Angewandte Chemie

DOI: 10.1002/anie.200605069

ansa-Metallocenes

A 1,8-Naphthylene-Bridged Bis(indenyl)zinc THF Adduct: Formation and Structure of an ansa-Zincocene Derivative**

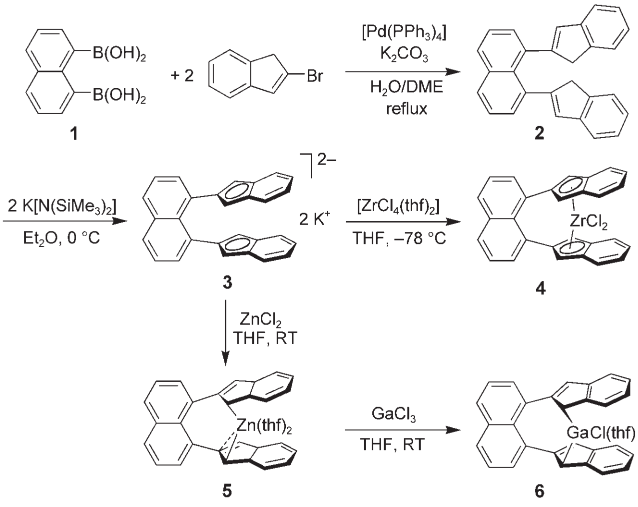
*Huadong Wang, Gerald Kehr, Roland Fröhlich, and Gerhard Erker**

Dedicated to Professor Peter Hofmann on the occasion of his 60th birthday

Cyclopentadienyl (Cp) zinc compounds can show great structural variation, as shown by the bis(cyclopentadienyl)dizinc complex prepared by Carmona and co-workers.[1] The CpZn derivatives occupy an intermediate position between the alkali-metal cyclopentadienides, whose geometric features are dominated by electrostatic ligand–metal interaction,[2] and the electropositive early-transition-metal Cp complexes.[3] Consequently, various structural types of Cp_2Zn derivatives have been described, ranging from the oligomeric chain structure of the Cp_2Zn parent[4] to (disordered) molecular η^1,η^5-type geometries in the $(Me_4RC_5)_2Zn$ series.[5–9] This situation suggests that it should be possible to influence the zincocene structural type by geometric control through the use of appropriate ligands, for example, by using the steric constraints introduced by ansa-ligands, which were so successfully applied in Group 4 metallocene Ziegler–Natta catalyst chemistry.[10] Herein we describe the synthesis of a new ansa-ligand system with some favorable geometric properties and its use in the synthesis of a novel ansa-zincocene derivative which shows some unprecedented structural and chemical features (Scheme 1).

1,8-Bis(indenyl)naphthalene (**2**) was prepared by $[Pd(PPh_3)_4]$-induced Suzuki–Miyaura coupling of naphthalene-1,8-diboronic acid with 2-bromoindene (ca. 30% yield).[11] Subsequent treatment of **2** with two molar equivalents of $K[N(SiMe_3)_2]$ gave the dianionic reagent **3** as its dipotassium salt.

Compound **3** was treated with $[ZrCl_4(thf)_2]$ in THF. The salt metathesis proceeded cleanly and gave the new ansa-zirconocene complex **4** in 55% yield after recrystallization. In $CDCl_3$ the ^1H NMR spectrum of **4** features a typical ABC pattern of the bridging 1,8-naphthylene unit at $\delta = 7.41$, 7.50, 7.84 ppm (each 2H). The ^1H NMR signals of the phenylene groups of the symmetry-equivalent 2-indenyl groups appear at $\delta = 7.21$ and 7.52 ppm and the indenyl H1/H3 singlet at $\delta = 6.41$ ppm (4H).



Scheme 1. Syntheses of ligand **3** and ansa-metallocenes **4–6**. DME = 1,2-dimethoxyethane.

The X-ray crystal structure analysis of **4** (single crystals from a $CHCl_3$ solution of **4** layered with pentane) shows a typical ansa-metallocene geometry. The rigid 1,8-naphthylene bridge is slightly tilted relative to the normal of the major plane (Cl1-Zr-Cl2) of the bent metallocene. There is a small tendency toward bond-length alternation within the bridging $C_{10}H_6$ subunit. The $C(sp^2)$–$C(sp^2)$ bonds to the indenyl units are slightly elongated (molecule A: 1.490(4)/1.495(5) Å [molecule B: 1.484(4)/1.487(4) Å]) but the overall ligand framework is barely distorted (angles [°]: C7-C8-C22 116.8(3) [116.2(3)], C2-C1-C12 117.2(3) [116.5(3)], C9-C8-C22 122.2(3) [121.8(3)], C9-C1-C12 121.1(3) [123.0(3)]; Figure 1). Both indenyl five-membered rings are uniformly η^5-coordinated to zirconium with bond lengths in a typical relatively narrow range: Zr–CH 2.461(3)–2.491(3) Å [2.472(3)–2.491(3) Å], Zr–C 2.490(3)–2.595(3) Å [2.486(3)–2.603(3) Å]. The C–C bonds inside the five-membered rings of the indenyl units are all very similar in length 1.429(4)–1.434(4) Å [1.402(5)–1.434(4) Å].

Activation of complex **4** with methylaluminoxane (MAO) gave an active homogeneous Ziegler–Natta catalyst for ethylene polymerization (under standard conditions at ambient temperature, activity ca. 1 (kg PE) $(mmol\,[Zr])^{-1}\,h^{-1}\,bar^{-1}$; PE = polyethylene).

Treatment of the potassium salt **3** with anhydrous $ZnCl_2$ in THF gave the ansa-zincocene complex **5** as a bis-THF adduct

---

[*] Dr. H. Wang, Dr. G. Kehr, Dr. R. Fröhlich,[+] Prof. G. Erker
Organisch-Chemisches Institut
Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)
Fax: (+49) 251-833-6503
E-mail: erker@uni-muenster.de

[+] X-ray crystal-structure analyses.

[**] Financial support from the Fonds der Chemischen Industrie and the Alexander von Humboldt foundation (fellowship to H.W.) is gratefully acknowledged. We thank BASF for the donation of solvents.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

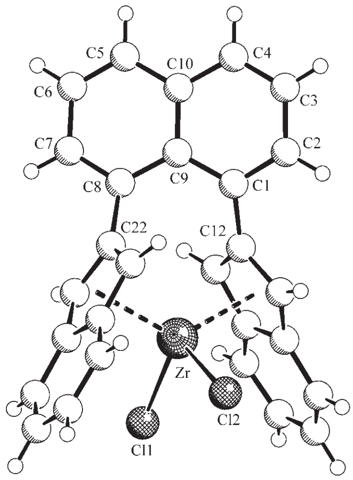


Figure 1. Molecular structure of the ansa-zirconocene complex **4**. Selected bond lengths [Å] in the naphthalene backbone: molecule A: C1–C2 1.375(5) [molecule B: 1.381(5)], C1–C9 1.427(5) [1.428(5)], C8–C7 1.375(5) [1.383(4)], C8–C9 1.423(5) [1.414(5)], C4–C3 1.356(6) [1.343(5)], C4–C10 1.412(6) [1.416(5)], C5–C6 1.353(6) [1.358(6)], C5–C10 1.413(5) [1.411(5)], C2–C3 1.417(5) [1.411(5)], C6–C7 1.425(5) [1.400(5)], C9–C10 1.425(5) [1.434(5)].

(isolated in 75% yield). Similar to the parent complex [Cp_2Zn], complex **5** is only sparingly soluble in apolar or weakly polar organic solvents, but is more soluble in THF, from which single crystals suitable for the X-ray crystal-structure analysis were obtained (Figure 2)

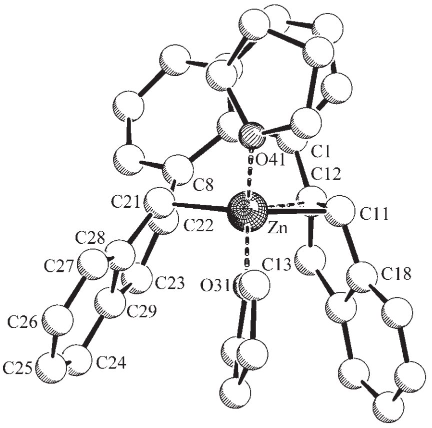


Figure 2. Molecular structure of the ansa-zincocene complex **5**. Hydrogen atoms are omitted for clarity.

Complex **5** features a zinc center has a pseudotetrahedral coordination environment. It is coordinated by two THF ligands (Zn−O bond lengths of the two crystallographically independent molecules: 2.074(3)–2.098(3) Å) and two indenyl ligands of the ansa-framework. The bridging 1,8-naphthylene unit shows structural features similar to those observed in the zirconium complex **4**, only that the angles to the indenyl units are slightly larger (123.7(3)–125.5(3)° [123.4(4)–126.3(4)°]) and the connecting bonds C1−C12 and C8−C22 are slightly shorter (1.470(5), 1.488(5) Å [1.469(5), 1.491(5) Å]).

One indenyl ligand of **5** (C21–C29) is η^1-coordinated to the Zn atom (Zn−C21 2.060(3) [2.056(4) Å]).[12] It features the typical C−C bond lengths of a substituted σ-metallated five-membered indenyl subunit (molecule A: C21−C22 1.474(5), C21−C28 1.480(5), C28−C29 1.419(5), C23−C29 1.431(5) Å) that contains a conjugated C22−C23 double bond (1.362(5) Å). The Zn-C21-C22 bond angle of this is characteristic of a σ-indenyl coordination (112.8(2)° [113.1(2)°]), the Zn-C21-C28 angle is 104.2(2)° [104.5(2)°]. In contrast the other indenyl ligand in **5** is $\eta^2(\sigma,\pi)$-bonded to the Zn atom in the solid state.[4,13] The corresponding Zn−C11 bond length is 2.081(3) Å [2.079(4) Å] and the adjacent Zn−C12 bond length is 2.562(4) Å [2.585(4) Å]. The characteristic coordination angle Zn-C11-C12 is considerably reduced at 90.9(2)° [91.7(2)°] (Zn-C11-C18 106.3(2)° [104.5(2)°]). Again, one bond in the indenyl five-membered ring is short (C12−C13 1.375(5) Å [1.368(5) Å]) with the remaining C−C bonds of this subunit are between 1.419(5) and 1.475(5) Å. In this coordination geometry the C(σ-indenyl)-Zn-O(thf) bond angles are in between 103.0(1)° and 111.8(1)°, whereas the C11-Zn-C21 angles are much larger (127.6(2)° [127.0(2)°]) and the O-Zn-O angles are much reduced (96.5(1)° [93.5(1)°]).

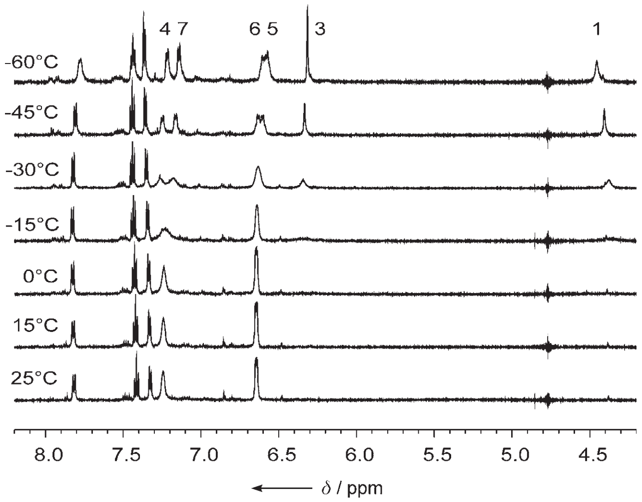
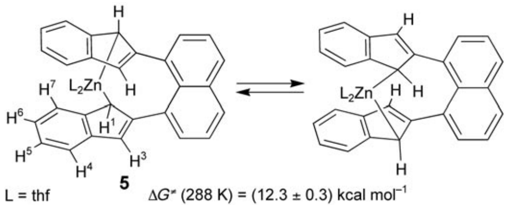


Figure 3. Temperature-dependent dynamic ^{1}H NMR spectra of the ansa-zincocene complex **5** (in [D_8]THF). Numbers assign signals to the indenyl protons (see Scheme 2).

In [D_8]THF solution the NMR spectra of the ansa-zincocene complex **5** indicate temperature-dependent dynamic behavior (Figure 3). At 40 °C the ^{1}H NMR signal of the H1/H3 indenyl protons of **5** appears as a very broad singlet at $\delta = 5.35$ ppm and the indenyl phenylene protons H4–H7 give rise to a slightly broadened AA′BB′ pattern at $\delta = 7.25$ and 6.64 ppm. The remaining set of downfield signals originate from the 1,8-naphthylene bridge. While these signals are almost temperature-invariant, the ^{1}H NMR signals of the indenyl unit decoalesce with decreasing temperature. At −45 °C we observe a 1:1 pair of signals for the H1

(δ 4.41 ppm) and H3 ($\delta = 6.33$ ppm) protons and an ABCD pattern for the corresponding phenylene proton resonances ($\delta = 7.25$, 7.16, 6.63, 6.61 ppm). Further lowering of the temperature (to −130 °C in $CDFCl_2$/[D_8]THF) did not result in further splitting of these signals. This dynamic behavior indicates a degenerative automerization process between chemically identical η^1,η^1-zincocene complexes that is frozen out on the NMR timescale. The automerization process results in a pair-wise equilibration of the respective positions of the indenyl subunits. From the H1/H3 coalescence we have estimated an activation barrier of $\Delta G^{\neq} = (12.3 \pm 0.3)$ kcal mol^{-1} ($T_{coal} = 288$ K, $\Delta\nu(228\ K) = 1158$ Hz) for this automerization process (Scheme 2). Consequently, the ^{13}C NMR spectra of **5** at the low-temperature limit shows resonance of carbon atom C1 (which is σ bonded to Zn) at $\delta = 62.1$ ppm (233 K) with a typical $^1J_{CH}$ coupling constant of 145 Hz, whereas the corresponding C3 resonance ($\delta = 115.0$ ppm (233 K)) shows a much larger $^1J_{CH} = 167$ Hz value typical of an olefinic sp^2-carbon center.



Scheme 2. Automerization process between chemically identical η^1,η^1-zincocene complexes **5**.

We have used the ansa-zincocene to prepare an ansa-bis(indenyl)gallium complex.[14] Treatment of the **5** with gallium trichloride gave the corresponding "ansa-gallocene" complex **6** in 55 % yield.[15,16] The C_s-symmetric product was identified spectroscopically and by an X-ray crystal-structure analysis (single crystals from a $CHCl_3$ solution of **6** layered with pentane), albeit of too poor quality for any detailed discussion of structural parameters. The ^{1}H/^{13}C NMR spectra in solution show features typical of a THF-stabilized η^1,η^1-coordinated ansa-bis(indenyl)gallium chloride complex. The corresponding signals for the indenyl protons H1 and H3 are at $\delta = 3.60$ ppm (C1 $\delta = 50.5$ ppm, $^1J_{CH} = 134$ Hz) and $\delta = 6.55$ ppm (C3 $\delta = 130.6$ ppm, $^1J_{CH} = 167$ Hz), respectively. The ^{1}H NMR resonances for the 1,8-naphthylene protons are at $\delta = 7.35$, 7.46, 7.90 ppm, and the resonances of the indenyl phenylene protons are at $\delta = 6.86$, 6.92, 7.15, 7.35 ppm.

Our study has made the new 1,8-naphthylene-bridged bis-indenyl ligand **2** available by a straightforward synthetic route. This ligand seems to be suited to accommodate the Group 12 metal zinc in a $\eta^1,\eta^2(\sigma,\pi)$-coordination mode that is uncommon for a molecular zincocene. The ansa-zincocene complex **5** is a suitable reagent for the synthesis of novel main-group ansa-metallocenes, as exemplified by the formation of the new gallium complex **6**. This approach using ansa-complexes will hopefully open new pathways to unusual structures of main-group metallocene systems.

Experimental Section

4: **3**·1.5 Et_2O (200 mg, 0.37 mmol) was treated with [$ZrCl_4(thf)_2$] (141 mg, 0.37 mmol) in THF (15 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and left at this temperature for 14 h. The solvent was then removed under vacuum, and the residue was extracted with toluene. Recrystallization from toluene yielded **4** (light yellow crystals, 104 mg, 55 %). ^{1}H NMR (599.7 MHz, $CDCl_3$, 298 K): $\delta = 6.41$ (s, 4 H, H1,3$_{(ind.)}$), 7.21 (m, 4 H, H5,6$_{(ind.)}$), 7.41 (d, $J = 7.1$ Hz, 2 H, H2,7$_{(naph.)}$), 7.50 (dd, $J = 8.2$, 7.1 Hz, 2 H, H3,6$_{(naph.)}$), 7.52 (m, 4 H, H4,7$_{(ind.)}$), 7.84 ppm (d, $J = 8.2$ Hz, 2 H, H4,5$_{(naph.)}$). ^{13}C{^{1}H} NMR (150.8 MHz, $CDCl_3$, 298 K): $\delta = 101.4$ ($^1J_{CH} = 176$ Hz, C1,3$_{(ind.)}$), 125.4 (C4,7$_{(ind.)}$), 125.9 (C3,6$_{(naph.)}$), 126.7 (C5,6$_{(ind.)}$), 128.7 (C-4,5$_{(naph.)}$), 128.8 (C9$_{(naph.)}$), 129.5 (C2,7$_{(naph.)}$), 129.9 (C-8,9$_{(ind.)}$), 132.6 (C1,8$_{(naph.)}$), 135.1 (C10$_{(naph.)}$), 136.9 ppm (C-2$_{(ind.)}$). Elemental analysis (%) calcd for $C_{28}H_{18}Cl_2Zr$: C 65.10, H 3.51; found: C 64.55, H 3.57.

Crystal data for **4**: $C_{28}H_{18}Cl_2Zr$, $M_r = 516.54$, monoclinic, space group Pc (No. 7), $a = 11.089(1)$, $b = 14.476(1)$, $c = 14.295(1)$ Å, $\beta = 110.29(1)°$, $V = 2152.3(3)$ Å^3, $\rho_{calcd} = 1.594$ g cm^{-3}, $\mu = 0.773$ mm^{-1}, $Z = 4$, $\lambda = 0.71073$ Å, $T = 198$ K, 14 340 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å^{-1}, 7757 independent ($R_{int} = 0.030$) and 7278 observed reflections [$I \geq 2\ \sigma(I)$], 559 refined parameters, $R = 0.028$, $wR^2 = 0.066$. CCDC-630677 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

5: A solution of $ZnCl_2$ (136 mg, 1.0 mmol) in THF (5 mL) was added to a suspension of **3**·1.5 Et_2O (543 mg, 1.0 mmol) in THF (5 mL) at room temperature. The mixture was stirred for 5 min and filtered though celite. The filtrate was evaporated to dryness under vacuum, affording complex **5** (421 mg, 75 %). ^{1}H NMR (599.7 MHz, [D_8]THF, 233 K): $\delta = 4.40$ (s, 2 H, H1$_{(ind.)}$), 6.33 (s, 2 H, H3$_{(ind.)}$), 6.60/6.63 (each m, 4 H, H5,6$_{(ind.)}$), 7.16 (d, $J = 7.0$ Hz, 2 H)/7.25 (d, $J = 7.2$ Hz, 2 H) (H4,7$_{(ind.)}$), 7.35 (dd, $J = 7.0$, 1.2 Hz, 2 H, H2,7$_{(naph.)}$), 7.44 (dd, $J = 8.0$, 7.0 Hz, 2 H, H3,6$_{(naph.)}$), 7.81 ppm (dd, $J = 8.0$, 1.2 Hz, 2 H, H4,5$_{(naph.)}$). ^{13}C NMR (125.7 MHz, [D_8]THF, 233 K): $\delta = 62.1$ ($^1J_{CH} = 145$ Hz, C1$_{(ind.)}$), 115.0 ($^1J_{CH} = 167$ Hz, C3$_{(ind.)}$), 118.2/117.7 (C5,6$_{(ind.)}$), 118.7/121.7 (C4,7$_{(ind.)}$), 125.2 (C3,6$_{(naph.)}$), 126.1 (C4,5$_{(naph.)}$), 129.7 ppm (C2,7$_{(naph.)}$); the ^{13}C NMR data are from a ^{1}H/^{13}C gradient heteronuclear single-quantum correlation (ghsqc) experiment.

Crystal data for **5**: $C_{28}H_{18}Zn{\cdot}2\,C_4H_8O$, $M_r = 564.00$, monoclinic, space group $P2_1/c$ (No. 14), $a = 21.233(1)$, $b = 15.088(1)$, $c = 19.247(1)$ Å, $\beta = 113.30(1)°$, $V = 5663.2(5)$ Å^3, $\rho_{calcd} = 1.323$ g cm^{-3}, $\mu = 0.898$ mm^{-1}, $Z = 8$, $\lambda = 0.71073$ Å, $T = 223$ K, 28 951 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 9956 independent ($R_{int} = 0.084$) and 5456 observed reflections [$I \geq 2\sigma(I)$], 703 refined parameters, $R = 0.056$, $wR^2 = 0.133$. CCDC-630678 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6: A solution of $GaCl_3$ (65 mg, 0.37 mmol) in THF (3 mL) was added to a solution of complex **5** (200 mg, 0.36 mmol) in THF (5 mL) at room temperature. The reaction mixture was stirred for 1 h. The resulting white precipitate was collected by filtration, rinsed with THF (10 mL) and dried under vacuum to yield **6** as a white powder (104 mg, 55 %). ^{1}H NMR (499.8 MHz, $CDCl_3$, 298 K): $\delta = 1.44$ (br, 4 H, THF), 3.35 (br, 4 H, THF), 3.60 (s, 2 H, H1$_{(ind.)}$), 6.55 (s, 2 H, H3$_{(ind.)}$), 6.86 (t, $J = 7.3$ Hz, 2 H)/6.92 (t, $J = 7.6$ Hz, 2 H) (H5,6$_{(ind.)}$), 7.15 (d, $J = 7.6$ Hz, 2 H)/7.35 (m, 2 H, H4,7$_{(ind.)}$), 7.35 (m, 2 H, H2,7$_{(naph.)}$), 7.46 (m, 2 H, H3,6$_{(naph.)}$), 7.90 ppm (d, $J = 8.0$ Hz, 2 H, H4,5$_{(naph.)}$). ^{13}C (125.7 MHz, $CDCl_3$, 298 K): δ 50.5 ($^1J_{CH} = 134$ Hz, C1$_{(ind.)}$), 120.3/122.2 (C4,7$_{(ind.)}$), 122.9/124.3 (C5,6$_{(ind.)}$), 124.7 (C3,6$_{(naph.)}$), 128.8 (C4,5$_{(naph.)}$), 129.8 (C2,7$_{(naph.)}$), 130.6 ppm ($^1J_{CH} =$

167 Hz, C3$_{(ind.)}$); the ^{13}C NMR data are from a ^{1}H/^{13}C ghsqc experiment.

Received: December 15, 2006

Keywords: ansa compounds · gallium · indenyl ligands · metallocenes · zinc

---

[1] a) I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* **2004**, *305*, 1136 – 1138; b) D. del Río, A. Galindo, I. Resa, E. Carmona, *Angew. Chem.* **2005**, *117*, 1270 – 1273; *Angew. Chem. Int. Ed.* **2005**, *44*, 1244 – 1247; c) A. Grirrane, I. Resa, A. Rodriguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Galindo, D. del Rio, R. A. Anderson, *J. Am. Chem. Soc.* **2007**, *129*, 693 – 703.
[2] a) P. Jutzi, *Adv. Organomet. Chem.* **1986**, *26*, 217 – 295; b) P. Jutzi, *J. Organomet. Chem.* **1990**, *400*, 1 – 17; c) E. Weiss, *Angew. Chem.* **1993**, *105*, 1565 – 1587; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1501 – 1523; d) D. Stalke, *Angew. Chem.* **1994**, *106*, 2256 – 2259; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2168 – 2171.
[3] a) J. W. Lauher, R. W. Hoffmann, *J. Am. Chem. Soc.* **1976**, *98*, 1729 – 1742; b) J. C. Green, *Chem. Soc. Rev.* **1998**, *27*, 263 – 271.
[4] P. H. M. Budzelaar, J. Boersma, G. J. M. van der Kerk, A. L. Spek, A. J. M. Duisenberg, *J. Organomet. Chem.* **1985**, *281*, 123 – 130.
[5] a) B. Fischer, P. Wijkens, J. Boersma, G. van Koten, W. J. J. Smeets, A. L. Spek, P. H. M. Budzelaar, *J. Organomet. Chem.* **1989**, *376*, 223 – 233; b) D. J. Burkey, T. P. Hanusa, *J. Organomet. Chem.* **1996**, *512*, 165 – 173.
[6] a) R. Fernández, I. Resa, D. del Río, E. Carmona, *Organometallics* **2003**, *22*, 381 – 383; b) A. Haaland, S. Samdal, N. V. Tverdova, G. V. Girichev, N. I. Giricheva, S. A. Shlykov, O. G. Garkusha, B. V. Lokshin, *J. Organomet. Chem.* **2003**, *684*, 351 – 358.
[7] H. V. Ly, T. D. Forster, D. Maley, M. Parvez, R. Roesler, *Chem. Commun.* **2005**, 4468 – 4470.
[8] V. M. Rayón, G. Frenking, *Chem. Eur. J.* **2002**, *8*, 4693 – 4707.
[9] E. Alvarez, A. Grirrane, I. Resa, D. del Rio, A. Rodriguez, E. Carmona, *Angew. Chem.* **2007**, *119*, 1381 – 1321; *Angew. Chem. Int. Ed.* **2007**, *46*, 1296 – 1299.
[10] a) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.* **1995**, *107*, 1255 – 1283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143 – 1170; b) See also: H.-R. H. Damrau, A. Geyer, M.-H. Prosenc, A. Weeber, F. Schaper, H.-H. Brintzinger, *J. Organomet. Chem.* **1998**, *553*, 331 – 343.
[11] See for a comparison: a) H. Wang, F. P. Gabbaï, *Angew. Chem.* **2004**, *116*, 186 – 189; *Angew. Chem. Int. Ed.* **2004**, *43*, 184 – 187; b) B. M. Foxman, D. A. Gronbeck, N. Khruschova, M. Rosenblum, *J. Org. Chem.* **1993**, *58*, 4078 – 4082; c) E. G. IJpeij, F. H. Beijer, H. J. Arts, C. Newton, J. G. de Vries, G.-J. M. Gruter, *J. Org. Chem.* **2002**, *67*, 169 – 176.
[12] a) B. Fischer, J. Boersma, G. van Koten, W. J. J. Smeets, A. L. Spek, *Organometallics* **1989**, *8*, 667 – 672; b) A. J. Arduengo III, F. Davidson, R. Krafczyk, W. J. Marshall, M. Tamm, *Organometallics* **1998**, *17*, 3375 – 3382.
[13] D. A. Walker, T. J. Woodman, M. Schormann, D. L. Hughes, M. Bochmann, *Organometallics* **2003**, *22*, 797 – 803.
[14] General review: P. Jutzi, N. Burford, *Chem. Rev.* **1999**, *99*, 969 – 990.
[15] See for a comparison: A. Dashti, K. Niediek, B. Werner, B. Neumüller, *Z. Anorg. Allg. Chem.* **1997**, *623*, 394 – 402.
[16] a) O. T. Beachley, Jr., R. B. Hallock, H. M. Zhang, J. L. Atwood, *Organometallics* **1985**, *4*, 1675 – 1680; b) H. Schumann, S. Nickel, R. Weimann, *J. Organomet. Chem.* **1994**, *468*, 43 – 47; c) C. L. B. Macdonald, J. D. Gorden, A. Voigt, A. H. Cowley, *J. Am. Chem. Soc.* **2000**, *122*, 11 725 – 11 726.