1,3-Doubly Bridged Group 4 Metallocenes by Intramolecular Reductive Coupling of Pendant Olefins

Timothy H. Warren, Gerhard Erker,* Roland Fröhlich,[†] and Birgit Wibbeling[†]

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

Received July 12, 1999

The new precursors $M(NMe_2)_2Cl_2(dme)$ (M = Zr (3), Hf (4)) react with the dilithium derivative of the silyl-bridged bis(1-indenyl) ligand bearing pendant 4-pentenyl groups Li₂- $[3,3'-{}^{5}R_{2}-SBI]$ (2) in toluene at -35 °C to provide the corresponding bis(dimethylamido) metallocenes with rac/meso ratios of 6-7:1. Subsequent treatment of the substantially *rac*enriched zirconocene mixture with excess TMS-CI in dichloromethane in the presence of a catalytic amount of anhydrous HCl provides rac-[3,3'-5R2-SBI]ZrCl2 (7) in 40% isolated yield free from its *meso* isomer. Similar reactions of $Li_2[SBI] \cdot OEt_2$ and of $Li_2[EBI] \cdot OEt_2$ with **3** and **4** also lead to selective formation of the *rac*-metallocenes with *rac/meso* ratios as high as 20:1 for [SBI]Zr(NMe₂)₂ (10). Sodium amalgam reduction of *rac*-[3,3'-⁵R₂-SBI]ZrCl₂ (7) in THF results in the intramolecular tail-to-tail coupling of the pendant olefins to provide the crystallographically characterized α, α' -disubstituted zirconacyclopentane 13 in 95% isolated yield. In contrast, reduction of rac-[3,3'-5R2-SBI]HfCl2 (8) (prepared from 2 and HfCl₄ in toluene) leads to both the symmetric α, α' -disubstituted and the unsymmetric α, β' substituted hafnacyclopentanes (14 and 15, respectively) in a 1:1 ratio. Zirconacycle 13 reacts with $[HNMe_2Ph]^+[OTf]^-$ to give the monotriflate 17, in which one of the 4-pentenyl arms is released and the other is formally protonated at its terminal carbon atom to give this thermally stable secondary alkyl complex. Formation of 17 is best understood as proceeding through a mono-olefin intermediate **16**, which can be trapped with 2-butyne to form the corresponding zirconacyclopentene 18. Reaction of 13 with the organometallic Lewis acid $B(C_6F_5)_3$ results in the formal abstraction of a hydride from the 3-position of one arm to form $[HB(C_6F_5)_3]^-$ and a THF-bound π -allyl cation **19**, in which one pendant alkene is also free.

Introduction

The C_2 -symmetric environment of group 4 *rac*-metallocenes based on symmetrically bridged indenyl or tetrahydroindenyl ligands plays host to a number of stereoselective C–C and/or C–H bond-forming processes.¹ Such reactions include isotactic α -olefin polymerization,² asymmetric hydrogenation of alkenes³ and imines,³ asymmetric hydrosilylation of ketones,⁵ asymmetric carbomagnesation of cyclic allyl ethers and amines,^{6a-c} enantioselective carboalumination of alkenes,^{6d} and asymmetric catalysis of Diels–Alder

- (1) For an overview, see: Hoveyda, A. H.; Morken, J. P. Angew. Chem. **1996**, 108, 1378–1401; Angew. Chem., Int. Ed. Engl. **1996**, 35, 1262–1284.
- (2) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. Angew. Chem. **1995**, *107*, 1255–1283; Angew. Chem., Int. Ed. Engl. **1995**, *34*, 1143–1170.
- (a) Jinotali, and Jingen. Cham. 1906, 101, 1200, 1200, 1200, 1100, 1100, 1000, 1100, 1100, 1100, 10000, 1000, 1000, 1000, 1000, 1000, 1000, 1000, 1000, 1000, 100
- (4) Willoughby, C. A.; Buchwald, S. L. J. Am. Chem. Soc. 1994, 116, 11703–11714.

(5) Carter, M. B.; Schiøtt, B.; Gutiérrez, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11667–11670.

(6) (a) Xu, Z. M.; Johannes, C. W.; Houri, A. F.; La, D. S.; Cogan D. A.; Hofilena, G. E.; Hoveyda, A. H. J. Am. Chem. Soc. 1997, 119, 10302–10316. (b) Heron, N. M.; Adams, J. A.; Hoveyda, A. H. J. Am. Chem. Soc. 1997, 119, 6205–6206. (c) Visser, M. S.; Heron, N. M.; Didiuk, M. T.; Sagal, J. F.; Hoveyda, A. H. J. Am. Chem. Soc. 1996, 118, 4291–4298. (d) Kondakov, D. Y.; Negishi, E. J. Am. Chem. Soc. 1995, 117, 10771–10772; 1996, 118, 1577–1578.

reactions.⁷ Many of the above applications employ C_2 -symmetric *ansa*-metallocenes, either in their racemic or optically resolved forms,^{6d,8} which emphasizes the importance of efficient routes to this important family of catalyst precursors.

Focusing on the extremely rapid C–C and C–H bondforming reactions that metallocene cations mediate in the polymerization of α -olefins, we became interested in exploring potentially new reactivity patterns⁹ that could result from the physical separation of the two equivalent sites in a metallocene complex. The X-ray structure of the *ansa*-zirconocene **1**, which bears an unusually long 12-carbon bridge, shows such a separation, as the bridge spans the front side of the coordination wedge rather than appearing opposite to it (Scheme 1).¹⁰ Unfortunately, this conformation is not maintained in solution due to rotation of the indenyl rings.¹¹ To ensure that this desired conformation is rigorously

[†] X-ray crystal structure analyses.

⁽⁷⁾ Jaquith, J. B.; Guan, J.; Wang, S.; Collins, S. Organometallics 1995, 14, 1079-1081.

^{(8) (}a) Ringwald, M.; Stürmer, R.; Brintzinger, H. H. J. Am. Chem. Soc. **1999**, *121*, 1524–1527, and references therein. (b) Kondakov, D. Y.; Negishi, E. J. Am. Chem. Soc. **1995**, *117*, 10771–10772. (c) Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermühle, D.; Krüger, C.; Nolte, M.; Werner, S. J. Am. Chem. Soc. **1993**, *115*, 4590–4601.

⁽⁹⁾ Bertuleit, A.; Fritze, C.; Erker, G.; Fröhlich, R. Organometallics 1997, 16, 2891–2899.

⁽¹⁰⁾ Erker, G.; Mollenkopf, C.; Grehl, M.; Fröhlich, R.; Krüger, C.; Noe, R.; Riedel, M. *Organometallics* **1994**, *13*, 1950–1955.



preserved in solution, we sought the synthesis of a 1,3doubly bridged analogue in which rotation of the indenyl rings would be prevented.

Although synthetic routes to 1,2-doubly bridged metallocenes have been developed to provide ansa-metallocenes with a greater degree of rigidity,12 these methods were not expected to be as successful in the preparation of a 1,3-doubly bridged metallocene due to the greater required length of the linker and the entropic challenges that entail. Our strategy was to employ silyl-bridged ansa-metallocenes bearing pendant groups in the 3- and 3'-positions which would be ammenable to coupling reactions, thus using the bent metallocene geometry as a template to bring these functionalities into mutual proximity. We describe herein our efforts utilizing terminal alkenyl pendants, chosen both for their compatibility with standard synthetic methods in the preparation of substituted indenyl ligands and their group 4 metallocenes¹³ and due to the wide range of potential methods to couple these functionalities.^{14,15}

Results and Discussion

Synthesis of Silyl-Bridged Ligands and ansa-Metallocene Complexes. The silvl-bridged ligand employed in this study bearing two 5-carbon pendant terminal olefin chains was prepared in a three-step reaction sequence (Scheme 2). Deprotonation of indene in THF with *n*-butyllithium followed by addition of 4-pentenyl tosylate afforded the corresponding 4-pentenyl indene, which was isolated primarily as its 1-substituted isomer after distillation. Subsequent deprotonation with *n*-butyllithium in ether followed by the addition of 0.5 equiv of Me₂SiCl₂ at -78 °C provided the silyl-bridged bis(indene) ligand H₂[3,3'-⁵R₂-SBI] as a yellow oil following flash chromatography. The corresponding dilithium salt Li₂[3,3'-⁵R₂-SBI] (2) was prepared by deprotonation of the bis(indene) system in pentane with *n*-butyllithium and is conveniently isolated by filtration in roughly 60% overall yield (two steps).



Warren et al.



^a(i) 1 equiv of BuLi/THF, then ROTs/0 °C; (ii) BuLi/Et₂O, then 0.5 equiv of $Me_2SiCl_2/-78$ °C to room temperature; (iii) 2 equiv of BuLi/pentane.



Scouting experiments were performed to determine suitable group 4 metal complex precursors that would allow the convenient isolation of the corresponding racmetallocene dichlorides derived from the dilithium salt **2**. Although the metallocenes may by be prepared by reaction between 2 and MCl₄ (M = Zr, Hf) in toluene, the overall conversion is low (ca. 35%) and devoid of stereoselectivity (radmeso = 1:1). In an attempt to boost the overall conversion using two metal-based "protecting groups",¹⁶ the known Zr(NEt₂)₂Cl₂(THF)₂¹⁷ reagent was used. This led to much higher formation (ca. 90% crude) of the red [3,3'-5R2-SBI]Zr(NEt2)2, but again as a 1:1 rad meso mixture.

Reaction of the lithium salt 2 with the new, toluenesoluble precursors $M(NMe_2)_2Cl_2(dme)$ (M = Zr (3), Hf (4)), which we prepared by reaction of M(NMe₂)₄ with 2 equiv of TMS-Cl in ether in the presence of 3-5 equiv of dme, led as well to high conversion to the corresponding $[3,3'-{}^{5}R_{2}-SBI]M(NMe_{2})_{2}$ (M = Zr (5), Hf (6)) complexes, but in much higher rac/meso ratios estimated at 6-7:1 (Scheme 3).¹⁸ Without requiring isolation, the bis(dimethylamido)zirconocene 5 may be conveniently converted to *rac*- $[3,3'-{}^{5}R_{2}-SBI]ZrCl_{2}$ (7) by reaction with excess TMS-Cl in the presence of a catalytic amount

⁽¹¹⁾ Mollenkopf, C. Dissertation, University of Münster, 1994.

^{(12) (}a) Mengele, W.; Diebold, J.; Troll, C.; Röll, W.; Brintzinger, H.-H. Organometallics 1993, 12, 1931-1935. (b) Cano, A.; Cuenca, T.; Gómez-Sal, P.; Royo, B.; Royo, P. Organometallics 1994, 13, 1688-1694.

^{(13) (}a) Alt, H. G.; Jung, M. J. Organomet. Chem. 1999, 580, 1-16. (b) Alt, H. G.; Jung, M. J. Organomet. Chem. 1998, 562, 229-253. (c) Spence, R. E. v. H.; Piers, W. E. Organometallics 1995, 14, 4617-4624.

⁽¹⁴⁾ Schuster, M.; Blechert, S. *Angew. Chem.* **1997**, *109*, 2124–2144; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2037–2056. (b) Marsella-M.

<sup>Angew. Chem., Int. Ed. Engl. 1997, 50, 2037–2036. (b) Marsend-M.
J.; Maynard, H. D.; Grubbs, R. H. Angew. Chem. 1997, 109, 1147–1150; Angew. Chem., Int. Ed. Engl. 1997, 36, 1101–1103.
(15) (a) Taber, D. F.; Louey, J. P.; Wang, Y.; Nugent, W. A.; Dixon, D. A.; Harlow, R. L. J. Am. Chem. Soc. 1994, 116, 9457–9463. (b) Negishi, E.; Takahashi, T. Acc. Chem. Res. 1994, 27, 124–130.</sup>

⁽¹⁶⁾ Warren, T. H.; Schrock, R. R.; Davis, W. M. Organometallics 1998, 17, 308-321

⁽¹⁷⁾ Brenner, S.; Kempe, R.; Arndt, P. Z. Anorg. Allg. Chem. 1995, 621, 2021-2024.

⁽¹⁸⁾ Similar diastereoselectivities were also observed using the known Zr(NMe₂)₂Cl₂(THF)₂, but the new M(NMe₂)₂Cl₂(dme) reagents employed here were chosen for their ease of preparation and better solubility in toluene.

Scheme 4^a



 $^a\!(i)$ 1 equiv of $Li_2[SBI]\text{·}OEt_2;$ (ii) 1 equiv of $Li_2[EBI]\text{·}OEt_2$ toluene/-35 °C to room temperature.

of anhydrous HCl. Although the zirconocene dichloride **7** may be isolated free from its *meso* isomer in ca. 40% yield, similar conversion of hafnocene **6** to the desired *rac*-[3,3'-⁵R₂-SBI]HfCl₂ (**8**) proved unreliable. *rac*-[3,3'-⁵R₂-SBI]HfCl₂ (**8**) is instead best prepared directly from **2** and HfCl₄ in toluene and is isolated isomerically pure in 10–15% yield following one recrystallization.

To test the generality of the stereoselectivity observed in the transmetalation of the bis(1-indenyl) ligand **2** observed above, a similar protocol was tried with two related bis(indenyl) ligands. Reactions of Li₂[SBI]·OEt₂ and Li₂[EBI]·OEt₂ with M(NMe₂)₂Cl₂(dme) (**3** and **4**) provide the corresponding bis(dimethylamido)metallocenes **9**–**12** in ca. 90% purity (¹H NMR) and in *rac*/*meso* ratios of over 20:1 in the case of [SBI]Zr(NMe₂)₂ (**9**) (Scheme 4). Simple removal of the volatiles in vacuo followed by recrystallization of the residue from toluene after filtration provided the pure *rac*-metallocenes in about 50% overall yield (unoptimized).

Intramolecular Reductive Olefin Coupling. Reduction of rac- $[3,3'-{}^{5}R_{2}-SBI]ZrCl_{2}$ (7) bearing the 5-carbon arms was effected with sodium amalgam in THF. It results in the intramolecular tail-to-tail coupling of the two pendant olefins to provide the C_2 -symmetric α, α' -disubstituted zironacyclopentane 13 in 90% isolated yield (Scheme 5). The ¹H NMR spectrum of 13 lacks characteristic terminal alkenyl resonances, and although two diastereomeric α, α' -disubstituted zironacyclopentanes are possible, singlets observed for the indenyl 2-H and Me_2 Si groups (δ 5.49 and 0.54 ppm, respectively) suggest the presence of a single diastereomer. In conjuction with ${}^{1}H{}^{-1}H$ correlation spectra, the single upfield resonance at δ -2.14 ppm is assigned to the secondary Zr-CHR groups. The metallacyclopentane formulation is further corroborated by the ${}^{1}J_{CH}$ coupling constants of 122.5 and 124.5 Hz for the carbon atoms α and β to zirconium, respectively.¹⁹ ¹H NOE NMR experiments as well as rudimentary molecular modeling studies favor the diastereomer shown in Scheme 5, and this was confirmed by an X-ray crystal structure analysis (see below).

In contrast, the analogous reduction of *rac*- $[3,3'-{}^{5}R_{2}-SBI]HfCl_{2}$ (8) leads to a ca. 1:1 ratio of two products in 90% overall yield (Scheme 5). The symmetric α, α' -



disubstituted hafnacyclopentane 14 could be identified from the ¹H NMR spectrum of this mixture by comparison of its three characteristic indenyl 2-H, Me₂Si, and Hf–C*H*R signals (δ 5.35, 0.55, and –1.99 ppm, respectively) with corresponding resonances from 13. Furthermore, the 600 MHz ¹H 1D-TOCSY NMR spectrum obtained by irradiation of the resonance assigned to the Hf–C*H*R group of the symmetric isomer **14** at δ –1.99 ppm reveals metallacycle resonances that are essentially superimposable on those appearing in the ¹H NMR spectrum of its zirconium analogue 13. In contrast to the symmetric **13** and **14**, the absence of *C*₂-symmetry in the other hafnacycle 15 results in two ¹H NMR signals at δ 5.51 and 5.29 ppm as well as at δ 0.64 and 0.47 ppm for its inequivalent indenyl 2-H and Me₂Si groups, respectively. Furthermore, complete assignment of the coupled pendants based on a series of ${}^{1}H{}^{-1}H$ and ¹H-¹³C correlation NMR spectra as well as ¹H 1D-TOCSY NMR spectra reveals both Hf-CHR (δ 1.11 ppm) and Hf– CH_aH_bR (δ –0.16 and –1.73 ppm) groups, identifiying metallacycle 15 as derived from the headto-tail coupling of the pendant olefins.

X-ray Crystal Structural Analyses. The asymmetric units of the isostructural complexes **13** and **14** contain both enantiomers of the corresponding C_2 -symmetric bis(indenyl) metallocene, of which one of these enantiomers shows positional disorder for the carbon atoms β and γ to the indenyl rings. The non-disordered molecule of zirconacyclopentane **13** (Figure 1) clearly shows the coupling of the two formerly pendant ω -alkenes to form a C–C single bond with a C(12)–C(32) distance of 1.541(7) Å [Hf complex **14**:

⁽¹⁹⁾ Takahashi, T.; Fischer, R.; Xi, Z.; Nakajima, K. *Chem. Lett.* **1996**, 357–358.



Figure 1. DIAMOND representation (50% probability level) of the nondisordered molecule found in the X-ray study of 13. Selected bond distances (Å) and angles (deg): Zr(1)-C(11), 2.286(5), Zr(1)-C(31) 2.294(5), C(12)-C(32)1.541(7), C(11)-C(12) 1.542(7), C(31)-C(32) 1.547(7), C(11)-Zr(1)-C(31) 87.36(17), Zr(1)-C(11)-C(12) 97.4(3), Zr(1)-C(12) 97.4(3), Zr(1)-C(12)C(31)-C(32) 99.2(3), C(11)-C(12)-C(32) 112.1(4), C(12)-C(32)-C(31) 115.0(4), Zr(1)-C(31)-C(30) 124.0(3), Zr(1)-C(11)-C(10) 125.2(3).



Figure 2. SCHAKAL representation of 13 highlighting the 10-carbon bridge which results upon metallacycle formation.

1.511(8) Å].²⁰ These bond distances lie comfortably within the range established, 1.502(5)-1.560(3) Å, for other structurally characterized group 4 metallacyclopentanes.^{15a,19,21,22} The Zr-C distances of 2.286(5) and 2.294(5) Å [Hf: 2.258(5), 2.282(5) Å] as well as the C-Zr-C angle of 87.36(17)° [Hf: 86.2(2)°] are also comparable to those distances and angles found in other related zirconacyclopentanes (2.275(2)-2.347(4) Å and 81.2(1)-89.2(1)°, respectively). There does not appear to be any appreciable ring strain in the metallacycle itself, as both 13 and 14 exhibit ring angles in the range 109–115°, and the Cp(centr)–M–Cp(centr) angles of 127.4(2)° (13) and 128.0(2)° (14) also reveal no unusual distortion. It would thus appear that the 4-pentenyl arms were ideally situated to couple, forming the α, α' disubstituted metallacyclopentanes 13 and 14.



 $^a\!(i)$ 1—5 equiv of [HMe2NPh]+[OTf]-/benzene- d_6 ; (ii) 10 equiv of 2-butyne/benzene- d_6 /overnight.

Reactivity of the Metallacyclopentanes. With closure of the two indenyl-bound alkenyl arms effected by the metallocene centers, we felt that we might be able to simply remove the coupled alkyl chains in 13-15 from the metal center by protonation with 2 equiv of an HCl source. Ideally, this would provide 1,3-doubly bridged metallocene dichlorides bearing either a 10 (from 13 and 14) or nine (from 15) carbon chain spanning the metallocene coordination wedge. Whereas reaction with anhydrous HCl in toluene did not lead to any tractible products at temperatures spanning from -78 °C to room temperature, the benzene-soluble [HNMe₂Ph]⁺[OTf]⁻ reacts slowly with zirconacycle 13 to produce the ring-opened product 17, in which one of the ω -alkenyl arms is released from the metal center and the terminal carbon of a bound pendant alkene is protonated (Scheme 6). The reaction is relatively slow, occurring over 20 min at room temperature in benzene d_6 (ca. 0.05 M in **13**, 0.3 M in [HNMe₂Ph]⁺[OTf]⁻), and the new secondary alkylmetallocene complex 17 is surprisingly stable in the presence of excess anilinium salt. Whereas olefinic ¹H NMR resonances centered at δ 5.73 and 4.95 ppm clearly reveal the dissociation of one pendant alkenyl arm, a multiplet of relative intensity 1 at δ -1.79 ppm shows that one secondary Zr-CH unit has remained intact. Protonation of the terminal carbon of this "bound" pendant has resulted in a doublet at δ 0.88 ppm coupled solely to the Zr-CH group (${}^{3}J_{\rm HH} = 8.4$ Hz). Furthermore, the unsymmetric nature of 17 is reflected in the observation of diastereotopic indenyl 2-H (δ 6.24 and 5.08 ppm) as well as *Me*₂Si groups (δ 0.65 and 0.53 ppm). In contrast to **13**, no reaction occurs between 14 or 15 and [HNMe₂Ph]⁺⁻ [OTf]⁻ over hours under similar conditions.

The surprising inertness of 13 toward protonolytic cleavage of the Zr–C σ -bond is probably due to severe steric crowding at the central core of the molecule. The observed mode of protonation of 13 seemed to indicate reversibility of the metallacycle formation and even the dissociation of a pendant olefin from the metallacycle to form the alleged mono-olefin metallocene intermediate 16 (Scheme 6). This assumption was supported by a trapping reaction with excess 2-butyne. Reaction of 13 with 10 equiv of 2-butyne in benzene slowly leads to the formation of zirconacyclopentene 18, in which 1

⁽²⁰⁾ Complete structural details from the X-ray crystal structure

 ^{(21) (}a) Knight, K. S.; Wang, D.; Waymouth, R. M.; Ziller, J. J. Am. Chem. Soc. 1994, 116, 1845–1854. (b) Mashima, K.; Sakai, N.; Takaya, H. Bull. Chem. Soc. Jpn. 1991, 64, 2475-2483. (c) Schmidt, J. R.; Duggan, D. M. Inorg. Chem. 1981, 20, 318-323.

⁽²²⁾ In the structures of the zirconacyclopentanes *rac*-[EBTHI]Zr-(CHPhCH₂CHPhCH₂) and *rac*-[EBTHI]Zr(C₄H₈), disorder in either one or both of the C_{β} atoms results in abnormally short $C_{\beta}-C_{\beta}$ distances of 1.331(6) and 1.451(7) Å, respectively. Mansel, S.; Thomas, D.; Lefeber, C.; Heller, D.; Kempe, R.; Baumann, W.; Rosenthal, U. *Organometallics* **1997**, *16*, 2886–2890.



equiv of alkyne formally adds to the intermediate **16**. In the ¹H NMR spectrum of **18**, two methyl resonances at δ 1.39 and 1.27 ppm indicate the incorporation of 1 equiv of 2-butyne into the metallacycle that still bears one secondary Zr–CH group (δ 0.26 ppm), and the olefinic multiplets centered at δ 5.74 and 4.95 ppm establish the dissociation of one pendant alkene. The observation of both two indenyl 2-*H* (δ 6.04 and 5.49 ppm) and two *Me*₂Si (δ 0.70 and 0.69 ppm) ¹H NMR signals serves to further illustrate the unsymmetric nature of **18**.

Although **14** and **15** do not readily incorporate 2-butyne under similar conditions, evidence that pendant olefin complexes are accessible in the hafnium system comes from heating a ca. 1:1 mixture of the hafnacycles **14** and **15** in benzene- d_6 . After 18 h at 65 °C, equilibrium is established in favor of the symmetric isomer **14** (K = 6), indicating that interconversion between these two hafnacycles does take place and is most reasonably mediated by an intermediate analogous to **16** (Scheme 7).

Reaction with the organometallic Lewis acid $B(C_6F_5)_3$ follows an unusual course. Rather than abstracting²³ a secondary carbon from the zirconacycle 13 or adding to the terminal carbon²⁴ in the mono-olefin intermediate 16, a hydride is formally abstracted from the middle carbon of one bound pendant arm (probably at the stage of the reactive intermediate **16**). The $[H-B(C_6F_5)_3]^$ anion results (¹¹B NMR: δ 24.9 ppm, (d))²⁵ as well as the π -allylmetallocene cation **19**, which is stable when generated in the presence of THF (Scheme 8). Whereas the allyl unit in **19** could be assigned by a combination of 1D-TOCSY NMR and correlation NMR spectra, its cationic nature is strongly suggested by the dramatic downfield shifts of the ¹³C NMR signals of the allylic carbon atoms (δ 88.2, 131.4, and 107.8 ppm) when compared to their resonances in the neutral zirconacycle

13 (δ 35.7, 65.1, and 29.6 ppm; C-10 to C-12, respectively).

In conclusion, we have demonstrated an effective new method for the stereoselective synthesis of *rac*-metallocenes through the reaction of dilithium salts of bridged bis(indenyl) systems with the easily prepared reagents $M(NMe_2)_2Cl_2(dme)$ (M = Zr (3), Hf (4)). Complementary to the route described by Jordan employing the free *ansa*-metallocene ligand and $M(NMe_2)_4$,²⁶ this new method holds promise in cases where the desired *ansa*-metallocene ligand is either too bulky or not acidic enough to undergo efficient and complete aminolysis.

The bent sandwich geometry of related silyl-bridged *ansa*-metallocenes rac-[3,3'- ${}^{5}R_{2}$ -SBI]MCl₂ (M = Zr (7), Hf (8)) may be used to bring substituents in the 3- and 3'-positions into mutual proximity. Simple reduction of 7 and 8 with sodium amalgam effects the coupling of the 4-pentenyl arms leading to 1,3-doubly bridged metallocenes through metallacyclopentane formation and illustrates how ligand systems may be further functionalized *after* transmetalation.

Experimental Section

All reactions involving butyllithium or group 4 metal compounds were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were purified by standard techniques, while deuterated NMR solvents were dried and stored over activated 4 Å molecular sieves before use. NMR spectra were recorded on either a Bruker AC 200P (1H, 200.13; ¹³C, 50.3 MHz; ¹¹B, 64.2 MHz) or on a Varian Unity Plus (¹H, 599.9; ¹³C, 150.8; ¹⁹F, 471.0 MHz) NMR spectrometer in which ¹H and ¹³C assignments were in some cases confirmed through GCOSY, GHSQC, GHMBC, and one-dimensional TOCSY spectra.²⁷ All NMR spectra were recorded at room temperature unless otherwise noted. Proton and carbon NMR spectra were referenced internally by the ¹H or ¹³C signal of the solvent relative to trimethylsilane. Fluorine and boron spectra were referenced externally to neat CFCl₃ and BF₃ etherate, respectively. Coupling constants J are reported in Hz. Melting points were obtained using a TA Instruments DSC 2010 differential scanning calorimeter, and elemental analyses were obtained using a Foss-Heraeus CHN-Rapid microanalyzer.

X-ray data sets were collected with a Nonius KappaCCD diffractometer, using a rotating anode generator FR591. Programs used: data collection Collect, data reduction Denzo-SMN, absorption correction SORTAV, structure solution SHELXS-97, structure refinement SHELXL-97, graphics DIA-MOND and SCHAKAL-92.²⁸

Tris(pentafluorophenyl)borane²⁹ as well as $M(NMe_2)_4$ (M = Zr,^{26e} Hf^{26b}) were prepared according to literature proceedures.

⁽²³⁾ Yang, X.; Stern, C. L.; Marks, T. J. J. Am. Chem. Soc. 1991, 113, 3623-3625.

⁽²⁴⁾ Sun, Y. M.; Piers, W. E.; Rettig S. J. Chem. Commun. **1998**, 127–128.

⁽²⁵⁾ Blaschke, U.; Erker, G.; Nissinen, M.; Wegelius, E.; Fröhlich, R. Organometallics **1999**, *18*, 1224–1234.

^{(26) (}a) Christopher, J. N.; Jordan, R. F.; Petersen, J. L.; Young, V.
G. Organometallics 1997, 16, 3044–3050. (b) Diamond, G. M.; Jordan,
R. F.; Petersen, J. L. Organometallics 1996, 15, 4030–4037. (c)
Christopher, J. N.; Diamond, G. M.; Jordan, R. F.; Petersen, J.
Organometallics 1996, 15, 4038–4044. (d) Diamond, G. M.; Jordan,
R. F.; Petersen, J. L. Organometallics 1996, 15, 4045–4053. (e)
Diamond, G. M.; Jordan, R. F.; Petersen, J. L. J. Am. Chem. Soc. 1996, 118, 8024–8033. (f) Diamond, G. M.; Rodewald, S.; Jordan, R. F.

⁽²⁷⁾ Braun, S.; Kalinowski, H.; Berger, S. *100 and More Basic NMR Experiments*; VCH: Weinheim, 1996, and references therein.

⁽²⁸⁾ Programs used: Data collection: COLLECT: Nonius B.V., 1998. Data reduction: Denzo-SMN: Otwinowski, Z.; Minor, W. Methods Enzymol. 1997, 276, 307–326. Absorption Correction: SORTAV: Blessing, R. H. Acta Crystallogr. 1995, A51, 33–37; J. Appl. Crystallogr. 1997, 30, 421–426. Structure Solution: SHELXS-97: Sheldrick, G. M. Acta Crystallogr. 1990, A46, 467–473. Sheldrick, G. M. Universität Göttingen, 1997. Structure refinement: SHELXL-97: Sheldrick, G. M. Universität Göttingen, 1997. Graphics: DIAMOND: Brandenburg, K. Universität Bonn, 1996; SCHAKAL-92: Keller, E. Universität Freiburg, 1997.

Directly before use, indene (Fluka, \geq 90%) was either freshly distilled or purified by passage of a ca. 10% v/v pentane solution through silica gel followed by removal of pentane in vacuo. Me₂SiCl₂ was distilled from *N*,*N*-dimethylaniline under argon after stirring overnight to remove HCl. Li₂[EBI]·OEt₂ and Li₂[SBI]·OEt₂ were prepared by adding 2 equiv of *n*butyllithium to the corresponding bis(indenes)^{26c,30} in ether and then isolating the product by filtration. [HNMe₂Ph]⁺[OTf]⁻ was prepared by adding freshly opened triflic acid (Aldrich, 98%) to a equimolar solution of *N*,*N*-dimethylaniline in pentane at 0 °C after decanting this solution from 4 Å molecular sieves.

4-Pentenyl Tosylate.³¹ Freshly ground potassium hydroxide (170 g, 2.95 mol) was slowly added over 30 min to a stirring solution of 4-penten-1-ol (21.2 g, 246 mmol) and tosyl chloride (56.3 g, 296 mmol) in 600 mL of ether at 0 °C. After stirring for an additional 1.5 h, the mixture was quenched with ice water (ca. 300 mL) until all of the remaining KOH dissolved. The organic fraction was separated and the aqueous phase washed with ether (2 \times 150 mL). After drying the combined organic extracts over MgSO₄, removal of the volatiles in vacuo afforded 55.4 g (94%) of the tosylate as colorless oil. ¹H NMR (CDCl₃, 200 MHz): δ 7.74 (d, 2, Ar–H), 7.30 (d, 2, Ar–H), 5.66 (m, 1, CH=CH₂), 4.92 (m, 2, CH=CH₂), 3.98 (t, 2, OCH₂), 2.40 (s, 3, Ar-CH₃), 2.03 (q, 2, CH₂), 1.69 (q, 2, CH₂). ¹³C NMR (CDCl₃, 50 MHz): δ 144.7, 136.6, 133.1, 129.8, 127.8, 115.8, 69.8, 29.3, 27.9, 21.6. Anal. Calcd for C12H16O3S (240.3): C, 59.98; H, 6.70. Found: C, 59.34; H, 6.72.

3-(4-Pentenyl)indene. Butyllithium (146 mL, 231 mmol, 1.58 M in hexane) was slowly added to a solution of indene (26.7 g, 230 mmol) in 250 mL of THF at 0 °C. After stirring for 3 h, a solution of 4-pentenyl tosylate (53.9 g, 224 mmol) in 50 mL of THF was added dropwise over 45 min at 0 °C. The solution was stirred overnight, allowing to slowly warm to room temperature. After addition of a few drops of water, the suspension was concentrated by rotary evaporation and then extracted with water (250 mL) and ether (400 mL). The organic phase was separated and the aqueous phase washed twice with ether (100 mL). The organic extracts were dried over MgSO₄ and then concentrated to dryness. A small amount of unreacted tosylate was removed by dissolving the orange oil in pentane (100 mL) and filtering through a pad of silica gel, which was then rinsed with pentane (300 mL). Fractional distillation (80 °C, 0.1 mbar) gave the product as a colorless liquid (28.1 g, 67%) containing a small amount (6%) of the 1,1disubstituted indene. ¹H NMR (CDCl₃, 200 MHz): δ 7.50– 7.15 (m, 4, Ar), 6.24 (t, 1, 2-H), 5.91 (m, 1, CH=CH₂), 5.07 (m, 2, CH=CH₂), 3.35 (d, 2, ring CH₂), 2.60 (t, 2, ind-CH₂), 2.21 (q, 2, CH₂), 1.83 (q, 2, CH₂). ¹³C NMR (CDCl₃, 50 MHz): δ 144.5, 144.3, 138.6, 133.0, 127.8, 125.9, 124.43, 123.7, 118.9, 114.7, 37.7, 33.6, 27.2, 27.1. (Extra peaks appear in this ¹³C NMR spectrum due to the presence of the disubstituted isomer and cannot be assigned with utmost certainty to the product.) Anal. Calcd for C₁₄H₁₆ (184.3): C, 91.26; H, 8.74. Found: C, 91.25; H, 9.16.

Li₂[Me₂Si(1-(3-(4-pentenyl)indene)₂)] (**Li₂[3,3'-⁵R₂-SBI]**) (2). Butyllithium (88.1 mL, 139 mmol, 1.58 M in hexane) was slowly added to a solution of 3-(4-pentenyl)indene (28.1 g, 139 mmol) in 150 mL of ether at 0 °C. After stirring for 3 h, the solution was chilled to -78 °C, and a solution of Me₂SiCl₂ (8.98 g, 69.6 mmol) in ether (50 mL) was added dropwise over 45 min. The solution was stirred overnight, slowly allowing to warm to room temperature. The volatiles were removed in vacuo, and the remaining oil was taken up in pentane (100 mL) and filtered through a pad of silica gel, which was then rinsed with pentane (300 mL). The volatiles were removed in vacuo to give a 1:1 rad meso mixture of Me₂Si(1-(3-(4-pentenyl)indene)₂). The yellow oil was then taken up in 250 mL of pentane and sparged with argon. Butyllithium (83 mL, 131 mmol, 1.58 M in hexane) was added at 0 °C, and after ca. 1 h the product began to precipitate. After 4 h, the precipitate was collected by filtration, rinsed with pentane, and dried in vacuo. The solid was then dispersed in pentane (200 mL), and the suspension was stirred for 3 h to remove all traces of butyllithium. The solid was again collected by filtration, washed with pentane (50 mL), and dried in vacuo to yield 18.8 g (62%) of the product as slightly off-white powder. ¹H NMR $(C_6D_6/THF-d_8, ca. 10:1, 200 MHz): \delta 8.08 (m, 2, Ar), 7.71 (m, 3.00 MHz)$ 2, Ar), 7.01 (s, 2, 2-H), 5.93 (m, 2, CH=CH2), 5.02 (m, 4, CH= CH2), 3.05 (t, 4, ind-CH2), 2.27 (q, 4, CH2), 1.93 (q, 4, CH2), 0.97 (SiMe₂). ¹³C NMR (C₆D₆/THF- d_8 , ca. 10:1, 50 MHz): δ 140.0, 134.5, 130.1, 123.9, 122.2, 118.3, 115.5, 115.2, 114.1, 109.9, 96.6, 34.7, 32.4, 28.4, 3.0. Anal. Calcd for C30H38Li2Si (440.6): C, 81.78; H, 8.69. Found: C, 81.54; H, 8.54.

Zr(NMe₂)₂Cl₂(dme) (3). Chlorotrimethylsilane (9.77 mL, 77.0 mmol) was added to a solution of Zr(NMe₂)₄ (10.30 g, 38.5 mmol) in ether (200 mL) with dme (20 mL). After stirring overnight, the solution was concentrated to ca. 30 mL and allowed to crystallize at -30 °C. Decanting the mother liquors followed by drying the very pale yellow crystals in vacuo gave a first crop of 8.89 g. A second crop of **3** could be obtained by further concentration and crystallization of the mother liquors to give a total yield of 10.35 g (76%). ¹H NMR (C₆D₆/THF-*d*₈, ca. 10:1, 200 MHz): δ 3.28 (br, 4, OC*H*₂), 3.27 (s, 12, N*M*e₂), 3.12 (s, 6, OC*H*₃). ¹³C NMR (C₆D₆/THF-*d*₈, ca. 10:1, 50 MHz): δ 74.9 (v br, O*C*H₂), 62.1 (O*C*H₃), 44.6 (N*M*e₂). Mp: 89 °C. Anal. Calcd for C₈H₂₂N₂Cl₂O₂Zr (340.4): C, 28.23; H, 6.51; N, 8.23. Found: C, 28.15; H, 6.71; N, 8.04.

Hf(NMe₂)₂Cl₂(dme) (4). Chlorotrimethylsilane (7.04 mL, 55.5 mmol) was added to a solution of Hf(NMe₂)₄ (9.85 g, 27.8 mmol) in ether (100 mL) with dme (15 mL). After stirring overnight, the solution was concentrated to ca. 30 mL and allowed to crystallize at -30 °C. Decanting the mother liquors followed by drying the colorless crystals in vacuo gave a yield of 9.50 g (80%). ¹H NMR (C₆D₆/THF-*d*₈, ca. 10/1, 600 MHz): δ 3.40 (s, 12 H, N*M*e₂), 3.10 (s, 6 H, OC*H*₃), 3.12 (s, 4 H, OCH₂). ¹³C NMR (C₆D₆/THF-*d*₈, ca. 10:1, 150 MHz): δ 71.6 (O*C*H₂), 62.1 (O*C*H₃), 44.2 (N*M*e₂). Mp: 95 °C. Anal. Calcd for C₈H₂₂N₂-Cl₂HfO₂ (427.7): C, 22.47; H, 5.18; N, 6.55. Found: C, 22.15; H, 4.90; N, 6.38.

rac-[3,3'-⁵R₂-SBI]ZrCl₂ (7). Chilled toluene (70 mL, -30 °C) was added to a solid mixture of 2 (5.53 g, 12.7 mmol) and 3 (4.32 g, 12.7 mmol). The suspension immediately became red and was allowed to warm to room temperature with stirring. After 2 h, the red solution was filtered through Celite and concentrated to ca. 10 mL. An aliquot measured by ¹H NMR spectroscopy showed that the major species in solution was rac-[3,3'-5R2-SBI]Zr(NMe2)2 (5), whose Me2Si resonance appears at δ 0.87 ppm. Integrating the largest indenyl 2-H resonance (δ 6.12 ppm) against the second largest (δ 6.20 ppm) in this region afforded a conservative estimate of 6:1 for the rac/meso ratio of this mixture. Dichloromethane (60 mL) was added followed by TMS-Cl (6.43 mL, 50.7 mmol). The solution was chilled to 0 °C, after which anhydrous HCl (0.63 mL, 0.63 mmol, 1.0 M in ether) was added with stirring. After 10 min, the red color of the solution faded to orange, signaling conversion to the dichloride. In some preparations the color did not change after addition of 5 mol % HCl, requiring the addition of another portion or two to effect complete conversion. The solution was concentrated to dryness, and the residue was washed with pentane and then crystallized from toluene to give 2.83 g (38%) of the product 7 as orange microcrystals. ¹H NMR (C₆D₆, 600 MHz): δ 7.38 (d of t, 2 H, 4-H), 7.27 (d of t, 2 H, 7-H), 7.14 (m, 2 H, 5-H), 6.88 (m, 2 H, 6-H), 5.72 (s, 2 H, 2-H), 5.67 (m, 2 H, 11-H), 4.92 (m, 4 H, 12-CH₂), 2.83 (t, 4 H, 8-CH₂), 1.92 (m, 4 H, 10-CH₂), 1.53 (m, 4 H, 9-CH₂), 0.65

⁽²⁹⁾ Massey, A. G.; Park, A. J. J. Organomet. Chem. 1964, 2, 245–250.

⁽³⁰⁾ Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. J. Organomet. Chem. 1988, 342, 21–29.

⁽³¹⁾ An established method was employed: Brandsma, L. *Preparative Acetylenic Chemistry*, 2 ed.; Elsevier: Amsterdam, 1988; pp 256– 257.

(SiMe₂). ¹³C NMR (C₆D₆, 150 MHz): δ 138.5 (C-11), 133.0 (C-3a), 131.4 (C-3), 128.2 (C-7a), 126.8 (C-5), 126.6 (C-6), 124.9 (C-7), 124.7 (C-4), 117.1 (C-2), 115.0 (C-12), 85.7 (C-1), 33.9 (C-9), 29.6 (C-10), 28.2 (C-8), -1.8 (SiMe₂). Mp: 200 °C. Anal. Calcd for C₃₀H₃₄Cl₂SiZr (584.8): C, 61.61; H, 5.86. Found: C, 61.67; H, 6.58.

rac-[3,3'-5R2-SBI]HfCl2 (8). Chilled (-35 °C) toluene (75 mL) was added to a solid mixture of HfCl₄ (2.95 g, 9.21 mmol) and 2 (4.02 g, 9.21 mmol). The suspension became yellow once stirring commenced and was allowed to warm to room temperature. After stirring overnight, the yellow suspension was filtered through Celite, concentrated to ca. 15 mL, and chilled to -35 °C. A first crop of ca. 1.5 g consisting of a 85:15 rad meso mixture was recrystallized from Et₂O/dichloromethane (50:50) to give 0.77 g (12%) of the product as bright yellow microcrystals. ¹H NMR (C₆D₆, 600 MHz): δ 7.37 (d of t, 2 H, 7-H), 7.33 (d of t, 2 H, 7-H), 7.11 (m, 2 H, 5-H), 6.87 (m, 2 H, 6-H), 5.69 (s, 2 H, 2-H), 5.67 (m, 2 H, 11-H), 4.92 (m, 4 H, 12-CH2), 2.83 (t, 4 H, 8-CH2), 1.92 (m, 4 H, 10-CH2), 1.53 (m, 4 H, 9-CH₂), 0.66 (SiMe₂). 13 C NMR (C₆D₆, 150 MHz): δ 138.5 (C-11), 132.2 (C-3a), 129.1 (C-3), 126.9 (C-7a), 126.7 (C-5), 126.5 (C-6), 124.9 (C-7), 124.5 (C-4), 115.3 (C-2), 114.9 (C-12), 86.1 (C-1), 33.9 (C-9), 29.6 (C-10), 28.1 (C-8), -1.7 (SiMe₂). Anal. Calcd for C₃₀H₃₈Cl₂SiHf (676.1): C, 53.29; H, 5.67. Found: C, 53.62; H, 5.11.

rac-[SBI]Zr(NMe₂)₂ (9). Chilled (-35 °C) toluene (25 mL) was added to a solid mixture of Li₂[SBI]·OEt₂ (0.593 g, 1.58 mmol) and **3** (0.593 g, 1.50 mmol). The suspension turned red rapidly and was allowed to warm to room temperature with stirring. After 3 h, the volatiles were removed in vacuo, and the residue was extracted with toluene (20 mL). The extracts were filtered through Celite, and the filtrate was concentrated to ca. 5 mL and was allowed to crystallize overnight at -30 °C. The mother liquors were then decanted and the crystals dried in vacuo to provide 0.49 g (66%, unoptimized) of the product as red crystallization indicated a *rac/meso* ratio of greater than 20.

rac-**[SBI]Hf(NMe₂)₂ (10). 10** was prepared analogously to **9** employing Li₂[SBI]·OEt₂ (0.51 g, 1.37 mmol) and **4** (0.65 g, 1.37 mmol) to provide 0.13 g (35%) of the product as orange-yellow crystals in two crops. ¹H NMR analysis²⁶ indicated an initial *rac/meso* ratio of ca. 16:1.

rac-[EBI]Zr(NMe₂)₂ (11). 11 was prepared analogously to 9 employing Li₂[EBI]·OEt₂ (0.52 g, 1.50 mmol) and 3 (0.51 g, 1.45 mmol) to provide 0.33 g (50%) of the product as red-orange crystals. ¹H NMR analysis²⁶ indicated an initial *rad meso* ratio of ca. 5:1.

rac-**[EBI]Hf(NMe₂)₂ (12). 12** was prepared analogously to **9** employing Li₂[EBI]·OEt₂ (0.34 g, 1.00 mmol) and **4** (0.43 g, 1.00 mmol) to provide 0.28 g (54%) of the product as yellow crystals. ¹H NMR analysis²⁶ indicated an initial *rac/meso* ratio of ca. 8:1.

Zirconacycle (13). Chilled THF (120 mL, -30 °C) was added to a solid mixture of 7 (2.16 g, 3.79 mmol) and freshly prepared sodium amalgam (63 g, 14 mmol, 0.5% Na in Hg). Rapid stirring at 0 °C resulted in a darkening of the solution and dispersion of the amalgam. After 1 h, the solution was dark orange and was stirred for another hour. The volatiles were removed in vacuo, the residue was extracted with toluene (50 mL), and then the extracts were filtered through Celite. Removal of the volatiles in vacuo provided 1.81 g (95%) of the product as orange microcrystals. Crystals suitable for X-ray analysis were obtained by slow evaporation of a benzene solution of 13. ¹H NMR (C₆D₆, 600 MHz): δ 7.39 (d of t, 2 H, 4-H), 7.03 (m, 2 H, 5-H), 6.91 (d of t, 2 H, 7-H), 6.69 (m, 2 H, 6-H), 5.49 (s, 2 H, 2-H), 2.99 (m, 2 H, 8-CH₂), 2.75 (m, 2, 8-CH₂), 2.00 (m, 2 H, 9-CH₂), 1.71 (m, 2 H, 10-CH₂), 1.57 (m, 2 H, 9-CH2), 1.42 (m, 2 H, 12-CH2), 1.33 (m, 2, 12-CH2), 1.28 (m, 4, 10-CH₂), 0.54 (s, 6 H, SiMe₂), -2.14 (m, 2 H, 11-H). ¹³C NMR (C₆D₆, 150 MHz): δ 127.9 (C-3a), 125.9 (C-7a), 124.2 (C-5),

123.7, 123.6 (C-6 and C-7), 123.1 (C-4), 122.6 (C-3), 118.9 (C-2), 79.9 (C-1), 65.1 (${}^{1}J_{CH} = 122.5$, C-11), 35.7 (${}^{1}J_{CH} = 122.0$, C-10), 29.6 (${}^{1}J_{CH} = 124.5$, C-12), 28.5 (C-9), 26.2 (C-8), -2.1 (SiMe₂). Mp: 147 °C (decomp). Anal. Calcd for C₃₀H₃₄SiZr (513.9): C, 70.12; H, 6.67. Found: C, 69.97; H 6.95. X-ray crystal structure analysis of 13: formula $C_{30}H_{34}SiZr$, M =513.88, 0.50 × 0.30 × 0.30 mm, a = 14.352(1) Å, b = 10.216-(1) Å, c = 32.489(1) Å, $\beta = 92.42(1)^{\circ}$, V = 4759.3(6) Å³, $\rho_{calc} =$ 1.434 g cm⁻³, $\mu = 5.29$ cm⁻¹, empirical absorption correction $(0.778 \le T \le 0.858)$, Z = 8, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, T = 198 K, ω and φ scans, 18828 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/ λ] = 0.67 Å⁻¹, 8784 independent ($R_{int} = 0.058$) and 7852 observed reflections [$I \ge$ 2 $\sigma(I)$], 619 refined parameters, R = 0.058, wR2 = 0.129, max. residual electron density 0.63 (-0.76) e Å⁻³, two independent molecules in the asymmetric unit being enantiomers, checking of $\lambda/2$ gives no indication of cell doubling, positional disorder in the carbon chain of the second molecules refined with restraints (0.57(1):0.43(1); 0.53(1):047(1)), hydrogens calculated and refined as riding atoms.

Hafnacyclopentanes 14 and 15. Chilled THF (120 mL, -30 °C) was added to a solid mixture of 8 (1.60 g, 2.38 mmol) and freshly prepared sodium amalgam (44 g, 9.5 mmol, 0.5% Na in Hg). Rapid stirring at 0 °C resulted in a darkening of the solution to forest green and dispersion of the amalgam. After ca. 1 h, the solution became yellow again and was stirred overnight. The volatiles were removed in vacuo, the residue was extracted with toluene (50 mL), and then the extracts were filtered through Celite. Removal of the volatiles in vacuo provided 1.28 g (89%) of the product as yellow microcrystals. Crystals of 14 suitable for an X-ray crystal structure analysis were obtained by slow evaporation of a benzene solution containing a mixture of 14 and 15. Spectral data for symmetric hafnacyclopentane 14: ¹H NMR (C₆D₆, 600 MHz, atom numbering as in Scheme 7): δ 7.45 (d of t, 2 H, 4-H), 7.04 (m, 2 H, 5-H), 6.93 (d of t, 2 H, 7-H), 6.70 (m, 2 H, 6-H), 5.39 (s, 2 H, 2-H), 2.99 (m, 2 H, 8-CH2), 2.74 (m, 2, 8-CH2), 2.11 (m, 2 H, 10-CH₂), 2.01 (m, 2 H, 9-CH₂), 1.67 (m, 2 H, 12-CH₂), 1.51 (m, 4 H, 9-CH2, 12-CH2), 1.38 (m, 2, 10-CH2), 0.55 (s, 6 H, SiMe2), -1.99 (m, 2 H, 11-H). ¹³C NMR (C₆D₆, 150 MHz): δ 127.7 (C-3a), 125.3 (C-7a), 124.5 (C-5), 124.0, 123.8 (C-6 and C-7), 123.5 (C-4), 121.9 (C-3), 117.8 (C-2), 82.3 (C-1), 67.0 (C-11), 35.3 (C-10), 30.1 (C-12), 28.4 (C-9), 25.9 (C-8), -2.1 (SiMe₂). Spectral data for the unsymmetrical isomer 15: ¹H NMR (C₆D₆, 600 MHz): δ 7.70 (d of t, 1 H, 4-H), 7.66 (d of t, 1 H, 4'-H), 7.29 (d of t, 1 H, 7'-H), 7.12 (d of t, 1 H, 7-H), 7.03 (m, 1 H, 5'-H), 6.93 (m, 2 H, 5-H), 6.69 (m, 2 H, 6-H and 6'-H), 5.51 (s, 1 H, 2'-H), 5.29 (s, 1 H, 2-H), 3.37 (m, 1 H, 8'-CH₂), 3.17 (m, 1 H, 8-CH₂), 2.97 (m, 1 H, 8'-CH2), 2.72 (m, 1 H, 11'-H), 2.54 (m, 1 H, 9'-CH₂), 2.18 (m, 2 H, 9-CH₂ and 10-CH₂), 2.03 (m, 1 H, 9'-CH₂), 1.98 (m, 1 H, 8-CH₂), 1.87 (m, 1 H, 10'-CH₂), 1.77 (m, 1 H, 12-CH₂), 1.67 (m, 1 H, 12-CH₂), 1.66 (m, 1 H, 10'-CH₂), 1.44 (m, 1 H, 9-CH₂), 1.11 (m, 1 H, 11-H), 0.64 (SiMe₂), 0.45 (SiMe₂), 0.28 (m, 1 H, 10-CH₂), -0.16 (m, 1 H, 12'-CH₂), -1.73 (m, 1 H, 12'-CH₂). ¹³C NMR (C₆D₆, 150 MHz): δ 131.1 (C-3a), 130.3 (C-3a'), 128.2 (C-7a), 126.7, 125.4, 125.1, 125.1, 124.9, 124.5 (C-7a'), 123.9, 123.7, 123.0, 122.8 (C-2'), 119.9 (C-3), 119.2 (C-3'), 117.9 (C-2), 86.1 (C-1'), 81.2 (C-1), 59.0 (C-12'), 58.7 (C-11), 39.0 (C-10'), 34.7 (C-12), 33.3 (C-11'), 33.1 (C-10), 29.5 (C-8'), 28.5 (C-8), 26.0 (C-9'), 25.5 (C-9), 0.3, -3.2 (SiMe₂) (four aromatic resonances could not be assigned unequivocally). Mp: 220 °C (decomp, crystals of 14). Anal. Calcd for C₃₀H₃₄-SiHf (601.2): C, 59.94; H, 5.70. Found C, 59.46; H, 5.88. X-ray crystal structure analysis of **14**: formula C₃₀H₃₄SiHf, $M = 601.15, 0.50 \times 0.30 \times 0.30$ mm, a = 14.346(1) Å, b =10.195(1) Å, c = 32.544(1) Å, $\beta = 92.62(1)^{\circ}$, V = 4754.8(6) Å³, $\rho_{\text{calc}} = 1.680 \text{ g cm}^{-3}, \ \mu = 44.55 \text{ cm}^{-1}, \text{ empirical absorption}$ correction (0.214 $\leq T \leq$ 0.348), Z = 8, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, T = 198 K, ω and φ scans, 18 862 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/ λ] = 0.71 Å⁻¹, 12 601 independent ($R_{int} = 0.024$) and 11 061 observed reflections $[I \ge 2 \ \sigma(I)]$, 619 refined parameters, R = 0.041, wR2 = 0.080, max. residual electron density 1.96 (-2.14) e Å⁻³ close to Hf, two independent molecules in the asymmetric unit being enantiomers, checking of $\lambda/2$ gives no indication of cell doubling, positional disorder in the carbon chain of the second molecules refined with restraints (0.57(1):0.43(1); 0.53(1):0.47(1)), hydrogens calculated and refined as riding atoms.

Monotriflate (16). A benzene- d_6 solution (ca. 0.7 mL) of 13 (0.030 g, 0.59 mmol) was added to a vial containing [HMe₂NPh]⁺[OTf]⁻ (0.030 g, 0.11 mmol) and was subsequently transferred to an NMR tube. After standing at room temperature for approximately an hour, conversion to the product 16 was complete. 16 is stable in the presence of excess anilinium for several hours at room temperature. ¹H NMR (C₆D₆, 600 MHz): δ 7.30, 7.24, 7.17, 6.92 (dd, 1 H each, 4-H, 4'-H, 7-H, 7'-H), 7.07, 7.05, 6.97, 6.92 (m, 1 H each, 5-H, 5'-H, 6-H, 6'H), 6.24 (s, 1 H, 2-H or 2'H), 5.73 (m, 1 H, 11'-H), 5.08 (s, 1 H, 2'-H or 2-H), 4.95 (m, 2 H, 12'-CH2), 3.30 (m, 1 H, 8'-CH2), 3.05 (m, 1 H, 8'-CH2), 2.64 (m, 1 H, 8-CH2), 2.43 (m, 1 H, 8-CH₂), 2.00 (m, 2 H, 10'-CH₂), 1.68 (m, 1 H, 9-CH₂), 1.59 (m, 2 H, 9'-CH₂), 1.49 (m, 1 H, 10-CH₂), 1.3 (m, 1 H, 10-CH₂), 1.10 (m, 1 H, 9-CH₂), 0.88 (d, ${}^{3}J_{HH} = 8.4$, 3 H, 12-CH₃), 0.64 (SiMe₂), 0.53 (SiMe₂), -1.79 (m, 1 H, 11-H). ¹³C NMR (C₆D₆, 150 MHz): δ 138.3 (C-11'), 134.3, 131.0, 129.6, 128.9, 127.3, 126.4, 126.1, 125.0, 124.3, 123.2, 122.9, 122.4, 119.5 (C-2 or C-2'), 115.1 (C-12'), 114.1 (C-2'or C2), 84.1, 82.7 (C-1 and C-1'), 71.6 (C-11), 35.9 (C-10), 33.8 (C-10'), 31.0 (C-9'), 28.1 (C-9), 27.2 (C-8'), 26.6 (C-8), 18.7 (12-CH₃), -0.7, -3.1 (SiMe₂) (the triflate CF₃ resonance was not found). ¹⁹F NMR (C₆D₆, 471 MHz): δ -75.1.

Zirconacyclopentene (18). 2-Butyne (15 µL, 0.19 mmol) was added to a solution of 13 (0.015 g, 0.029 mmol) in 0.7 mL of benzene- d_6 and transferred to an NMR tube and sealed with a Teflon cap. The solution was allowed to stand at room temperature overnight, after which conversion to the monoinsertion product 18 was complete. Removal of the volatiles in vacuo provided spectra free of excess 2-butyne. ¹H NMR (C₆D₆, 600 MHz): δ 7.48 (d of t, 1 H, 4-H), 7.43 (d of t, 1 H, 4'-H), 7.37 (d of t, 1 H, 7-H), 7.21 (d of t, 1 H, 7'-H), 6.96 (m, 1 H, 5'-H), 6.83 (m, 1 H, 6-H), 6.79 (m, 1 H, 5-H), 6.73 (m, 1 H, 6'-H), 6.04 (s, 1 H, 2'-H), 5.74 (m, 1 H, 11'-H), 5.49 (s, 1 H, 2-H), 4.97 (m, 2 H, 12'-CH2), 2.95 (m, 1 H, 8-CH2), 2.77 (m, 1 H, 8'-CH₂), 2.60 (m, 1 H, 8'-CH₂), 2.37 (m, 1, 8-CH₂), 2.02 (q, 2 H, 10'-CH₂), 1.96 (m, 2 H, 9-CH₂ and 12-CH₂), 1.71 (m, 2 H, 9'-CH2), 1.64 (m, 1 H, 10-CH2), 1.46 (d of d, 1 H, 12-CH2), 1.39 (s, 3 H, 16-CH₃), 1.32 (m, 1 H, 9-CH₂), 1.26 (s, 3, 14-CH₃), 1.00, (m, 1 H, 10-CH₂), 0.70 (SiMe₂), 0.69 (SiMe₂), 0.26 (m, 1 H, 11-H). ¹³C NMR (C₆D₆, 150 MHz): δ 183.7 (C-15), 138.7 (C-11'),

132.3 (C-13), 129.7, 128.9, 128.2, 126.7, 125.6, 125.3, 125.1, 124.7, 124.4, 123.8, 123.5, 123.2, 123.2, 121.8, 119.7, 118.3, 114.9 (aromatic), 83.6 (C-1'), 82.4 (C-1), 61.0 (C-11), 36.2 (C-12), 34.1 (C-9'), 33.3 (C-10), 30.1 (C-10'), 28.3 (C-9), 27.4 (C-8'), 26.7 (C-8), 22.0 (C-16), 19.9 (C-14), -0.2 (SiMe₂), -2.6 (SiMe₂).

Cationic π -allylzirconocene (19). A chilled (-35 °C) solution of $B(C_6F_5)_3$ (0.013 g, 0.025 mmol) in ca. 0.7 mL of toluene- d_8 was added to a chilled solution of **13** (0.012 g, 0.024 mmol) in ca. 0.7 mL of toluene- d_8 containing 10 μ L (4 equiv) of THF- d_8 . The solution darkened to red, and a portion of the solution was immediately transferred to an NMR tube and cooled to -78 °C. ¹H NMR spectra at -35 °C showed incomplete conversion to product. Warming to room temperature affored spectrally clean conversion to product, and later inspection of the NMR tube revealed a red-purple oil, which had separated. ¹H NMR (toluene- d_8 , 600 MHz): δ 7.05, 6.99, 6.93, 6.87 (d of t, 1 H each, 4-H, 4'-H, 7-H, 7'-H), 7.05, 6.75, 6.67, 6.62 (m, 1 each, 5-H, 5'-H, 6-H, 6'-H), 5.89 (s, 1 H, 2-H or 2'-H), 5.65 (m, 1 H, 11'-H), 5.16 (m, 1 H, 11-H), 4.94 (m, 2, 12'-CH2), 4.78 (s, 1 H, 2'-H or 2-H), 4.34 (d, 1 H, 12-CH2), 3.25 (d, 1H, 12-CH₂), 2.73 (m, 2 H, 8'-CH₂ and 8-CH₂), 2.63 (dd, 1 H, 9-CH₂), 2.48 (dd, 1 H, 9-CH₂), 2.20 (m, 1 H, 8'-CH₂), 1.91 (q, 2 H, 10'-CH₂), 1.67 (m, 1 H, 9-CH₂), 1.51 (m, 2 H, 9'-CH₂), 0.73 (s, 3 H, SiMe₂), 0.66 (s, 3, SiMe₂), -1.75 (dd, 1H, 10-H). Partial ¹³C NMR (toluene- d_8 , 600 MHz): δ 131.4 (C-11), 127.0, 126.1, 123.6, 121.0, 121.02, 120.4, 120.1, 116.8, 115.6 (C-12'), 107.8 (C-12), 107.5 (C-2'or C-2), 90.1 (C-1 or C-1'), 88.2 (C-10), 84.9 (C-1'or C-1), 34.5 (C-9), 33.3 (C-10'), 30.7, 26.2, 25.9, 23.4 (C-8), -1.0 (SiMe₂), -4.1 (SiMe₂). (B(C₆F₅)₃ resonances omitted) ¹¹B NMR (toluene- d_8 , 64.2 MHz): δ –24.9 (d).

Acknowledgment. Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. T.H.W expresses gratitude to NSF-NATO, DAAD, and the Alexander von Humboldt Foundation for their generous support of his stay in Germany and thanks Dr. Klaus Bergander for many stimulating discussions as well as assistance in obtaining high-field NMR spectra.

Supporting Information Available: Additional NMR data for complexes **7**, **8**, and **13–19**. Details on the X-ray crystal structure determinations of complexes **13** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9905411