexation of bis(trimethylsilyl)acetylene by *rac*-[1,2-ethylene-1,1′-bis(η^5-tetrahydroin-

---

[†] Present address: Max-Planck-Gesellschaft, Arbeitsgruppe "CO_2-Chemie" an der Universität Jena.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.

(1) For reviews, see: (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (b) Buchwald, S. L.; Fisher, R. A. *Chem. Scr.* **1989**, *29*, 417. (c) Negishi, E. *Chem. Scr.* **1989**, *29*, 457. (d) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124. (e) Ohff, A.; Pulst, S.; Lefeber, C.; Peulecke, N.; Arndt, P.; Burlakov, V. V.; Rosenthal, U. *Synlett* **1996**, 111 and references cited therein. (f) Wild, F. W. R. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *288*, 63. (g) Halterman, R. L. *Chem. Rev.* **1992,** *92*, 965 and references cited therein.

(2) (a) Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006. (b) Demerseman, B.; Mahe, R.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1394. (c) Shur, V. B.; Burlakov, V. V.; Vol'pin, M. E. *J. Organomet. Chem.* **1988**, *347*, 77.

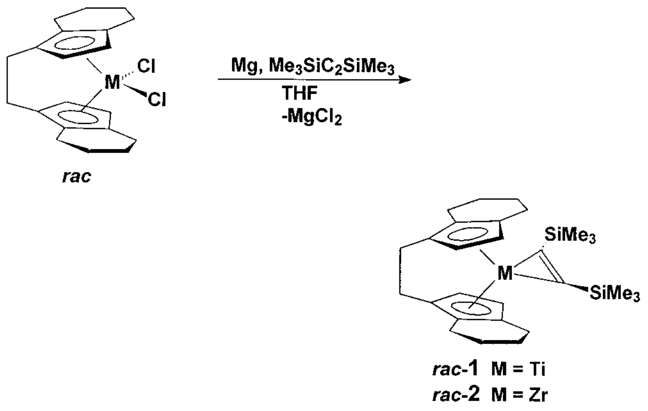
(3) (a) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281. (b) Lamaire, S. J. Ph.D. Thesis, Chemistry Department, MIT, 1989. (c) Threlkel, R. S. Ph.D. Thesis, California Institute of Technology, 1980.

(4) (a) Burlakov, V. V.; Polyakov, A. V.; Yanovsky, A. I.; Shur, V. B.; Vol'pin, M. E.; Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1994**, *476*, 197 and references therein. (b) Lefeber, C.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *J. Organomet. Chem.* **1995**, *501*, 189, (c) Varga, V.; Mach, K.; Polásek, M.; Sedmera, P.; Hiller, J.; Thewalt, U.; Troyanov, S. I. *J. Organomet. Chem.* **1996**, *506*, 241.

(5) (a) Rosenthal, U.; Ohff, A.; Michalik, M; Görls, H.; Burlakov, V. V.; Shur, V. B. *Angew. Chem.* **1993**, *105*, 1228; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1193. (b) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 77.

S0276-7333(96)00034-9 CCC: $12.00

Scheme 1



denyl)]zirconium to yield the first zirconocene−alkyne complex that does not contain an additional stabilizing ligand, *rac*-(EBTHI)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$), **2** [EBTHI = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)].

Results and Discussion

The reduction of *rac*-(EBTHI)TiCl$_2$[6] with equimolar amounts of magnesium in the presence of Me$_3$SiC$_2$SiMe$_3$ in THF at room temperature (Scheme 1) gave, after workup, golden-yellow needles of *rac*-(EBTHI)Ti(η^2-Me$_3$SiC$_2$SiMe$_3$), **1**, in 64% yield. Under analogous conditions, the reaction of *rac*-(EBTHI)ZrCl$_2$[7] afforded dark-green plates of *rac*-(EBTHI)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$), **2**, which did not contain a THF ligand, in 72% yield.

The absorption bands due to the complexed C≡C bond (**1**, 1594 cm^{-1}; **2**, 1534 cm^{-1}) in the IR spectra and the signals of the acetylenic C atoms in the ^{13}C NMR spectra (**1**, 244.5 ppm; **2**, 259.7 ppm) are consistent with a metallacyclopropene structure for **1** and **2**. These data suggest that the strength of the coordination of the C≡C bond increases from the *ansa*-titanocene **1** to the *ansa*-zirconocene−alkyne complex **2**. In complexes of type Cp$_2$Zr(L)(η^2-Me$_3$SiC$_2$SiMe$_3$), which contain an additional ligand, the relevant IR bands [L = THF, 1581 cm^{-1};[5a] L = py, 1579/99 (uncertain assignment) cm^{-1} [5b]] and ^{13}C NMR resonances (L = THF, 212.9 ppm;[5a] L = py, 195.3, 220.5 ppm;[5b] L = PMe$_3$, 177.3, 205.1 ppm[8]) are less shifted from those of the free bis(trimethyl)acetylene (2107 cm^{-1}; 113.8 ppm) in comparison to the data for the zirconacyclopropene **2**, which does not contain an additional ligand. That indicates weaker bonding of the acetylene in the donor ligand-containing complexes.

The crystal structure of **2** (Figure 1) clearly shows the absence of an additional ligand. Table 1 lists crystallographic data. The nearly symmetric structure exhibits, within experimental error, *cis* geometry of the complexed alkyne. The bond distance of the coordinated C [C1−C2 = 1.302(8) Å] is close to the generally accepted value of a C═C double bond (1.34 Å[9]).

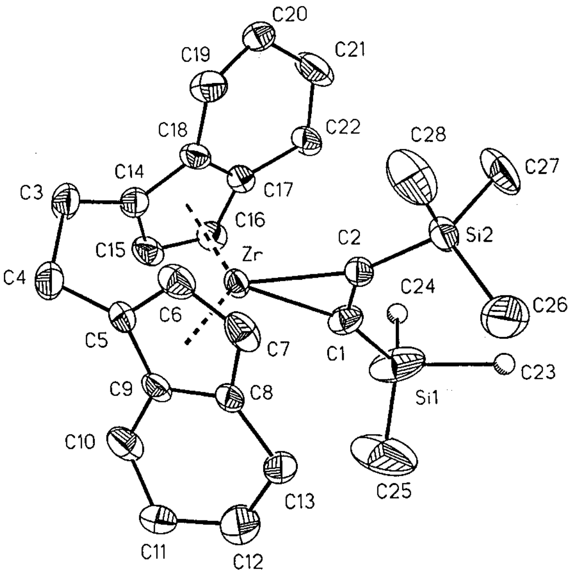


Figure 1. Molecular structure of complex **2**, shown by an ORTEP plot. The thermal ellipsoids correspond to 50% probability. Selected bond distances (Å) and angles (deg): C1−C2, 1.300(10); C2−Si2 1.851(7); C1−Si1, 1.848(7); Zr−C1, 2.211(7); Zr−C2, 2.199(7); C1−Zr−C2, 34.3(3); C2−C1−Zr, 72.3(4); C1−C2−Zr, 73.4(5); C2−C1−Si1, 136.3(7); C1−C2−Si2, 139.4(6); Si2−C2−Zr, 145.7(4); Si1−C1−Zr 150.5(5).

Table 1. Crystallographic Data for 2 and 6

	2	6·2C$_4$H$_{10}$O
formula	C$_{28}$H$_{42}$Si$_2$Zr	C$_{96}$H$_{102}$N$_4$OZr$_2$
mol mass	526.02	1510.26
cryst color, habit	green, prismatic	violet, prismatic
cryst system	orthorhombic	monoclinic
space group	Pccn	$P2_1/c$
lattice consts		
a (Å)	17.461(3)	19.002(3)
b (Å)	34.813(7)	15.101(2)
c (Å)	9.212(2)	27.342(5)
α (deg)	90	90
β (deg)	90	94.630(10)
γ (deg)	90	90
Z	8	8
temp (K)	183(2)	293(2)
μ(Mo Kα) (cm^{-1})	4.9	3.2
θ range (deg)	2.33−27.41	1.72−24.35
no. of rflns (measd)	6360	53 951
no. of rflns (indep)	6360	12 064
no. of rflns (obsd)	6358	4611
no. of params	290	904
R_1 ($I > 2\sigma(I)$)	0.071	0.053
wR2 (all data)	0.147	0.113

Table 2. Structural Parameters of the Complexes 2 and Cp$_2$Zr(L)(η^2-Me$_3$SiC$_2$SiMe$_3$)

		Cp$_2$Zr(L)(η^2-Me$_3$SiC$_2$SiMe$_3$)	
	2	L = THF	L = pyridine
		Distances (Å)	
C1−C2	1.300(10)	1.302(9)	1.312(3)
Zr−C1	2.211(7)	2.260(7)	2.224(2)
Zr−C2	2.199(7)	2.204(7)	2.216(2)
		Angles (deg)	
C1−C2−Si2	139.0(5)	143.5(6)	138.7(2)
C2−C1−Si1	137.0(6)	134.4(6)	135.5(2)

Comparison of the analogous structural data for the complexes Cp$_2$Zr(L)(η^2-Me$_3$SiC$_2$SiMe$_3$) in contrast to the spectroscopic data provides no information concerning the different complexation strengths in ligand-containing and ligand-free complexes (Table 2). This is in agreement with studies reported recently which showed that NMR and IR spectroscopy are better suited for the

---

[6] Wild, F. W. R. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233.

[7] Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *J. Organomet. Chem.* **1988**, *342*, 21.

[8] Binger, P.; Müller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Krüger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035.

[9] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Guy Orpen, A.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, S1−S19.

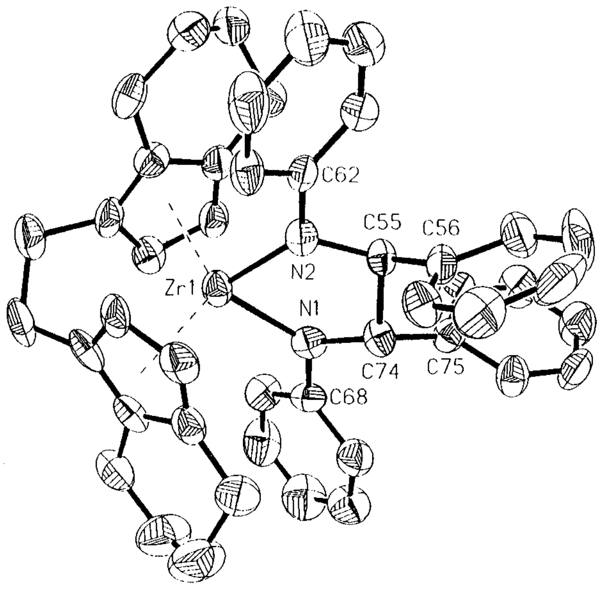


Figure 2. Molecular structure of complex **6**, shown by an ORTEP plot. The thermal ellipsoids correspond to 40% probability. Selected bond distances (Å) and angles (deg): Zr−N1, 2.135(5); Zr−N2, 2.105(5); N1−C74, 1.510(7); N1−C68, 1.414(8); N2−C62, 1.439(8); C74−C75, 1.516(8); C55−C56, 1.516(8); Zr1−N1−C74, 112.1(4); Zr1−N2−C55, 114.0(4); Zr1−N1−C68, 128.4(4); Zr1−N2−C62, 133.2(4); N1−Zr1−N2, 81.4(2).

Scheme 2

characterization of the complexed alkyne than an X-ray structure analysis.[10]

In complexes **1** and **2** the metallocene fragment is an unstable 14-electron species with the metal atom in the +2 oxidation state. The binding of an alkyne produces a 16-electron complex for which the extreme resonance forms **A** and **B** are shown in Scheme 2.

Titanium and zirconium are more stable in the +4 oxidation state, which is achieved by back-bonding from the filled Zr orbital to a π^* orbital of the coordinated alkyne. Thus Ti(IV) and Zr(IV) better describe the oxidation state of the metals in these complexes (**B**).[1b,10]

Complex **2** undergoes three types of reactions also found for unbridged zirconocene−bis(trimethylsilyl)acetylene complexes: addition of a donor ligand,[5b] insertion of carbonyl compounds,[11] and loss of the alkyne in the course of reactions with other substrates[12] (Scheme 3).

Compound **2** reacts with pyridine and (*S*)-(−)-nicotine to form alkyne complexes with an additional ligand, *rac*-(EBTHI)Zr(L)(η^2-$Me_3SiC_2SiMe_3$) (L = pyridine, **3**; L = (*S*)-(−)-nicotine **4**) (Scheme 3). All attempts to separate the diastereomers (*R,R,S*)-**4** and (*S,S,S*)-**4** by recrystallization have not been successful to date. In NMR experiments complexes **3** and **4** show the dynamic behavior found and discussed for the unbridged pyridine complex $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$.[5b] Acetone inserts into a Zr−C bond of **2** to yield yellow *rac*-(EBTHI)-ZrOCMe$_2$C(SiMe$_3$)=C(SiMe$_3$), **5**. In the reaction with 2 equiv of the Schiff base PhN=CHPh with complex **2** the bis(trimethylsilyl)acetylene ligand is displaced, and **2** is reacting as a source of the "*rac*-(EBTHI)Zr" fragment. Two C=N units are coupled in the coordination sphere of the metal to give *rac*-(EBTHI)ZrNPhCHPh-CHPhNPh, **6**.[12d] Here **2** reacts analogously to $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$, which serves as a source of zirconocene "Cp_2Zr" under mild conditions.[12] Complex **6** was obtained in 86% yield as violet crystals. The ^{1}H NMR spectrum exhibited, in addition to the signals due to the EBTHI ligand and the Ph groups, only the resonance due to two equivalent protons (5.18 ppm) for the metallacycle, indicating that, as found also in the Cp_2Zr complex (4.86 ppm), only one isomer is present in solution. The structure of the racemic complex **6** (Figure 2) was established by X-ray crystal structure analysis. It crystallized from diethyl ether in two symmetrically independent molecules together with one uncoordinated ether molecule. The molecular structure is composed of a bent zirconocene moiety, (EBTHI)Zr, to which two, within experimental error, equivalent nitrogen atoms are coordinated as a part of a 1,3-diaza-2-zirconacyclopentane. The Zr−N bond distances [Zr1−N1 2.135(5), Zr1−N2 2.105(5), Zr2−N3 2.134(5), Zr2−N4 2.138(5) Å] are very similar to those of the unbridged zirconocene complex of the same type [Zr−N 2.138(η^2) Å] and are typical for a zirconium−nitrogen single bond. The angles Zr−N−Cβ [112.1(4), 114.0(4), 115.5(4), 114.8(4)°] indicate sp^3 hybridization of the nitrogen atoms.

Conclusion

The metallocenes with unsubstituted Cp ligands on reaction with $Me_3SiC_2SiMe_3$ give only in the case of titanium products that do not contain an additional ligand, e.g., $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$[4b] whereas for zirconium the complexes $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (L = THF,[5a] py[5b]) result. When using the EBTHI ligand in place of Cp, both metals give complexes that do not contain an additional ligand, (EBTHI)M(η^2-$Me_3SiC_2SiMe_3$), **1** and **2**. Spectroscopic data suggest that the acetylene ligand is less strongly bonded to the metal in the complexes that contain an additional ligand.

The special feature of the bis(trimethylsilyl)acetylene ligand to favor substitution reactions gives these EBTHI complexes the ability to act as a preparative source for the "(EBTHI)Zr" and "(EBTHI)Ti" moieties under mild conditions. The alkyne complexes **1** and **2** can react in this manner with different substrates, and if the optically pure systems (*R,R* and *S,S*) are used instead of *rac*-EBTHI, these complexes should possess high synthetic potential for stereoselective reactions.

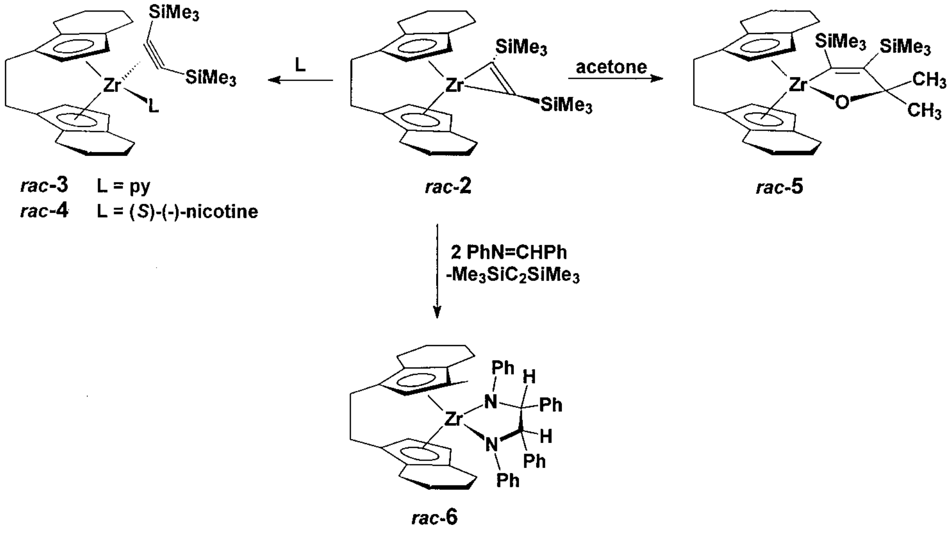
---

(10) Rosenthal, U.; Nauck, C.; Arndt, P.; Pulst, S.; Baumann, W.; Burlakov, V. V.; Görls, H. *J. Organomet. Chem.* **1994**, *484*, 81 and references therein.

(11) (a) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Görls, H.; Burlakov, V. V.; Shur, V. B. *J. Organomet. Chem.* **1994**, *484*, 203. (b) Peulecke, N.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *Organometallics* **1996**, *15*, 1340.

(12) (a) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Organometallics* **1994**, *13*, 2903. (b) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Angew. Chem.* **1994**, *106*, 1678; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1605. (c) *Ibid.* **1994**, *106*, 1946; **1994**, *33*, 1850. (d) Lefeber, C.; Arndt, P.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *Organometallics* **1995**, *14*, 3090. (e) Burlakov, V. V.; Ohff, A.; Lefeber, C.; Tillack, A.; Baumann, W.; Kempe, R.; Rosenthal, U. *Chem. Ber.* **1995**, *128*, 1967.

Scheme 3



Experimental Section

All operations were carried out under inert atmosphere (argon) with standard Schlenk techniques. Prior to use solvents were freshly distilled from sodium tetraethylaluminate under argon. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled, and stored under argon. The following spectrometers were used: NMR, Bruker ARX 400; IR, Nicolet Magna 550 (Nujol mulls using KBr plates); MS, AMD 402. Melting points were measured in sealed capillaries on a Büchi 535 apparatus. Elemental analyses were carried out with a Leco CHNS-932 elemental analyzer.

X-ray Crystallographic Study of Complexes 2 and 6. Diffraction data were collected on a CAD4 MACH3 diffractometer using graphite-monochromated Mo Kα radiation and a STOE-IPDS diffractometer. The structures were solved by direct methods (SHELXS-86[13]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93[14]). The hydrogen atoms were included at calculated positions. In complex **2** the indenyl carbon atoms C11 and C20 are disordered. The disorder could be resolved. The carbon atoms C23 and C24 only were refined isotropically. All other non-hydrogen atoms were refined anisotropically. Cell constants and other pertinent data were collected and recorded in Table 1. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. Further details of the crystal structure investigations are available upon request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ, U.K., on quoting the full journal citation.

Preparation of *rac*-(EBTHI)Ti(η^2-Me$_3$SiC$_2$SiMe$_3$) (1). To a suspension of 0.53 g (0.92 mmol) of *rac*-(EBTHI)TiCl$_2$ in 15 mL of THF was added 0.02 g (0.96 mmol) of magnesium cuttings and 0.21 mL (0.92 mmol) of bis(trimethylsilyl)-acetylene. The mixture was stirred at 45 °C until the color changed from red to black-brown. After that, the solution was stirred at room temperature for 2 h. The solvent was removed *in vacuo*, and the solid residue was resolved in 15 mL of *n*-hexane. After filtration and repeated removal of the solvent, 0.28 g (64%) of golden-yellow needles of **1** were isolated, mp 158–162 °C. Anal. Calcd for $C_{28}H_{42}Si_2Ti$ (482.69): C, 69.67; H, 8.77. Found: C, 68.42 (acceptable in view of the formation of titanium carbides);[15] H, 8.93. MS: *m/z* 482 (M$^+$). IR (Nujol mull): 1594 cm^{-1}. ^{1}H-NMR (benzene-d_6): δ -0.03 (s, 18H, SiMe$_3$), 0.17–0.35, 0.91–0.99, 1.44–1.68, 1.85–2.06, 3.19–3.26, 3.45–3.53 (m, 20H, CH$_2$), 3.98 (d, J = 3.2 Hz, 2H, CH═CH), 8.58 (d, J = 3.2 Hz, 2H, CH═CH). ^{13}C{^{1}H} NMR (benzene-d_6): δ 2.6 (SiMe$_3$), 23.3, 23.5, 24.1, 25.7, 26.0 (CH$_2$), 113.1, 115.2 (CH═CH), 124.5, 126.1, 128.2 (q-C), 244.5 (*C*-SiMe$_3$).

Preparation of *rac*-(EBTHI)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$) (2). Using the same procedure as described for **1**, a mixture of 1.00 g (2.35 mmol) of *rac*-(EBTHI)ZrCl$_2$, 0.07 g (2.67 mmol) of magnesium cuttings, and 0.42 mL (1.91 mmol) of bis(trimethylsilyl)acetylene was prepared. While the mixture was stirred at 45 °C, the color changed from colorless to dark violet. After the mixture was stirred for 2 h at room temperature the color changed to green. After removal the solvent *in vacuo*, dissolution of the residue in *n*-hexane, filtration, and repeated removal of solvent, 0.89 g (72 %) of the dark green complex **2** was obtained, mp 137–142 °C. Anal. Calcd for $C_{28}H_{42}Si_2Zr$ (524.19): C, 64.01; H, 8.08. Found: C, 63.51; H, 8.14. MS: *m/z* 524 (M$^+$). IR (Nujol mull): 1534 cm^{-1}. ^{1}H-NMR (benzene-d_6): δ 0.18 (s, 18H, SiMe$_3$), 0.92–0.98, 1.23–1.31, 1.41–1.58, 1.67–1.75, 2.01–2.18, 2.23–2.33 (m, 16H, CH$_2$), 2.93 (m, AA′BB′, 4H), 4.68 (d, J = 3.2 Hz, 2H, CH═CH), 7.54 (d, J = 3.2 Hz, 2H, CH═CH). ^{13}C{^{1}H} NMR (benzene-d_6): δ 2.6 (SiMe$_3$), 23.4, 23.5, 24.4, 24.9, 26.5 (CH$_2$), 108.7, 110.2 (CH═CH), 123.7, 124.0, 128.2 (q-C), 259.7 (*C*-SiMe$_3$).

Preparation of *rac*-(EBTHI)Zr(py)(η^2-Me$_3$SiC$_2$SiMe$_3$) (3). To a solution of 0.42 g (0.80 mmol) of *rac*-(EBTHI)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$), **2**, in 15 mL of *n*-hexane was added 0.30 mL of pyridine. The color changed from green to dark blue. After evaporation of the solvent *in vacuo*, 0.20 g (43%) of the dark blue solid **3** was isolated, mp 139–142 °C. Anal. Calcd for $C_{33}H_{47}NSi_2Zr$ (605.13): C, 65.50; H, 7.83. Found: C, 65.55; H, 7.99. MS: *m/z* 524 (M$^+$ – py), 354 [(EBTHI)Zr], 79 (py). IR (Nujol mull): 1565 cm^{-1}. ^{1}H-NMR (benzene-d_6): the NMR spectrum exhibited broad signals at room temperature, and not all carbon resonances could be detected [a behavior as discussed previously for the analogous complex Cp$_2$Zr(py)(η^2-Me$_3$SiC$_2$SiMe$_3$)[5b]], δ 0.89 (s, 18H, SiMe$_3$), 1.31, 1.39, 1.47, 1.62, 2.19, 2.45, 2.72 (m, 20H, CH$_2$), 5.21 (bs, 2H, CH═CH), 5.90 (bs, 2H, CH═CH), 6.47 (m, 2H, meta-py), 6.79 (m, 1H, para-py), 8.30 (m, 2H, ortho-py).

Preparation of *rac*-(EBTHI)Zr[S(-)-nicotine](η^2-Me$_3$SiC$_2$SiMe$_3$) (4). To a solution of 0.32 g (0.61 mmol) of *rac*-(EBTHI)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$), **2**, in 10 mL of *n*-hexane was added 89 μL (0.61 mmol) of *S*-(–)-nicotine, and the solution was stirred at room temperature. The color changed from green to black-blue. The solvent was removed *in vacuo*, and the solid residue was recrystallized from *n*-hexane to yield 0.12

---

[13] Sheldrick, G. M. SHELXS-86, University of Göttingen, Göttingen, Germany, 1986.

[14] Sheldrick, G. M. SHELXL-93, University of Göttingen, Göttingen, Germany, 1993.

[15] Samuel, E.; Mu, Y.; Harrod, J. F.; Dromzee, Y.; Jeannin, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3435 and references cited therein.

g (29%) of black-violet crystals of **4**, mp 91−94 °C. Anal. Calcd for $C_{38}H_{56}Si_2N_2Zr$ (688.27): C, 66.31; H, 8.20; N, 4.07. Found: C, 65.99; H, 8.30; N, 3.95. IR (nujol): 1560 cm^{-1}. This compound shows similar spectroscopic behavior to complex **3** [discussed in detail for the analogous complex $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$[5b]]. ^1H NMR (400 MHz, benzene-d_6): δ 0.37 (s, 18H, $SiMe_3$), 1.25, 1.43, 1.68, 1.85 (m, 12H, CH_2), 2.02 (d, 3H, CH_3), 2.23, 2.52, 2.78, 2.98 (m, 14H, CH_2), 5.27 (bs, 2H, CH═CH), 5.90 (bs, 2H, CH═CH), 6.63, 7.40, 8.32, 8.60 (m, 4H, ar).

Preparation of 5. *rac*-(EBTHI)Zr(η^2-$Me_3SiC_2SiMe_3$), **2** (0.35 g (0.66 mmol)), was dissolved in 10 mL of *n*-hexane, and 0.1 mL of acetone was added. The color changed from green to yellow. After 2 d at −30 °C, 0.32 g (84%) yellow crystals of **5** deposited, mp 161−163 °C. Anal. Calcd for $C_{31}H_{48}Si_2OZr$ (582.23): C, 63.89; H, 8.31. Found: C, 63.71; H, 8.49. MS: *m*/*z* 524 (M^+ − acetone). ^1H NMR (benzene-d_6): δ 0.36 (s, 18H, $SiMe_3$), 1.45 (s, 3H, Me), 1.62 (s, 3H, Me), 1.42−1.52, 1.62−1.68, 1.71−1.80, 1.90−1.97, 2.00−2.07, 2.15−2.31, 2.52−2.63, 2.77−2.85, 3.04−3.15 (m, 20H, CH_2), 5.08 (d, J = 2.8 Hz, 1H, CH═CH), 5.46 (d, J = 3.1 Hz, 1H, CH═CH), 6.47 (d, J = 3.1 Hz, 1H, CH═CH), 6.95 (d, J = 2.8 Hz, 1H, CH═CH). ^{13}C NMR (benzene-d_6): δ 5.0 ($SiMe_3$), 6.6 ($SiMe_3$), 22.7, 22.9, 23.3, 23.4, 23.5, 24.6, 25.0, 26.7, 26.8 (CH_2), 28.6, 33.2 (CH_3), 88.7, 106.3, 108.3, 109.0, 115.7, 121.9, 122.4, 122.7, 125.3, 127.2, 129.5, 129.6, 193.4, 217.6.

Preparation of *rac*-(EBTHI)$\overline{\text{ZrNPhCHPhCHPhN}}$Ph (6). A solution of 0.14 g (0.76 mmol) of *N*-benzylideneaniline in 10 mL of THF was added to a solution of 0.20 g (0.38 mmol) of *rac*-**2** in 15 mL of THF. The solution was stirred for 10 min at 40 °C. The color changed from green to violet. After the solution was stirred 1 h at room temperature the solvent was removed *in vacuo*. The foamy solid residue was dissolved in boiling ether, and 0.24 g (86%) of violet crystals of **6** deposited overnight at room temperature, mp >280 °C. Anal. Calcd for $C_{49}H_{51}N_2O_{0.5}Zr$ (755.13): C, 76.46; H, 6.82; N, 3.72. Found: C, 76.44; H, 6.49; N, 3.99. ^1H NMR (benzene-d_6): δ −0.15 to −0.10, 0.98−1.02, 1.10−1.15, 1.27−1.31, 2.15−2.20, 2.49−2.55, 2.64−2.72, 2.92−2.95 (m, 20H, CH_2), 5.18 (s, 2H, CHPh), 5.78 (d, J = 2.6 Hz, 2H, CH═CH), 6.58 (d, J = 2.6 Hz, 2H, CH═CH), 6.56−6.59, 6.90−7.00, 7.06−7.12 (m, 20H, ar). ^{13}C NMR (benzene-d_6): δ 20.0, 23.1, 24.1, 26.1 (CH_2), 73.0, 108.6, 115.7, 117.8, 120.7, 126.0, 126.5, 127.8, 128.1, 129.4, 130.4, 132.2, 145.9, 152.9.

Acknowledgment. This research was supported by the Max-Planck-Gesellschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystal structure parameters and details of data collection, bond angles and distances, and atomic positional and thermal parameters and ORTEP diagrams for **2** and **6** (28 pages). Ordering information is given on any current masthead page.

OM9600349