Chiral silicon-bridged 2-(*N*,*N*-dialkylamino)ethyl-substituted indenes as potential precursors for *ansa*-zirconocenes[1]

Timo Hagemeister, Peter Jutzi, Anja Stammler, and Hans-Georg Stammler

Abstract: Chiral amino-functionalized silicon-bridged indene derivatives **4a**–**4c** were synthesized from 3-(2-(*N*,*N*-dialkylamino)ethyl)indenes **2a**–**2c**. The C-Si coupling reactions are regioselective, leading exclusively to the formation of 1,3-disubstituted isomers in a *rac*/*meso* ratio of 1:1, as indicated by NMR spectroscopy. The solid-state structure of the dimethylsilyl-bridged bisindene (*R*,*R*)-**4a** is described. The formation of corresponding *ansa*-zirconocenes via amine elimination chemistry was monitored by ^{1}H NMR spectroscopy.

Key words: amino-functionalized indenes, silicon-bridged, *ansa*-metallocenes, chirality, regioselectivity, amine elimination chemistry.

Résumé : Utilisant les 3-(2(*N*,*N*-dialkylamino)éthyl)indènes **2a**–**2c** comme produits de départ, on a réalisé la synthèse des dérivés chiraux de l'indène à pont de silicium et portant une fonction amine **4a**–**4c**. Les réactions de couplage C-Si sont régiosélectives et elles conduisent exclusivement à la formation d'isomères 1,3-disubstitués qui, d'après la spectroscopie RMN, sont dans un rapport *rac*/*méso* égal à l'unité. On a déterminé la structure en phase solide du bisindène (*R*,*R*)-**4a** à pont diméthylsilyle. La formation des *ansa*-zirconocènes correspondants par le biais de la chimie d'élimination d'amine a été suivie par spectroscopie RMN du ^{1}H.

Mots clés : indène portant une fonction amine, pont de silicium, *ansa*-métallocènes, chiralité, régiosélectivité, chimie d'élimination d'amine.

Introduction

Donor-functionalized cyclopentadienes have recently attracted considerable attention as starting materials for the synthesis of corresponding complexes with elements from the *s*-, *p*-, *d*-, and *f*-blocks (1). In contrast, only a few examples of donor-functionalized indenes are known (2). Such compounds are promising substrates for the synthesis of chiral *ansa*-metallocenes.

Concerning *ansa*-metallocenes of group IV metals, potential applications include a wide variety of synthetic transformations, for instance olefin hydrogenation (3), epoxidation (4) and isomerization (5), allylation of aldehydes (6), ketone reduction (7), catalysis of Diels–Alder reactions (8), and dehydrogenative phenylsilane oligomerization (9).

In addition, transition metal complexes with pendant amino groups have been shown to provide special characteristics as precatalysts in olefin polymerization reactions. The option to heterogenize homogenous precatalysts due to interaction of the amino groups with Lewis or Broensted acidic surfaces is given (10). Furthermore, quaternization of the amino groups leads to a dramatically increased solubility in polar solvents and can enable the recycling of precatalysts by simple extraction procedures (11). Some recently described switchable catalyst systems exhibit a temperature-controlled allosteric effect, based on a reversible coordination of the cocatalyst MAO by the pendant donor function. As a consequence, either high- or low-molecular weight polymer products become accessable by employing an amino-substituted precatalyst (12).

Here we report on the regioselective preparation and on structural properties of chiral, silicon-bridged indene derivatives, which are substituted at the indene moiety by a dialkylaminoethyl group. New *ansa*-zirconocenes bearing such indenyl ligands are shown to be accessable via an amine elimination reaction.

Results and discussion

The 3-(2-(*N*,*N*-dialkylamino)ethyl)indenes (**2a**–**2c**), which were first described in 1967 but have been characterized only incompletely (13), served as starting compounds. Their synthesis was carried out according to a procedure introduced by Wang et al. and modified by Jutzi and Bangel for the preparation of the analogous cyclopentadienes (Scheme 1) (14).

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Dedicated to Professor John F. Harrod in recognition of his seminal contributions to the field of organometallic chemistry.

T. Hagemeister, P. Jutzi,[2] A. Stammler, and H.-G. Stammler. Faculty of Chemistry, University of Bielefeld, 33615 Bielefeld, Germany.

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[2]Corresponding author (e-mail: peter.jutzi@uni-bielefeld.de).

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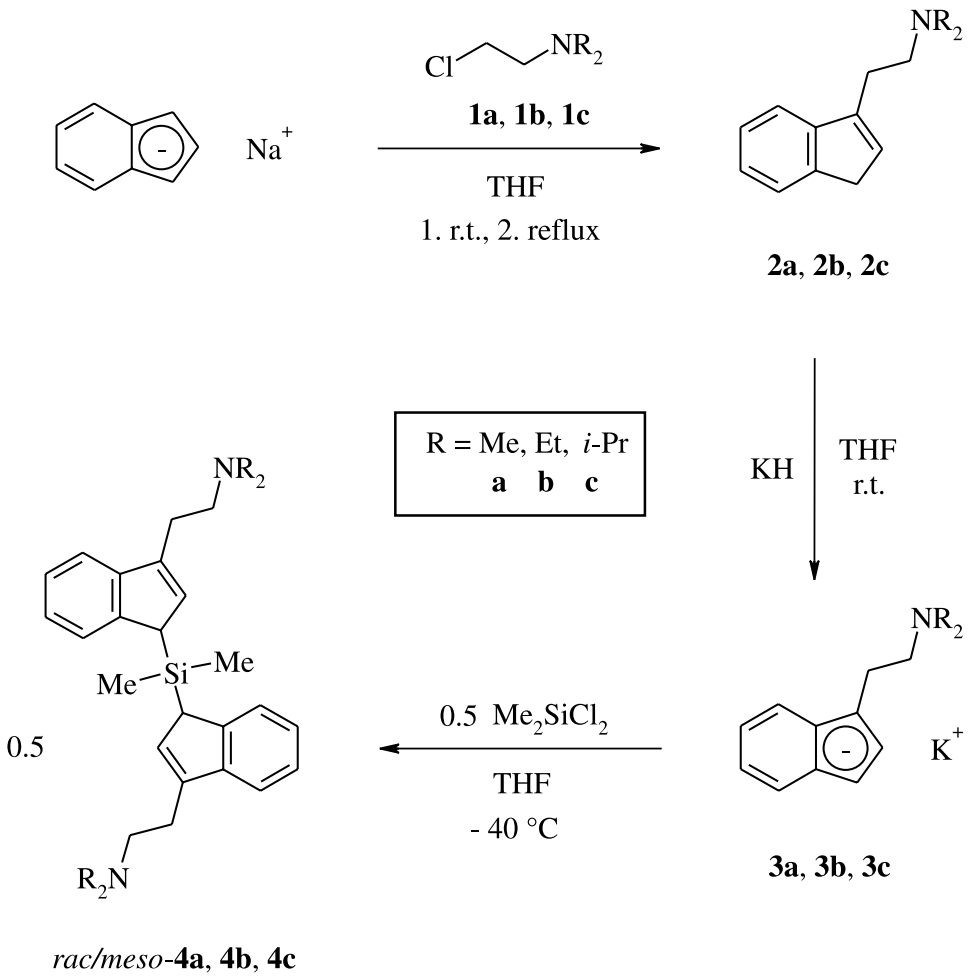
Scheme 1.



Reaction of the (2-chloroethyl)dialkylamines (**1a**–**1c**) with indenyl sodium in THF yielded the (dialkylaminoethyl)indenes **2a**, **2b**, and **2c** as colourless, distillable, and viscous liquids in analytical purity. The ^{1}H NMR data gave clear evidence that substitution exclusively occurred in position 3. This correlates with earlier observations (15) that the regioselectivity of coupling reactions is solvent-dependent. Reactions with electrophiles in nonpolar solvents predominantly take place at C(1), and in more polar media such as THF, mainly at C(3).

The compounds **2a**–**2c** were converted almost quantitatively into the intensively coloured potassium (dialkylaminoethyl)indenides **3a**–**3c** by reaction with KH in THF. Subsequent C—Si bond formation was achieved by metathesis of the salts with a slight excess of dimethyldichlorosilane (Scheme 1). After conventional work-up, the resulting chiral 1,3-bis(indenyl)dimethylsilanes **4a**–**4c** were obtained as pure, viscous orange-brown oils in 60–70% yields. The new compounds were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, mass spectrometry, as well as elemental analysis. They turned out to be remarkably air- and moisture stable; for instance stirring in water for 18 h did not lead to decomposition.

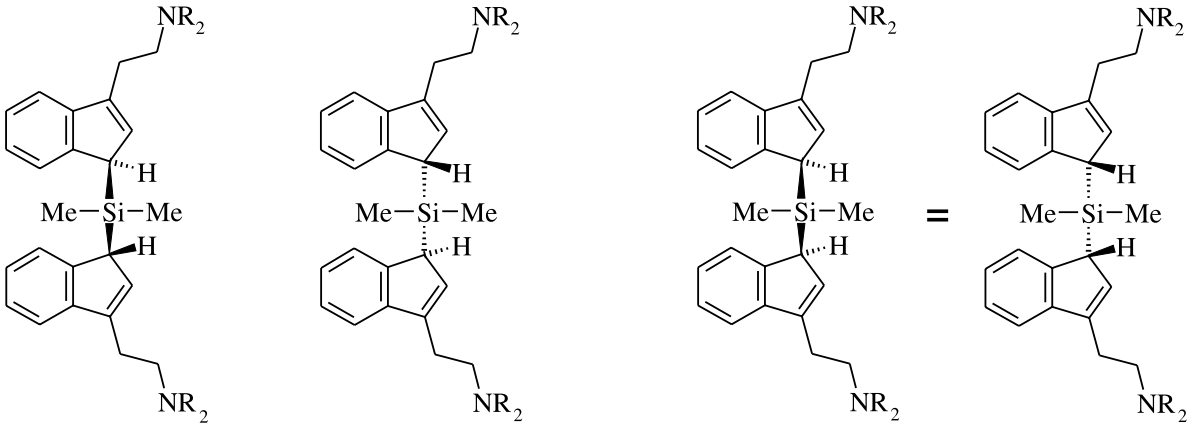
The ^{1}H NMR data of **4a**–**4c** indicated the regioselective introduction of the silicon-bridge under retention of the double bond position. The 1,3-substitution pattern was proved by the observed AB spin-system leading to two doublets with equal intensities and ^3J (H_A, H_B) = 1.1 Hz. The presence of the double bond between C(2) and C(3) was most clearly demonstrated by ^{13}C NMR data. With $\delta_{C(2)}$ = 129.9–130.2 ppm and $\delta_{C(3)}$ = 145.2–146.1 ppm, the resonances for these carbon atoms remained almost unshifted relative to the parent compounds **2a**–**2c**.

The compounds **4a**–**4c** possess two asymmetric centres at C(1) and C(1′). Therefore, three stereoisomers are conceivable: the (*R*,*R*)- and the (*S*,*S*)-enantiomers forming a racemate and a meso compound (Scheme 2).

The NMR data were consistent with the presence of the three possible stereoisomers. The *rac*/*meso* ratio of 1:1 was most easily determined from ^{1}H NMR integrals of the cleanly separated signals for the silicon bridge protons (Fig. 1 for **4a**). In the *meso* compound, one methyl group (Me_H) was located between the annellated benzene rings, causing a proton resonance shifted to higher field. The other methyl group (Me_D) lies distant from the C_6-perimeters, which resulted in a downfield shifted signal of equal intensity. In the racemic compounds the bridge protons are equivalent. This led to an averaged signal with doubled intensity (Fig. 1).

In accordance with earlier investigations (16), two independent signal sets were found for all other proton and carbon resonances, which can be assigned to the *rac* and *meso*

Scheme 2.



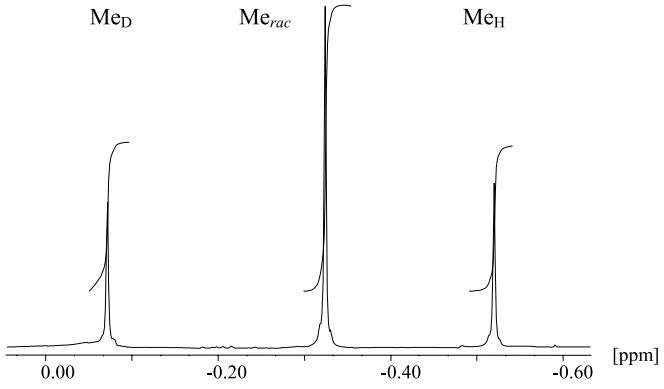
R = Me, Et, *i*-Pr

4a, **4b**, **4c**

(*R*,*R*) (*S*,*S*) (*R*,*S*) = (*S*,*R*)

rac ***meso***

Fig. 1. Part of the ^{1}H NMR spectrum (C_6D_6, TMS_{int}) of *rac*/*meso*-**4a** (resonances of the Si-CH_3-protons).



isomers. As expected, the ^{29}Si NMR data of **4a**–**4c** also exhibited two resonances each.

In addition to NMR spectroscopy and elemental analysis, the compounds **4a**–**4c** were characterized by mass spectrometry. Electron impact MS data showed the appearance of each $[CH_2NR_2]^+$ fragment with intensities of 100%. These fragments are typical of moieties containing (β-*N*,*N*-dialkylaminoethyl) substituents (17).

So far, no solid-state structure of a dimethylsilyl-bridged bisindene has been cited in the literature. Thus, the dimethylamino-substituted derivative **4a** was characterized by single crystal X-ray diffraction studies; crystallographic data are presented in Table 1, selected bond lengths and bond angles are listed in Table 2.

The analysis confirmed the assumptions based on NMR investigations; all bond lengths and angles were in the expected range. The solid-state structure of the (*R*,*R*)-enantiomer of **4a** is illustrated in Fig. 2.[3]

In a preliminary experiment the bridged bisindene *rac*/*meso*-**4b** was employed for the synthesis of corresponding group IV metal complexes. The reaction of **4b** with $Zr(NMe_2)_4$ was carried out in *n*-octane at 126 °C under a continuous argon stream. In regular intervals of 2 h, the reaction atmosphere was removed under reduced pressure and replaced with fresh argon. After a total reaction time of 8 h and complete removal of the volatiles in vacuo, a mixture of the chiral zirconocene bis(amide) *rac*-**6**, of its achiral diastereomer *meso*-**6**, and of the corresponding half-sandwich complexes **5** was obtained as a highly air- and moisture-sensitive red oil (Scheme 3). The formation of the new *ansa*-metallocenes was monitored by ^{1}H NMR spectroscopy.

From ^{1}H NMR integrals of the cleanly separated signals for the $Zr(NMe_2)_2$ groups, the overall NMR yield of *rac*-**6** and *meso*-**6** was determined as 40% with a *rac*/*meso* ratio of 4:1. This demonstrates the predominant formation of the desired racemic isomer, which in comparable situations is generally observed under the chosen reaction conditions (18).

In detail, after a reaction time of 4 h, the resonances of the free ligand *rac*/*meso*-**4b** almost disappeared due to the formation of the half-sandwich complex **5** in its two diastereomeric forms; unfortunately, their signals were par-

[3] Supplementary data may be purchased from the Directory of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www/nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 190217 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement for (*R*,*R*)-**4a**.

Empirical formula	$C_{28}H_{38}N_2Si$
Formular weight	430.69
Colour	Colourless plates
Crystal size (mm)	0.30 × 0.23 × 0.10
Crystal system, space group	Triclinic *P*–1
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Unit cell dimensions	
a (Å)	10.9650(2)
b (Å)	11.7740(3)
c (Å)	11.8160(3)
α (°)	92.9690(11)
β (°)	107.2550(11)
γ (°)	115.5181(11)
Volume (Å^3)	1285.84(5)
Z; calculated density (g/cm^3)	2; 1.112
Absorption coefficient (mm^{-1})	0.108
θ Range (°)	3–30
Index ranges	$-15 \le h \le 13$, $-15 \le k \le 16$, $-15 \le l \le 16$
No. reflections collected / unique	37 432 / 7450 (R(int) = 0.0168)
No. of data / restraints / parameters	7450 / 0 / 432
Abs. correction	Multiscan
Goodness-of-fit on F^2	1.008
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0432, wR_2 = 0.0997 (5574)
R indices (all data)	R_1 = 0.0674, wR_2 = 0.1123
Largest difference peak andhole (e Å^{-3})	0.320 and –0.216
Diffractometer used	Nonius Kappa CCD
Refinement method	Full-matrix least-squares on F^2

Table 2. Selected bond lengths (Å) and bond angles (°) for (*R*,*R*)-**4a**.

Bond lengths (Å)	
Si(1)—C(1)	1.8982(13)
C(1)—C(2)	1.5011(18)
C(1)—C(9)	1.5069(17)
C(2)—C(7)	1.4099(17)
C(7)—C(8)	1.4697(17)
C(8)—C(9)	1.3474(18)
Si(1)—C(14)	1.9046(13)
C(14)—C(15)	1.5006(17)
C(14)—C(22)	1.5016(17)
C(15)—C(20)	1.4122(17)
C(20)—C(21)	1.4652(18)
C(21)—C(22)	1.3509(18)
Bond angles (°)	
C(1)-Si(1)-C(27)	109.11(6)
C(1)-C(9)-C(8)	111.74(11)
C(2)-C(1)-C(9)	102.15(10)
C(7)-C(8)-C(9)	108.54(11)
C(14)-Si(1)-C(28)	108.53(6)
C(14)-C(22)-C(21)	111.73(11)
C(15)-C(14)-C(22)	102.32(10)
C(20)-C(21)-C(22)	108.25(11)

tially overlapped and obscured. A prolonged reaction time accompanied by periodical exchange of the reaction atmosphere led to the appearance of new signal multiplicities caused by the *rac* and *meso* isomer of **6**. Whereas the characteristic $Zr(NMe_2)_2$ groups exhibited only one singlet at δ = 2.39 ppm for *rac*-**6**, they showed two resonances at δ = 1.73 and 3.00 ppm for *meso*-**6** because of the prochirality of these moieties; an identical signal pattern was observed for the silicon bridge protons of these complexes.

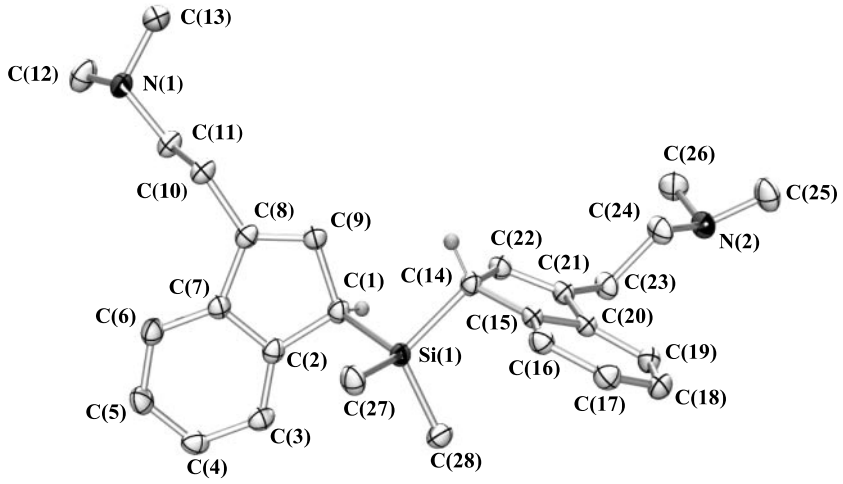
Based on the ^{1}H NMR data, an intra- or intermolecular coordination of the metal centers by the pendent dimethylamino groups can be excluded, although *rac*-**6** and *meso*-**6** are formally 16-VE-complexes. This result is supported by earlier studies, which have proved a partial double bond character for the M-amido bonds in comparable group IV metallocenes (19). As a consequence of this N → M π-donation, an additional coordination of the metal centers by the pendant donor functionalities should not be observed in the neutral complexes.

It is noteworthy that more drastic reaction conditions are required for the formation of the amino-functionalized *ansa*-zirconocenes than for the synthesis of the nonfunctionalized complexes (18). Thus, substantially higher reaction temperatures and the removal of the evolved amine are necessary to enrich the *ansa*-metallocenes *rac*-**6** and *meso*-**6** in the complex equilibrium mixture.

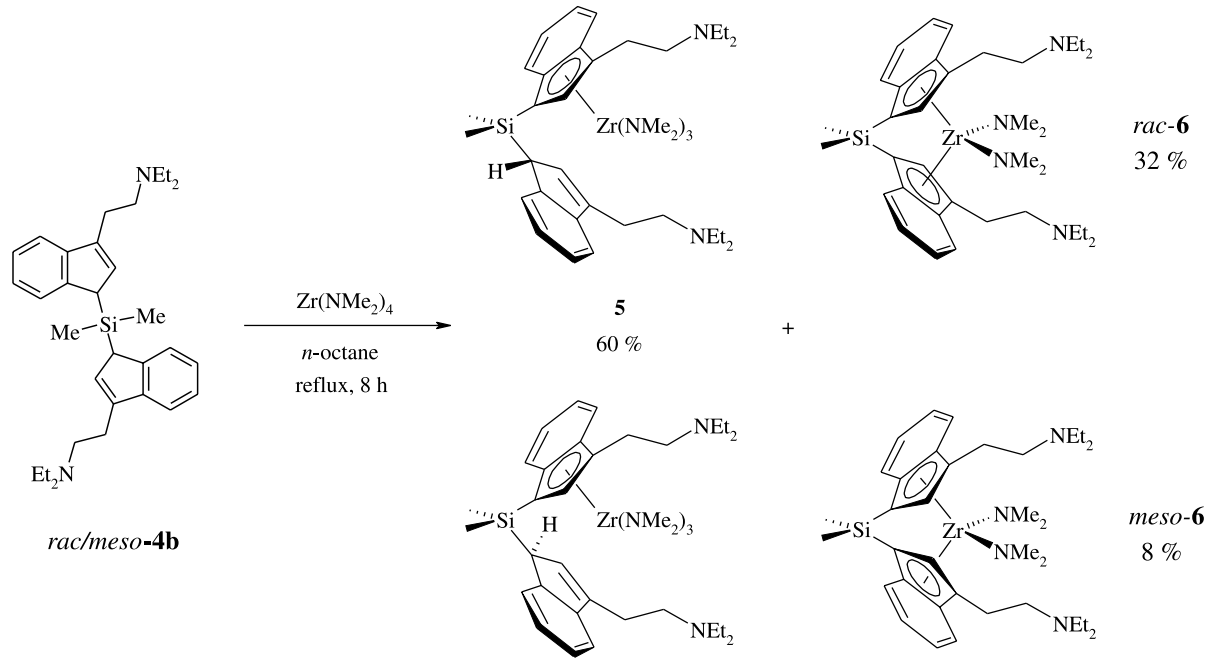
Summary

In this paper we have described the synthesis of novel chiral silicon-bridged indene derivatives which are selectively substituted in position 3 by a 2-(*N*,*N*-dialkylamino)ethyl group. The employed strategy yields the air-

Fig. 2. Molecular structure of (*R*,*R*)-**4a** (ORTEP diagram; 50% probability ellipsoids). Hydrogen atoms have been omitted for clarity except for H(1) and H(14).



Scheme 3.



and moisture-stable functionalized bisindenes in analytical purity without further extensive purification steps. The first solid-state structure of a dimethylsilyl-bridged bisindene has been presented. The diethylamino-functionalized derivative was shown to be a useful precursor for the synthesis of new *ansa*-zirconocenes via an amine elimination reaction. The extension of this approach to the preparation and isolation of other *ansa*-metallocenes containing the novel ligands will be described in subsequent contributions.

Experimental

All reactions were performed under purified Ar atmosphere using standard Schlenk techniques. The commercially available solvents were purified by conventional means and distilled immediately prior to use. Indenyl sodium (14) and $Zr(NMe_2)_4$ (18) were synthesized according to the literature. Yields refer to analytically pure samples. Isomer ratios were determined from suitable ^1H NMR integrals of cleanly separated signals. Elemental analyses were carried out at the Microanalytical Laboratory of the Universität Bielefeld. The NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer at 300 K (^1H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz). Chemical shifts are referenced to the solvent as internal standard and are reported in ppm.

3-(2-(*N*,*N*-Dimethylamino)ethyl)indene (2a)

Typical procedure

(2-Chloroethyl)dimethylamine (**1a**) (42.50 g, 395.0 mmol) was generated via a solid-phase reaction of (2-chloroethyl)dimethylamine hydrochloride and powdered so-

dium hydroxide (1:2 molar ratio) followed by a vacuum distillation using a liquid N_2 cooled trap (14). At 0 °C, the solution of (2-chloroethyl)dimethylamine in THF (80 mL) was added dropwise to a suspension of indenyl sodium (55.3 g, 400.0 mmol) in THF (200 mL). Stirring overnight at room temperature (r.t.) and subsequent refluxing for 2 h gave a green reaction mixture. The volatile components were evaporated and the residue was hydrolyzed with cooled H_2O (400 mL). After extraction of the resulting maroon solution with petrol ether (bp 35/80) (4 × 125 mL), the combined organic phases were washed with H_2O (3 × 300 mL) and dried (Na_2SO_4). The solvent was removed in vacuo and the crude product was distilled to give **2a** as a colourless, slightly viscous liquid (25.16 g, 134.3 mmol, 34%), bp 77 °C (0.5 mbar). ^{1}H NMR ($CDCl_3$) δ: 2.37 (s, 6H, N-C*H*$_3$), 2.67 (t, 2H, $^3J_{H,H}$ = 7.7 Hz, N-CH$_2$-C*H*$_2$-), 2.79 (t, 2H, $^3J_{H,H}$ = 7.7 Hz, N-C*H*$_2$-CH$_2$-), 3.35 (d, 2H, $^3J_{H,H}$ = 1.5 Hz, allyl-*H*), 6.27 (t, 1H, $^3J_{H,H}$ = 1.5 Hz, vinyl-*H*), 7.24 (pseudo t, 1H, $^3J_{H,H}$ = 7.5 Hz, *H*5), 7.34 (pseudo t, 1H, $^3J_{H,H}$ = 7.5 Hz, *H*6), 7.42 (d, 1H, $^3J_{H,H}$ = 7.5 Hz, *H*4), 7.48 (d, 1H, $^3J_{H,H}$ = 7.5 Hz, *H*7). ^{13}C NMR ($CDCl_3$) δ: 26.0 (N-CH$_2$-*C*H$_2$-), 37.6 (*C*1), 45.3 (N-*C*H$_3$), 58.2 (N-*C*H$_2$-CH$_2$-), 118.6 (*C*4), 123.4 (*C*7), 124.3 (*C*6), 125.8 (*C*5), 128.1 (*C*2), 142.2 (*C*8), 144.1 (*C*9), 145.1 (*C*3). MS (EI, 70 eV) *m*/*z* (%): 187(1) [M$^+$], 129(4) [IndCH$_2^+$], 115(6) [Ind$^+$], 58(100) [Me$_2$NCH$_2^+$]. Anal. calcd. for $C_{13}H_{17}N$ (187.30): C 83.37, H 9.15, N 7.48; found: C 83.40, H 9.44, N 7.05.

3-(2-(*N*,*N*-Diethylamino)ethyl)indene (2b)

In the same manner as described above, **2b** was obtained by reaction of (2-chloroethyl)diethylamine (**1b**) (62.4 g, 460 mmol) with indenyl sodium (64.9 g, 470 mmol) in 59% yield, bp 87 °C (0.5 mbar). ^{1}H NMR ($CDCl_3$) δ: 1.09 (t, 6H, $^3J_{H,H}$ = 7.2 Hz, N-CH$_2$-C*H*$_3$), 2.64 (q, 4H, $^3J_{H,H}$ = 7.2 Hz, N-C*H*$_2$-CH$_3$), 2.74 (t, 2H, $^3J_{H,H}$ = 7.4 Hz, N-CH$_2$-C*H*$_2$-), 2.81 (t, 2H, $^3J_{H,H}$ = 7.4 Hz, N-C*H*$_2$-CH$_2$-), 3.33 (b, 2H, *H*1), 6.24 (b, 1H, *H*2), 7.20 (pseudo t, 1H, $^3J_{H,H}$ = 7.4 Hz, *H*5), 7.30 (pseudo t, 1H, $^3J_{H,H}$ = 7.4 Hz, *H*6), 7.39 (d, 1H, $^3J_{H,H}$ = 7.4 Hz, *H*4), 7.45 (d, 1H, $^3J_{H,H}$ = 7.4 Hz, *H*7). ^{13}C NMR ($CDCl_3$) δ: 11.6 (N-CH$_2$-*C*H$_3$), 25.0 (N-CH$_2$-*C*H$_2$-), 37.3 (*C*1), 45.3 (N-*C*H$_2$-CH$_3$), 51.2 (N-*C*H$_2$-CH$_2$-), 118.4 (*C*4), 123.3 (*C*7), 124.1 (*C*6), 125.6 (*C*5), 127.7 (*C*2), 142.4 (*C*8), 143.8 (*C*9), 145.0 (*C*3). MS (EI, 70 eV) *m*/*z* (%): 215(1) [M$^+$], 143(10) [IndCH$_2$CH$_2^+$], 115(6) [Ind$^+$], 86(100) [Et$_2$NCH$_2^+$]. Anal. calcd. for $C_{15}H_{21}N$ (215.34): C 83.67, H 9.83, N 6.50; found: C 83.54, H 9.90, N 6.44.

3-(2-(*N*,*N*-Diisopropylamino)ethyl)indene (2c)

Compound **2c** was prepared according to the procedures described for **2a** and **2b** from (2-chloroethyl)diisopropylamine (**1c**) (79.6 g, 486 mmol) and indenyl sodium (67.7 g, 490 mmol) in 62% yield, bp 110 °C (0.5 mbar). ^{1}H NMR ($CDCl_3$) δ: 1.09 (d, 12H, $^3J_{H,H}$ = 6.6 Hz, N-CH-(C*H*$_3$)$_2$), 2.71 (t, 2H, $^3J_{H,H}$ = 6.5 Hz, N-CH$_2$-C*H*$_2$-), 2.77 (t, 2H, $^3J_{H,H}$ = 6.5 Hz, N-C*H*$_2$-CH$_2$-), 3.12 (sept, 2H, $^3J_{H,H}$ = 6.6 Hz, N-C*H*-(CH$_3$)$_2$), 3.35 (b, 2H, *H*1), 6.26 (b, 1H, *H*2), 7.22 (pseudo t, 1H, $^3J_{H,H}$ = 7.5 Hz, *H*5), 7.33 (pseudo t, 1H, $^3J_{H,H}$ = 7.5 Hz, *H*6), 7.41 (d, 1H, $^3J_{H,H}$ = 7.5 Hz, *H*4), 7.48 (d, 1H, $^3J_{H,H}$ = 7.5 Hz, *H*7). ^{13}C NMR ($CDCl_3$) δ: 20.8 (N-CH-(*C*H$_3$)$_2$), 30.7 (N-CH$_2$-*C*H$_2$-), 37.8 (*C*1), 44.7 (N-*C*H$_2$-CH$_2$-), 48.9 (N-*C*H-(CH$_3$)$_2$), 118.9 (*C*4), 123.7 (*C*7), 124.4 (*C*6), 126.0 (*C*5), 128.0 (*C*2), 143.2 (*C*8), 144.3 (*C*9), 145.6 (*C*3). MS (EI, 70 eV) *m*/*z* (%): 243(1) [M$^+$], 228(2) [M$^+$ – CH$_3$], 115(14) [Ind$^+$], 114(100) [*i*-Pr$_2$NCH$_2^+$]. Anal. calcd. for $C_{17}H_{25}N$ (243.40):C 83.89, H 10.35, N 5.75; found: C 83.63, H 10.39, N 5.78.

Potassium [1-(2-(*N*,*N*-dialkylamino)ethyl)indenide] salts (3a–3c)

General procedure

The solutions of the 3-(2-dialkylaminoethyl)indenes **2a**–**2c** (50 mmol) in 20 mL THF were added slowly to a suspension of potassium hydride (2.01 g, 50.1 mmol) in THF (60 mL) at –40 °C. The reaction mixtures were allowed to warm up to r.t. and stirred for 18 h. The solvent was removed in vacuo and the residues washed with *n*-hexane (2 × 50 mL). After removal of the solvent, the potassium salts were obtained as green (**3a**) (49.1 mmol, 98%), yellow (**3b**) (40.6 mmol, 81%), or brown (**3c**) (46.1 mmol, 92%) solids.

(3a)

^{1}H NMR ([D]$_8$ THF) δ: 1.89 (s, 6H, N-C*H*$_3$), 2.35 (t, 2H, $^3J_{H,H}$ = 6.3 Hz, N-CH$_2$-C*H*$_2$-), 2.77 (t, 2H, $^3J_{H,H}$ = 6.3 Hz, N-C*H*$_2$-CH$_2$-), 5.56 (d, 1H, $^3J_{H,H}$ = 3.2 Hz, *H*2), 6.06 (d, 1H, $^3J_{H,H}$ = 3.2 Hz, *H*1), 6.27–6.31 (m, 2H, *H*4, *H*7), 7.05–7.12 (m, 2H, *H*5, *H*6). ^{13}C NMR ([D]$_8$ THF) δ: 26.9 (N-CH$_2$-*C*H$_2$-), 45.2 (N-*C*H$_3$), 62.9 (N-*C*H$_2$-CH$_2$-), 91.4 (*C*2), 104.9 (*C*1), 112.9 (*C*7), 113.6 (*C*4), 116.8 (*C*6), 117.5 (*C*5), 119.4 (*C*3), 126.0 (*C*8), 128.9 (*C*9).

(3b)

^{1}H NMR ([D]$_8$ THF) δ: 0.93 (t, 6H, $^3J_{H,H}$ = 7.2 Hz, N-CH$_2$-C*H*$_3$), 2.50 (q, 4H, $^3J_{H,H}$ = 7.2 Hz, N-C*H*$_2$-CH$_3$), 2.62 (t, 2H, $^3J_{H,H}$ = 7.1 Hz, N-CH$_2$-C*H*$_2$-), 2.84 (t, 2H, $^3J_{H,H}$ = 7.1 Hz, N-C*H*$_2$-CH$_2$-), 5.61 (d, 1H, $^3J_{H,H}$ = 3.3 Hz, *H*2), 6.16 (d, 1H, $^3J_{H,H}$ = 3.3 Hz, *H*1), 6.33–6.35 (m, 2H, *H*4, *H*7), 7.12 –7.15 (m, 2H, *H*5, *H*6). ^{13}C NMR ([D]$_8$ THF) δ: 11.5 (N-CH$_2$-*C*H$_3$), 26.5 (N-CH$_2$-*C*H$_2$-), 46.6 (N-*C*H$_2$-CH$_3$), 56.0 (N-*C*H$_2$-CH$_2$-), 91.5 (*C*2), 105.1 (*C*1), 112.8 (*C*7), 113.2 (*C*4), 116.8 (*C*6), 117.6 (*C*5), 119.5 (*C*3), 126.3 (*C*8), 128.9 (*C*9).

(3c)

^{1}H NMR ([D]$_8$ THF) δ: 1.13 (d, 12H, $^3J_{H,H}$ = 6.6 Hz, N-CH-(C*H*$_3$)$_2$), 2.59 (t, 2H, $^3J_{H,H}$ = 8.5 Hz, N-CH$_2$-C*H*$_2$-), 2.82 (t, 2H,$^3J_{H,H}$ = 8.5 Hz, N-C*H*$_2$-CH$_2$-), 3.17 (sept, 2H, $^3J_{H,H}$ = 6.6 Hz, N-C*H*-(CH$_3$)$_2$), 5.64 (d, 1H, $^3J_{H,H}$ = 3.3 Hz, *H*2), 6.29 (d, 1H, $^3J_{H,H}$ = 3.3 Hz, *H*1), 6.32–6.36 (m, 2H, *H*4, *H*7), 7.13 (dd, 1H, $^3J_{H5,H4}$ = 3.8 Hz, $^3J_{H5,H6}$ = 2.5 Hz, *H*5), 7.19 (dd, 1H, $^3J_{H6,H7}$ = 3.8 Hz, $^3J_{H6,H5}$ = 2.5 Hz, *H*6). ^{13}C NMR ([D]$_8$ THF) δ: 21.7 (N-CH-(*C*H$_3$)$_2$), 32.4 (N-CH$_2$-*C*H$_2$-), 49.3 (N-*C*H$_2$-CH$_2$-), 49.5 (N-*C*H-(CH$_3$)$_2$), 91.2 (*C*2), 105.9 (*C*1), 112.4 (*C*7), 113.0 (*C*4), 117.0 (*C*6), 117.9 (*C*5), 118.9 (*C*3), 126.6 (*C*8), 128.9 (*C*9).

rac/*meso*-[Bis(3,3′-(2-(*N*,*N*-dimethylamino)ethyl)indenyl)]dimethylsilane (4a)

Typical procedure

Potassium [1-(2-(*N*,*N*-dimethylamino)ethyl)indenide] (**3a**) (5.00 g, 22.2 mmol) was dissolved in THF (35mL) and cooled to –40 °C. After dropwise addition of dimethylchlorosilane (1.15 g, 8.91 mmol) in THF (25 mL), the ma-

roon mixture was allowed to warm to r.t. Stirring was continued for 18 h and subsequent removal of the solvent gave a residue that was extracted with *n*-hexane (70 mL). After filtration the solvent was again removed in vacuo yielding a *rac*/*meso* mixture of **4a** as an orange-red oil (2.57 g, 5.97 mmol, 67%). Crystals of the (*R*,*R*)-enantiomer suitable for X-ray structure analysis were obtained by storage at 4 °C for 6 weeks. ^{1}H NMR (C_6D_6) δ: –0.52, –0.32, –0.07 (3 × s, 6H, Si-CH_3), 2.16, 2.18 (2 × s, 12H, N-CH_3), 2.51–2.83 (m, 8H, N-CH_2-CH_2-), 3.47 (b, 2H, *H*1), 6.08, 6.29 (2 × b, 2H, *H*2), 7.17–7.49 (m, 8H, *H*5, *H*6, *H*4, *H*7). ^{13}C NMR (C_6D_6) δ: –7.0, –5.9, –4.5 (Si-*C*H_3), 26.6, 26.8 (N-CH_2-*C*H_2-), 43.8, 43.9 (*C*1), 45.5, 45.5 (N-*C*H_3), 59.2, 59.3 (N-*C*H_2-CH_2-), 119.6, 119.6 (*C*4), 123.4, 123.4, 124.3, 124.3, 125.3, 125.3 (*C*7, *C*6, *C*5), 130.2, 130.2 (*C*2), 140.6, 140.8 (*C*8), 145.1, 145.2 (*C*9), 145.9, 146.0 (*C*3). ^{29}Si NMR (C_6D_6) δ: 5.5, 6.0. MS (EI, 70 eV) *m*/*z* (%): 430(4) [M^+], 372(8) [M^+ – Me_2NCH_2], 58(100) [$Me_2NCH_2^+$]. Anal. calcd. for $C_{28}H_{38}N_2Si$ (430.72): C 78.08, H 8.89, N 6.50; found: C 78.21, H 9.17, N 6.33.

rac/*meso*-[Bis(3,3′-(2-(*N*,*N*-diethylamino)ethyl)indenyl)]dimethylsilane (4b)

According to the procedure described above, **4b** was prepared by reaction of potassium [1-(2-(*N*,*N*-diethylamino)ethyl)indenide] (**3b**) (5.63 g, 22.2 mmol) with Me_2SiCl_2 (1.15 g, 8.91 mmol). The oily orange-brown product was obtained as a mixture of both diastereomers (2.67 g, 5.48 mmol, 62%). ^{1}H NMR (C_6D_6) δ: –0.50, –0.32, –0.06 (3 × s, 6H, Si-CH_3), 0.99–1.03 (m, 12H, N-CH_2-CH_3), 2.49–2.54 (m, 8H, N-CH_2-CH_3), 2.71–2.84 (m, 8H, N-CH_2-CH_2-), 3.48, 3.50 (2 × d, 2H, $^3J_{H,H}$ = 1.1 Hz, *H*1), 6.09, 6.32 (2 × d, 2H, $^3J_{H,H}$ = 1.1 Hz, *H*2), 7.17–7.53 (m, 8H, *H*5, *H*6, *H*4, *H*7). ^{13}C NMR (C_6D_6) δ: –6.9, –5.9, –4.5 (Si-*C*H_3), 12.6, 12.6 (N-CH_2-*C*H_3), 26.3, 26.4 (N-CH_2-*C*H_2-), 43.8, 43.9 (*C*1), 47.3, 47.3 (N-*C*H_2-CH_3), 52.8, 53.0 (N-*C*H_2-CH_2-), 119.6, 119.6 (*C*4), 123.4, 123.5, 124.3, 124.4, 125.3, 125.3 (*C*7, *C*6, *C*5), 130.1, 130.2 (*C*2), 141.0, 141.2 (*C*8), 145.2, 145.3 (*C*9), 146.0, 146.0 (*C*3). ^{29}Si NMR (C_6D_6) δ: 5.3, 5.7. MS (EI, 70 eV) *m*/*z* (%): 486 (3) [M^+], 400 (10) [M^+ – Et_2NCH_2], 86 (100) [$Et_2NCH_2^+$]. Anal. calcd. for $C_{32}H_{46}N_2Si$ (486.83): C 78.95, H 9.52, N 5.75; found: C 78.44, H 9.76, N 5.75.

rac/*meso*-[Bis(3,3′-(2-(*N*,*N*-diisopropylamino)ethyl)indenyl)]dimethylsilane (4c)

The *rac*/*meso* mixture of **4c** was prepared in the same manner as described above from potassium [1-(2-(*N*,*N*-diisopropylamino)ethyl)indenide] (**3c**) (6.25 g, 22.2 mmol) and Me_2SiCl_2 (1.15 g, 8.91 mmol) as a highly viscous brown oil (2.90 g, 5.35 mmol, 60%). ^{1}H NMR (C_6D_6) δ: –0.47, –0.29, –0.03 (3 × s, 6H, Si-CH_3), 1.01–1.03 (m, 24H, N-CH-(CH_3)$_2$), 2.75–3.05 (m, 12H, N-CH_2-CH_2-, N-C*H*-(CH_3)$_2$), 3.48, 3.52 (2 × b, 2H, *H*1), 6.11, 6.35 (2 × b, 2H, *H*2), 7.17–7.59 (m, 8H, *H*5, *H*6, *H*4, *H*7). ^{13}C NMR (C_6D_6) δ: –6.9, –5.7, –4.2 (Si-*C*H_3), 21.1, 21.2 (N-CH-(*C*H_3)$_2$), 31.0, 31.0 (N-CH_2-*C*H_2-), 43.8, 43.8 (*C*1), 45.2, 45.3 (N-*C*H_2-CH_2-), 48.7, 48.8 (N-*C*H-(CH$_3$)$_2$), 119.7, 119.7 (*C*4), 123.5, 123.5, 124.3, 124.4, 125.4, 125.4 (*C*7, *C*6, *C*5), 129.9, 130.0 (*C*2), 141.4, 141.6 (*C*8), 145.4, 145.4 (*C*9), 145.9, 146.0 (*C*3). ^{29}Si NMR (C_6D_6) δ: 5.3, 5.7. MS (EI, 70 eV) *m*/*z* (%): 114 (100) [*i*-$Pr_2NCH_2^+$]. Anal. calcd. for $C_{36}H_{54}N_2Si$ (542.92): C 79.64, H 9.80, N 5.16; found: C 79.26, H 9.80, N 5.14.

Formation of *rac*/*meso*-dimethylsilanediyl[bis(3,3′-(2-(*N*,*N*-diethylamino)ethyl)-indenyl)]zirconocenebis(dimethylamide) (*rac*/*meso*-6)

In a reaction flask fitted with a fractional distillation column (30 cm × 1.5 cm) $Zr(NMe_2)_4$ (0.30 g, 1.12 mmol) was dissolved in *n*-octane (20 mL). At r.t. *rac*/*meso*-**4b** (0.55 g, 1.12 mmol) was added via a syringe. After refluxing for 2 h under a continuous argon stream a ^{1}H NMR spectrum was recorded, which indicated the formation of the half-sandwich complexes **5**. Subsequently, the reaction was heated for a further 6 h under repetitive removal of $HNMe_2$ in vacuo. During this procedure a successive discolouration of the solution from yellow to red was observed. Removal of the volatiles in vacuo yielded a mixture of the half-sandwich complexes **5** (60%) as well as of the *ansa*-zirconocenes *rac*-**6** (32%) and *meso*-**6** (8%) as a highly air- and moisture-sensitive red oil. The key ^{1}H NMR data of **5**, *rac*-**6**, and *meso*-**6** are listed below.

(*5*)

^{1}H NMR (C_6D_6) δ: –0.04, 0.14, 0.32, 0.59 (4 × s, 4 × 3H, Si-CH_3), 2.77, 2.78 (2 × s, 2 × 18H, N-CH_3).

(rac-*6*)

^{1}H NMR (C_6D_6) δ: 0.63 (s, 6H, Si-CH_3), 2.39 (s, 12H, N-CH_3), 6.20 (s, 2H, *H*2).

(meso-*6*)

^{1}H NMR (C_6D_6) δ: 0.46 (s, 3H, Si-CH_3), 1.04 (s, 3H, Si-CH_3), 1.73 (s, 6H, N-CH_3), 3.00 (s, 6H, N-CH_3).

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References

1. (*a*) C. Müller, D. Vos, and P. Jutzi. J. Organomet. Chem. **600**, 127 (2000), and cited literature; (*b*) C. Müller and P. Jutzi. Synthesis, **3**, 389 (2000); (*c*) I.L. Fedushkin, S. Dechert, and H. Schumann. Organometallics, **19**, 4066 (2000); (*d*) H. Schumann, F. Erbstein, J. Demtschuk, and R. Weimann. Z. Anorg. Allg. Chem. **625**, 1457 (1999); (*e*) H. Schumann, E.C.E. Rosenthal, and J. Demtschuk. Organometallics, **17**, 5324 (1998); (*f*) H. Schumann, J.A. Meese-Marktscheffel, and L. Esser. Chem. Rev. **95**, 865 (1995), and cited literature; *(g)* P. Jutzi and U. Siemeling. J. Organomet. Chem. **500**, 175 (1995); (*h*) P. Jutzi, J. Dahlhaus, and M.O. Kristen. J. Organomet. Chem. **450**, C1 (1993); (*i*) R. Anwander, W.A. Herrmann, W. Scherer, and F.C. Munck. J. Organomet. Chem. **462**, 163 (1993); (*j*) C. Quian, J. Guo, C. Yl, J. Sun, and P. Zheng. J. Chem. Soc., Dalton Trans. 3441 (1993).
2. (*a*) A. Döhring, J. Göhre, P.W. Jolly, B. Kryger, J. Rust, and G.P.J. Verhovnik. Organometallics, **19**, 388 (2000); (*b*) E. Barsties, S. Schaible, M.-H. Prosenc, U. Rief, W. Röll, O. Weyand, B. Dorer, and H.H. Brintzinger. J. Organomet. Chem. **520**, 63 (1996); (*c*) H.J.G. Luttikhedde, R.P. Leino, C.-E.

Wilén, J.H. Näsman, M.J. Ahlgrén, and T.A. Pakkanen. Organometallics, **15**, 3092 (1996).
3. (*a*) R.D. Broene and S.L. Buchwald. J. Am. Chem. Soc. **115**, 12569 (1993); (*b*) R. Waymouth and P. Pino. J. Am. Chem. Soc. **112**, 4911 (1990).
4. (*a*) S.R. Hitchcock, J.J. Situ, J.A. Covel, M.M. Olmstead, and M.H. Nantz. Organometallics, **14**, 3732 (1995); (*b*) R.L. Halterman and T.M. Ramsey. Organometallics, **12**, 2879 (1993); (*c*) S.L. Colletti and R.L. Halterman. Tetrahedron Lett. **33**, 1005 (1992).
5. Z. Chen and R.L. Halterman. J. Am. Chem. Soc. **114**, 2276 (1992).
6. (*a*) S. Collins, B.A. Kuntz, and Y. Hong. J. Org. Chem. **54**, 4154 (1989); (*b*) F. Sato, S. Iijima, and M. Sato. J. Chem. Soc., Chem. Commun. 180 (1981).
7. (*a*) M.B. Carter, B. Schiøtt, A. Gutiérrez, and S.L. Buchwald. J. Am. Chem. Soc. **116**, 11 667 (1994); (*b*) R.L. Halterman, T.M. Ramsey, and Z. Chen. J. Org. Chem. **59**, 2642 (1994).
8. (*a*) J.B. Jaquith, J. Gaun, S. Wang, and S. Collins. Organometallics, **14**, 1079 (1995); (*b*) Y. Hong, B.A. Kuntz, and S. Collins. Organometallics, **12**, 964 (1993).
9. J.P. Banovetz, K.M. Stein, and R.M. Waymouth. Organometallics, **10**, 3430 (1991).
10. P. Jutzi and T. Redeker. Eur. J. Inorg. Chem. 663 (1998).
11. P. Jutzi and T. Redeker. Organometallics, **16**, 1343 (1997).
12. C. Müller, D. Lilge, M.O. Kristen, and P. Jutzi. Angew. Chem. **112**, 800 (2000).
13. J.C. Winter, P.K. Gessner, and D.D. Godse. J. Med. Chem. **10**, 856 (1967).
14. (*a*) P. Jutzi and M. Bangel. J. Organomet. Chem. **480**, C18 (1994); (*b*) T.-F. Wang, T.-Y. Lee, J.-W. Chou, and C.-W. Ong. J. Organomet. Chem. **439**, 155 (1992); (*c*) W.S. Rees, Jr. and K.A. Dippel. Org. Prep. Proced. Int. **24**, 527 (1992).
15. T.E. Ready, J.C.W. Chien, and M.D. Rausch. J. Organomet. Chem. **519**, 21 (1996).
16. (*a*) S.S. Rigby, L. Girard, A.D. Bain, and M.J. McGlinchey. Organometallics, **14**, 1798 (1995); (*b*) S.S. Rigby, H.K. Gupta, N.H. Werstiuk, A.D. Bain, and M.J. McGlinchey. Polyhedron, **14**, 2787 (1995); (*c*) Y.X. Chen, M.D. Rausch, and J.C.W. Chien. Organometallics, **12**, 4607 (1993); (*d*) E. Marechal and J.P. Tortal. C. R. Acad. Sci. Paris, **267**, 467 (1968); (*e*) L.H. Sommer and N.S. Marans. J. Am. Chem. Soc. **73**, 5135 (1951).
17. H. Schumann, F. Erbstein, D.F. Karasiak, I.L. Fedushkin, J. Demtschuk, and F. Girgsdies. Z. Anorg. Allg. Chem. **625**, 781 (1999).
18. (*a*) J.N. Christopher, G.M. Diamond, R.F. Jordan, and J.L. Petersen. Organometallics, **15**, 4038 (1996); (*b*) G.M. Diamond, R.F. Jordan, and J.L. Petersen. Organometallics, **15**, 4030 (1996); (*c*) G.M. Diamond, R.F. Jordan, and J.L. Petersen. J. Am. Chem. Soc. **118**, 8024 (1996); (*d*) G.M. Diamond, S. Rodewald, and R.F. Jordan. Organometallics, **14**, 5 (1995).
19. (*a*) D.M. Giolando, K. Kirschbaum, L.J. Graves, and U. Bolle. Inorg. Chem. **31**, 3887 (1992); (*b*) R.A. Andersen, D.B. Beach, and W.L. Jolly. Inorg. Chem. **24**, 2741 (1985); (*c*) M.F. Lappert, P.P. Power, A.R. Sanger, and R.C. Srivastava. Metal and matalloid amides. Ellis Horwood, Chichester, West Sussex. 1980; (*d*) D.C. Bradley and M.H. Chisholm. Acc. Chem. Res. **9**, 273 (1976).