Neutral Tripodal Amidozirconium Alkyls and Hydride. Synthesis, Structures, and Catalytic Olefin Insertions

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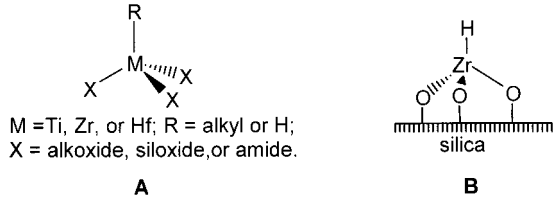
Summary: *Synthesis, structural characterization, and preliminary reactivity studies of the title compounds are reported. The ethylene polymerization and diene cyclization activities that these complexes have shown are unprecedented for neutral molecules of the type* X_3MR *(X = amide, alkoxide, or siloxide; M = group 4 metal; R = alkyl or hydride).*

Group 4 d^0 organometallic molecules of the type **A** have been studied since the 1970s.[1] Despite of the



apparent electronic unsaturation of these complexes, very little reactivity has been observed.[1] On the other hand, Basset recently suggested on EXAFS evidence that the neutral tetra-coordinate species **B** is the active component in his silica-supported catalysts, which polymerize ethylene and hydrogenolyze polyolefins.[2] In an attempt to "model" Basset's catalysts, Duchateau found on the contrary that benzyltitanium silsesquioxide did not react with ethylene or even form acetonitrile adducts.[1g] The apparent analogy and yet drastic reactivity differences between **A** and **B** and the fact that most homogeneous olefin polymerization catalysts are cationic[3−6] raise an interesting question as to what structural characteristics may significantly activate the neutral molecules **A**.

One possibility seems to be the coordination geometry. We reasoned that reduction of the X−M−X angles in **A** would open up the coordination sites cis to metal−alkyl and thus possibly improve the reactivity.[7] We wish to report here the synthesis and initial observations on the catalytic activities of a few compounds of the general type **A**, which feature unusually small N−Zr−N angles.[9]

Tripodal ligand **1** (Scheme 1), which was developed by Gade along with a series of other tripodal amide ligands,[10,11] has been chosen to create the small-angle geometry. Aminolysis of tetrabenzylzirconium[12] with **1** affords **2** in high yield (Scheme 1).[13] The single-crystal structure of **2** shows that the N−Zr−N angles are indeed

(1) (a) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1724. (b) Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1984**, *3*, 977. (c) Chestnut, R. W.; Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting K.; Huffman, J. C. *Polyhedron* **1987**, *6*, 2026. (d) Cummins, C.; Van Duyne, G. D.; Schaller, C. P.; Wolczanski, P. T. *Organometallics* **1991**, *10*, 164. (e) Schaller, C. P.; Cummins, C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591. (f) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696. (g) Duchateau, R.; Abbenhuis, H. C. L.; van Santen, R. A.; Meetsma, A.; Thiele, S. K. H.; van Tol, M. F. H. *Organometallics* **1998**, *17*, 5663.

(2) (a) Lefebvre, F.; De Mallmann, A.; Basset, J.-M. *Eur. J. Inorg. Chem.* **1999**, *3*, 361. (b) Dufaud, V.; Basset, J.-M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 806. (c) Corker, J.; Lefebvre, F.; Lécuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J.-M. *Science* **1996**, *271*, 966. (d) Quignard, F.; Lécuyer, C.; Choplin, A.; Basset, J.-M. *J. Chem. Soc., Dalton Trans.* **1994**, 1153.

(3) Recent reviews of cationic metallocenes and olefin polymerization: (a) Abbenhuis, H. C. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1058. (b) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (c) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413. (d) Montagna, A. A.; Dekmezian, A. H.; Burkhart, R. M. *CHEMTECH* **1997**, *27*, 26. (e) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (f) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (g) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57. (h) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(4) Cationic olefin polymerization catalysts containing amide ligands: (a) Liang, L.-C.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797. (b) Guerin, F.; McConville, D. H.; Vittal, J. J.; Yap, G. A. P. *Organometallics* **1998**, *17*, 5172. (c) Wright, J. M.; Landis, C. R.; Ros, M. A. M. P.; Horton, A. D. *Organometallics* **1998**, *17*, 5031.

(5) Neutral group 4 compounds isoelectronic to cationic metallocenes have been demonstrated to catalyze ethylene polymerization and/or alkyne hydrogenation, see: (a) Pindado Jimnez, G.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **1998**, *120*, 6816. (b) Pastor, A. Kiely, A. F.; Henling, L. M.; Day, M. W.; Bercaw, J. E. *J. Organomet. Chem.* **1997**, *528*, 65. (c) Yoshida, M.; Crowther, D. J.; Jordan, R. F. *Organometallics* **1997**, *16*, 1349.

(6) Neutral d^2 group 4 compounds active for ethylene oligomerization: Hessen, D.; van der Heijden, H. *J. Am. Chem. Soc.* **1996**, *118*, 11670.

(7) A common structural feature of molecules X_3MR is that the X−M−X angles are larger than the ideal tetrahedral angle 109.5°.[1,9] Such large angles cannot be explained by steric effects alone since the N−M−N angles in the $(TMS_2N)_3MCl$ series (114.3°, 114.1(1)°, and 115.4(2)° for M = Ti, Zr, and Hf, respectively)[8b] do not follow the trend in metal ionic radii, which determines the degree of steric congestion around the metal in this homologous series. It seems likely that the large-angle coordination geometry is adopted in part because it facilitates the X(p)−M(d) π donation. Conversely, small-angle geometry may decrease the X(p)−M(d) π donation and increase the electrophilicity of the metal. We are currently investigating the geometric effect on the electrophilicity of the metal center using both experimental (zirconium and nitrogen XPS) and theoretical approaches.

(8) (a) Turner, H. W.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1979**, *18*, 1221. (b) Airoldi, C.; Bradley, D.; Chudzynska, H.; Hursthouse, M. B.; Mali, A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010. (c) Latesky, S. L.; R. W.; Keddington, J.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 995.

(9) Communicated in part: Jia, L.; Ding, E. *Abstracts of Papers*; 218th National Meeting of the American Chemical Sosiety, New Orleans, LA, 1999; American Chemical Society: Washington, DC, 1994; INOR 165.

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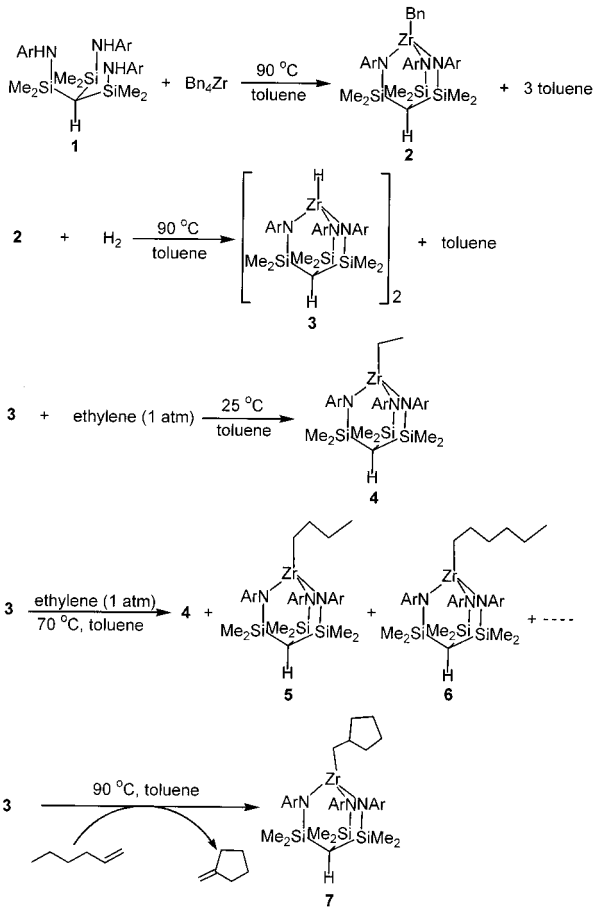
Scheme 1. Synthesis and Reactions of Tripodal Amidozirconium Alkyls and Hydride



exceptionally small (Figure 1).[14a] The Zr−N bond lengths are long but in the normal range.[1,8,10] The benzyl group is bonded to the electrophilic zirconium in an η^2 fashion in the solid state. This bonding mode is retained in solution as indicated by the high-field ortho ^{1}H chemical shift (δ 6.04 ppm) and the large CH_2 coupling constant ($^1J_{C-H}$ = 129 Hz) of the benzyl group.[15] Compound **2** undergoes quantitative hydrogenolysis to give **3** (Scheme 1).[16] The single-crystal structure of **3** reveals a dimer in the solid state with two Zr atoms bridged by two μ-hydrides (Figure 2).[14b] The N atoms and the Zr atoms in different monomer units are separated well beyond bonding distances.

Compounds **2** and **3** polymerize ethylene (activity = 30 g PE·(mol Zr)$^{-1}$·h^{-1}, N_t = 1.1 h^{-1}, at 90 °C under 1 atm ethylene).[17] The polyethylene produced by **2** and **3**

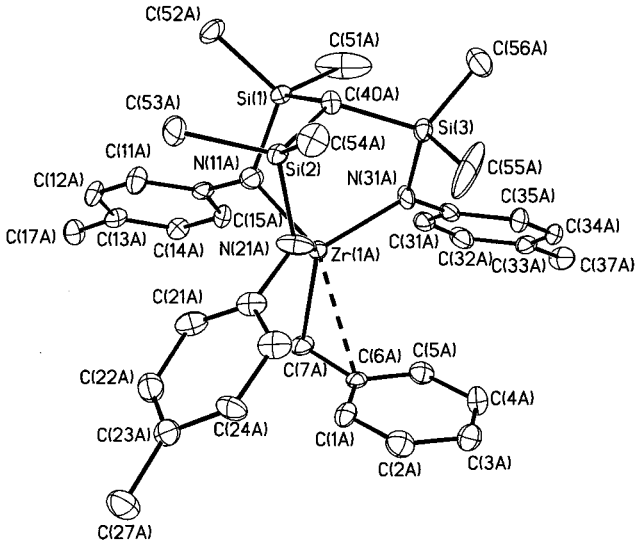


Figure 1. ORTEP diagram of **2**. Thermal ellipsoid drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Zr(1A)−C(7A), 2.274(8); Zr(1A)−C(6A), 2.753(7); Zr(1A)−N(11A), 2.089(7); Zr(1A)−N(21A), 2.075(7); Zr(1A)−N(31A), 2.082(7); Zr(1A)−C(7A)−C(6A), 91.4(5); N(11A)−Zr(1A)−N(21A), 96.9(3); N(11A)−Zr(1A)−N(31A), 99.3(3); N(31A)−Zr(1)−N(21A), 106.3(3).

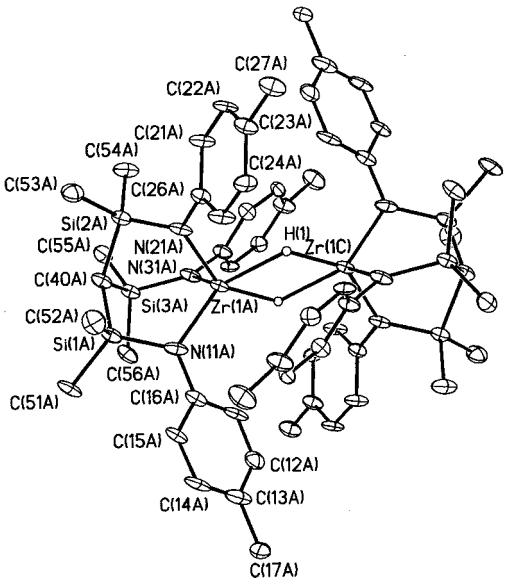


Figure 2. ORTEP diagram of **3**. Thermal ellipsoid drawn at 30% probability.

is completely soluble in hot toluene and thus has low molecular weight. No branches or end groups are

(10) (a) Renner, P.; Galka, C.; Memmler, H.; Kauper, U.; Gade, L. H. *J. Organomet. Chem.* **1999**, *591*, 71. (b) Schneider, A.; Gade, L. H.; Breuning, M.; Bringmann, G.; Scowen, I. J.; McPartlin, M. *Organometallics* **1998**, *17*, 1643. (c) Memmler, H.; Kauper, U.; Gade, L. H.; Scowen, I. J.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1996**, 1751. (d) Findeis, B.; Schubart, M.; Platzek, C.; Gade, L. H.; Scowen, I. J.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1996**, 219. (e) Memmler, H.; Kevin, W.; Gade, L. H.; Lauher, J. W. *Inorg. Chem.* **1995**, *34*, 4062. (f) Schubart, M.; Findeis, B.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Chem. Ber.* **1995**, *128*, 329. (g) Friedrich, S.; Memmler, H.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 676. (h) Gade, L. H.; Becker, C.; Lauher, J. W. *Inorg. Chem.* **1993**, *32*, 2308.

(11) For the related atrazane chemistry: (a) Schrock, R. R *Acc. Chem. Res.* **1997**, *30*, 9. (b) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483.

(12) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *260*, 357.

(13) A solution of $Zr(CH_2C_6H_5)_4$ (114 mg, 0.25 mmol) and **1** (127 mg, 0.25 mmol) in 20 mL of toluene was stirred at 60 °C for 24 h under Ar in the dark. Removal of the solvent under vacuum resulted in an off-white powder. The off-white powder was redissolved in hot hexamethyldisiloxane (∼15 mL) and filtered. Cooling the solution to room temperature and then −40 °C yielded pale yellow crystals of **2** (154 mg, 90%). Anal. Calcd for $C_{35}H_{47}N_3Si_3Zr$: C, 61.35; H, 6.91; N, 6.13. Found: C, 61.20; H, 6.42; N, 6.02. ^{1}H NMR (20 °C, C_6D_6): δ −0.50 (s, 1H, C*H*≡), 0.36 (s, 18H, [(CH_3)$_2$Si−]$_3$), 2.13 (s, 2H, ZrCH_2C$_6$H$_5$), 2.16 (s, 9H, [4-C$_6$H$_4$CH_3]$_3$), 6.04 (d, J = 7.2 Hz, 2H, ortho ZrCH$_2$C$_6$*H*$_5$), 6.59 ("t", J = 7.4 Hz, 2H, meta ZrCH$_2$C$_6$*H*$_5$), 6.70 (t, J = 7.5 Hz, 1H, para ZrCH$_2$C$_6$*H*$_5$), 6.96 (d, J = 7.2 Hz, 6H, [4-C$_6$*H*$_4$CH$_3$]$_3$), 7.01 (d, J = 7.2 Hz, 6H, [4-C$_6$H$_4$CH$_3$]$_3$). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 4.1 ([(*C*H$_3$)$_2$Si−]$_3$), 4.2 (HC≡), 20.8 ([4-C$_6$H$_4$*C*H$_3$]$_3$), 73.3 (Zr*C*H$_2$C$_6$H$_5$), 123.3 (para ZrCH$_2$*C*$_6$H$_5$), 125.4 (ortho or meta [4-*C*$_6$H$_4$CH$_3$]$_3$), 126.5 (ortho or meta ZrCH$_2$*C*$_6$H$_5$), 130.2 (ortho or meta ZrCH$_2$*C*$_6$H$_5$), 130.5 (ortho or meta [4-*C*$_6$H$_4$CH$_3$]$_3$), 131.9 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$), 139.7 (ipso ZrCH$_2$*C*$_6$H$_5$), 146.5 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$).

detectable by ^{1}H NMR, indicating that the product is linear and averages no less than 50 ethylene units per polymer chain. The process of ethylene insertion can be monitored by ^{1}H NMR and ^{13}C NMR. Exposure of a benzene solution of **3** to ethylene (1 atm) at 70 °C for 2 h yields a mixture of **4**, **5**, and **6** in an approximately 1:4:2 ratio according to ^{13}C signal integrations.[18] The ethyl derivative **4** can be isolated by reaction of **3** with ethylene at room temperature for 5 min and is a monomer in benzene solution, determined cryoscopically.[19,20] The identities of butyl **5** and hexyl **6** are verified by independently generating **5** and **6** via reaction of **3** with 1-butene and 1-hexene, respectively.[21] Compound **3** also catalyzes cyclization of 1,5-hexadiene to methylenecyclopentane.[22−24] Cyclization of 100 equiv of 1,5-hexadiene was completed in 18 h at 90 °C (average $N_t = 5.5\ h^{-1}$), and the catalyst was cleanly converted to **7**.[25] Despite their apparently strained coordination geometry, the alkyls **2** and **4**−**7** as well as the hydride **3** are all stable at 100 °C in toluene. No β-agostic interaction can be detected in any of the alkyls.

In summary, the new tripodal amidozirconium compounds have shown activities for ethylene polymerization and diene cyclization. Alkene insertion into a neutral Zr−C bond is rare[5,6] and to our knowledge unprecedented for group 4 d^0 metel complexes not in metallocene-like frameworks. We tentatively attribute the reactivity to the open and perhaps strained coordination geometry. Quantitative kinetic studies of the catalytic reactions and polymerizations in the presence of various organoaluminum cocatalysts are under way.

Supporting Information Available: NMR spectra of multiple ethylene insertion products and X-ray crystallographic characterizations (including tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement coefficients). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Complete X-ray experimental details are given in the Supporting Information. The unit cells of both **2** and **3** contain two independent, chemically equivalent molecules. The Si atoms of **2** are positionally disordered and are refined in 65/35 and 70/30 occupancy ratios for the two independent molecules, respectively. The bridging hydrides of **3** are located from the difference map. (a) Crystallographic data for **2**: $C_{35}H_{47}N_3Si_3Zr$, colorless block, MW = 697.14, orthorhombic, $Pca2_1$; a = 20.3524(3) Å, b = 10.7398(2) Å, c = 34.0023(3) Å, V = 7432.26(16) Å^3, Z = 8, T = 173(2) K, D_{calc} = 1.225 g/cm^3, GOF = 1.345, $R(F)$ = 5.91% for 10 786 observed independent reflections ($4° \le 2\theta \le 48°$). (b) Crystallographic data for **3**: $C_{56}H_{82}N_6Si_6Zr_2$, yellow plate, MW = 1190.26, triclinic, $P\bar{1}$, a = 11.6729(2) Å, b = 13.9372(2) Å, c = 20.9042(3) Å, α = 75.9066(6)°, β = 76.7090(8)°, γ = 70.3894(9)°, V = 3066.02(7) Å^3, Z = 2, T = 223(2) K, D_{calc} = 1.289 g/cm^3, GOF = 1.994, $R(F)$ = 8.83% for 15 270 observed independent reflections ($4° \le 2\theta \le 48°$).

(15) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P. *Organometallics* **1985**, *4*, 902.

(16) A solution of compound **2** (500 mg, 0.73 mmol) in 50 mL of toluene was stirred at 90 °C for 5 days under H_2 (1 atm). After hot filtration, the solution was slowly cooled to −78 °C, yielding a yellow crystalline solid of **3** (total yield of three crops: 280 mg, 85%). Anal. Calcd for $C_{56}H_{82}N_6Si_6Zr_2$: C, 56.51; H, 6.94; N, 7.06. Found: C, 56.46; H, 7.13; N, 7.35. ^{1}H NMR (20 °C, C_6D_6): δ −0.39 (s, 1H, C*H*≡), 0.28 (s, 18H, [(CH_3)$_2$Si−]$_3$), 2.30 (s, 9H, [4-C$_6$H$_4$CH_3]$_3$), 6.54 (d, J = 7.2 Hz, 6H, [4-C$_6H_4$CH$_3$]$_3$), 7.09 (d, J = 7.2 Hz, 6H, [4-C$_6H_4$CH$_3$]$_3$), 8.06 (s, 1H, Zr−*H*). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 4.1 ([(*C*H$_3$)$_2$Si−]$_3$), 4.6 (H*C*≡), 20.8 ([4-C$_6$H$_4$*C*H$_3$]$_3$), 123.5 (ortho or meta [4-*C*$_6$H$_4$CH$_3$]$_3$), 130.5 (ortho or meta [4-*C*$_6$H$_4$CH$_3$]$_3$), 130.9 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$), 147.6 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$).

(17) In a typical experiment, catalyst **2** (30 mg, 44 μmol) was loaded into a 100 mL flask in the glovebox. The flask was attached to a vacuum line and evacuated, and toluene (~20 mL) was condensed into the flask. The solution was exposed to ethylene (1 atm) and stirred for 72 h at 90 °C. Methanol (2 mL) was added to quench the polymerization. The hot polymer solution was filtered to remove the decomposed catalyst and was then cooled to room temperature to precipitate the polymer. White polyethylene was collected by filtration, dried under vacuum, and weighed (97(±4) mg).

(18) See Supporting Information for the ^{13}C spectrum and assignments of the insertion products. The octyl derivative seems also to be present.

(19) A slurry of **3** (200 mg, 0.33 mmol) in toluene (10 mL) was exposed to ethylene (1 atm) at room temperature and stirred for 5 min. Then, ethylene and toluene were removed under vacuum. The resulting off-white powder was redissolved in hexane (~25 mL). After filtration, the volume of the hexane solution was reduced to 10 mL. Cooling the solution to room temperature and then −40 °C yielded colorless crystals of **4** (123 mg, 60%). Anal. Calcd for $C_{30}H_{45}N_3Si_3Zr$: C, 57.88; H, 7.23; N, 6.75. Found: C, 57.59; H, 7.25; N, 6.75. ^{1}H NMR (20 °C, C_6D_6): δ −0.59 (s, 1H, C*H*≡), 0.43 (s, 18H, [(CH_3)$_2$Si−]$_3$), 0.55 (q, J = 8.1 Hz, 2H, ZrCH_2CH$_3$), 0.76 (t, J = 8.1 Hz, 3H, ZrCH$_2$CH_3), 2.10 (s, 9H, [4-C$_6$H$_4$CH_3]$_3$), 7.00 (d, J = 8.3 Hz, 6H, [4-C$_6H_4$CH$_3$]$_3$), 7.05 (d, J = 8.3 Hz, 6H, [4-C$_6H_4$CH$_3$]$_3$). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 3.8 (H*C*≡), 4.2 ([(*C*H$_3$)$_2$Si−]$_3$), 9.2 (ZrCH_2*C*H$_3$), 20.8 ([4-C$_6$H$_4$*C*H$_3$]$_3$), 60.9 (Zr*C*H$_2$CH$_3$), 124.8 (ortho or meta [4-*C*$_6$H$_4$CH$_3$]$_3$), 130.8 (ortho or meta [4-*C*$_6$H$_4$CH$_3$]$_3$), 131.9 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$), 144.6 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$).

(20) Alkene insertion into a Zr−H bond is common. For example, hydrozirconation: Schwartz, J. *Pure Appl. Chem.* **1980**, *52*, 733.

(21) (a) NMR data for **5**. ^{1}H NMR (20 °C, C_6D_6): δ −0.57 (s, 1H, C*H*≡), 0.43 (s, 18H, [(CH_3)$_2$Si−]$_3$), 0.48 (t, J = 7.2 Hz, 2H, ZrCH_2(CH$_2$)$_2$CH$_3$), 0.66 (t, J = 7.8 Hz, 3H, ZrCH$_2$(CH$_2$)$_2$CH_3), 0.75 ("sexet", J = 7.6 Hz, 2H, ZrCH$_2$CH$_2$CH_2CH$_3$), 1.03 ("pentet", J = 7.6 Hz, 2 H, ZrCH$_2$CH_2-CH$_2$CH$_3$), 2.11 (s, 9H, [4-C$_6$H$_4$CH_3]$_3$), 7.02 (d, J = 8.3 Hz, 6H, [4-C$_6H_4$-CH$_3$]$_3$), 7.07 (d, J = 8.3 Hz, 6H, [4-C$_6H_4$CH$_3$]$_3$). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): 3.8 (H*C*≡), 4.8 ([(*C*H$_3$)$_2$Si−]$_3$), 13.7 (ZrCH$_2$(CH$_2$)$_2$*C*H$_3$), 20.7 ([4-C$_6$H$_4$*C*H$_3$]$_3$), 27.2 (ZrCH$_2$(*C*H$_2$)$_2$CH$_3$), 28.6 (ZrCH$_2$(*C*H$_2$)$_2$CH$_3$), 70.1 (Zr*C*H$_2$(CH$_2$)$_2$CH$_3$), 125.0 (ortho or meta [4-*C*$_6$H$_4$CH$_3$]$_3$), 130.7 (ortho or meta [4-*C*$_6$H$_4$CH$_3$]$_3$), 131.9 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$), 144.7 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$). (b) NMR data for **6**. ^{1}H NMR (20 °C, C_6D_6): δ −0.57 (s, 1H, C*H*≡), 0.43 (s, 18H, [(CH_3)$_2$Si−]$_3$), 0.67 (t, J = 7.8 Hz, 2H, ZrCH_2(CH$_2$)$_4$CH$_3$), 0.76 (t, J = 7.2 Hz, 3H, ZrCH$_2$(CH$_2$)$_4$CH_3), 0.99 (pentet, 2H, ZrCH$_2$CH_2(CH$_2$)$_3$CH$_3$), 1.28 (m, 6H, ZrCH$_2$CH$_2$(CH_2)$_3$CH$_3$), 2.13 (s, 9H, [4-C$_6$H$_4$CH_3]$_3$), 7.02 (d, J = 8.3 Hz, 6H, [4-C$_6H_4$CH$_3$]$_3$), 7.07 (d, J = 8.3 Hz, 6H, [4-C$_6H_4$CH$_3$]$_3$). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): 3.8 (H*C*≡), 4.2 ([(*C*H$_3$)$_2$Si−]$_3$), 14.2 (ZrCH$_2$(CH$_2$)$_4$*C*H$_3$), 20.7 ([4-C$_6$H$_4$*C*H$_3$]$_3$), 22.8 (ZrCH$_2$(*C*H$_2$)$_4$CH$_3$), 26.4 (ZrCH$_2$(*C*H$_2$)$_4$CH$_3$), 32.0 (ZrCH$_2$(*C*H$_2$)$_4$-CH$_3$), 33.9 (ZrCH$_2$(*C*H$_2$)$_4$CH$_3$), 70.5 (Zr*C*H$_2$(CH$_2$)$_4$CH$_3$), 125.1 (ortho or meta [4-*C*$_6$H$_4$CH$_3$]$_3$), 130.7 (ortho or meta [4-*C*$_6$H$_4$CH$_3$]$_3$), 131.9 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$), 144.8 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$).

(22) Diene cyclization: Barta, N. S.; Kirk, B. A.; Stille, J. R. *J. Organomet. Chem.* **1995**, *487*, 47.

(23) 1, 5-Hexadiene polymerization: Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91, and references therein.

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(25) NMR data for **7**. ^{1}H NMR (20 °C, C_6D_6): δ −0.59 (s, 1H, C*H*≡), 0.42 (s, 18H, [(CH_3)$_2$Si−]$_3$), 0.83 (d, J = 7.20 Hz, 2H, ZrCH_2), 1.14 (m, 4H, ZrCH$_2$CH (CH_2)$_4$), 1.23 (m, 4H, ZrCH$_2$CH (CH_2)$_4$), 1.40 (m, 1H, ZrCH$_2$C*H* (CH$_2$)$_4$), 2.12 (s, 9H, [4-C$_6$H$_4$CH_3]$_3$), 7.03 (d, J = 7.9 Hz, 6H, [4-C$_6H_4$CH$_3$]$_3$), 7.10 (d, J = 7.9 Hz, 6H, [4-C$_6H_4$CH$_3$]$_3$). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): 3.8 (H*C*≡), 4.2 ([(*C*H$_3$)$_2$Si−]$_3$), 20.8 ([4-C$_6$H$_4$*C*H$_3$]$_3$), 24.8 (ZrCH$_2$CH(*C*H$_2$)$_4$), 36.7 (ZrCH$_2$CH(*C*H$_2$)$_4$), 39.8 (ZrCH$_2$*C*H(CH$_2$)$_4$), 78.2 (ZrCH$_2$*C*H(CH$_2$)$_4$), 125.4 (ortho or meta [4-C$_6$H$_4$CH$_3$]$_3$), 130.7 (ortho or meta [4-*C*$_6$H$_4$CH$_3$]$_3$), 132.1 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$), 145.0 (para or ipso [4-*C*$_6$H$_4$CH$_3$]$_3$).