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Porphodimethene−Zirconium: A New Entry into Zirconium Macrocycle Organometallic Chemistry

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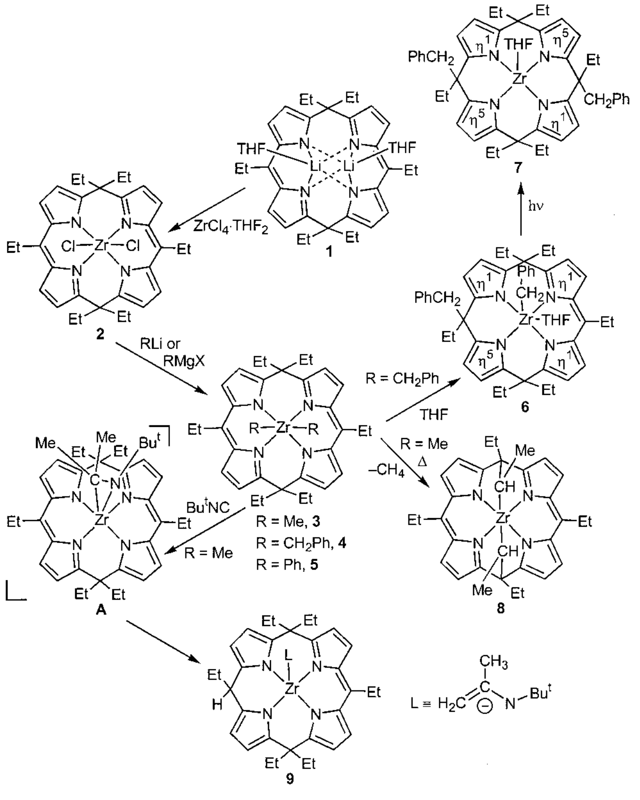
Summary: The cis-dichloro-meso-hexaethylporphodimethene−zirconium(IV) complex has been functionalized to the corresponding dialkyl derivatives [$R = Me, PhCH_2, Ph$], ***3***−***5****, displaying a variety of migratory pathways. In the case of benzyl derivative* ***4****, the spontaneous migration of the first benzyl to the ligand,* ***6****, is followed by the second one, photochemically induced, thus forming a Zr−porphyrinogen complex,* ***7****. The methyl derivative undergoes thermally induced methane elimination with the metalation of the meso ethyl chains,* ***8****. Migration of both methyl groups has been observed in the reaction of* ***3*** *with Bu^{t}NC, with the preliminary formation of η^2-imine, rearranging to the corresponding enamine,* ***9****.*

Macrocycles have had a remarkable development quite recently as ancillary ligands in the early transition metallorganic chemistry.[1] The metal *par excellence* chosen within the context has so far been zirconium in combination with tmtaa [tmtaa = dibenzotetramethyltetraaza[14]annulene],[2] calix[4]arenes,[3] azatranes,[4] porphyrinogens,[5] and porphyrins.[6] A quite recent synthetic methodology has made available the possibility of large-scale production of the dianionic macrocycle *meso*-hexaethylporphodimethene (see Scheme 1),[7] which paves the way from porphyrinogen to porphyrin and combines some of the features of both skeletons.

Scheme 1



This is a preliminary report on the organic chemistry of zirconium based on the porphodimethene ligand, with the purpose of emphasizing (i) the synthesis of Zr−C functionalities, (ii) the migration of an alkyl group from the metal either to the macrocyclic ligand or to an incoming substrate, and (iii) the intramolecular metalation of aliphatic C−H bonds.

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(1) For leading references on organometallic chemistry based on macrocyclic ligands see refs 2−6.

(2) For tmtaa [dibenzotetramethyltetraaza[14]annulene], see: (a) Mountford, P. *Chem. Soc. Rev.* **1998**, *27*, 105, and references therein. (b) Floriani, C.; Ciurli, S.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 70. (c) Solari, E.; De Angelis, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 96. (d) De Angelis, S.; Solari, E.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 2520. (e) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2204. (f) Giannini, L.; Solari, E.; De Angelis, S.; Ward, T. R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 5801. (g) Black, D. G.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1995**, *14*, 3539. (h) Blake, A. J.; Mountford, P.; Nikonov, G. I.; Swallow, D. *Chem. Commun.* **1996**, 1835. (i) Schumann, H. *Inorg. Chem.* **1996**, *35*, 1808. (j) Nikonov, G. I.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 1107. (k) Black, D. G.; Jordan, R. F.; Rogers, R. D. *Inorg. Chem.* **1997**, *36*, 103. (l) Martin, A.; Uhrhammer, R.; Gardner, T. G.; Jordan, R. F. *Organometallics* **1998**, *17*, 382.

(3) For calix[4]arenes, see: (a) Floriani, C. *Chem. Eur. J.* **1999**, *5*, 19. (b) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9198 and 9709. (c) Caselli, A.; Giannini, L.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1997**, *16*, 5457. (d) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 437. (e) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, C.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 823. (f) Giannini, L.; Solari, E.; Dovesi, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1999**, *121*, 2784. (g) Giannini, L.; Guillemot, G.; Solari, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1999**, *121*, 2797. (h) Giannini, L.; Dovesi, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed.* **1999**, *38*, 807. (i) Castellano, B.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Chem. Eur. J.* **1999**, *5*, 722.

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Complex **2**, which represents the entry into the zirconium−porphodimethene organometallic chemistry, has been synthesized according to Scheme 1.[8] The cis arrangement of the two chloride atoms is particularly appropriate for the metal functionalization, as was the case for a variety of other macrocyclic ancillary ligands such as tmtaa,[2] calix[4]arenes,[3b] and porphyrins.[6] The cis arrangement of the two chloride atoms is the consequence of the saddle shape conformation of the ligand having two sp^3 and two sp^2 meso-carbons and with the metal 0.932(2) Å out of the N_4 plane.[9] Particularly significant are the Zr···CH_2 short contacts with two meso-ethyl groups, thus suggesting a structural intermediate in the metal-assisted aliphatic C−H activation (see below). The alkylation of **2** led to the bis-alkyl derivatives, two of them, **3**[10] and **5**, being isolated and characterized, while **4**, which might not be isolated, led to the migration of one benzyl group to the monosubstituted meso-position,[11] thus forming the trianionic porphomethene ligand[7] in complex **6**.[12] The structure of **6** (Figure 1)[13] shows the η^1:η^1:η^1:η^5 bonding mode of the tetrapyrrolic ligand and the η^1 bonding mode of the benzyl group. The migration of the second benzyl group was photochemically induced, thus forming **7**, where zirconium is η^5:η^1:η^5:η^1 bonded[5] to the *meso*-hexaethylbisbenzylporphyrinogen tetraanion. The bonding mode of the macrocyclic ligand in both **6** and **7** has been confirmed by the ^{1}H NMR spectra in solution and the X-ray analysis in the solid state.

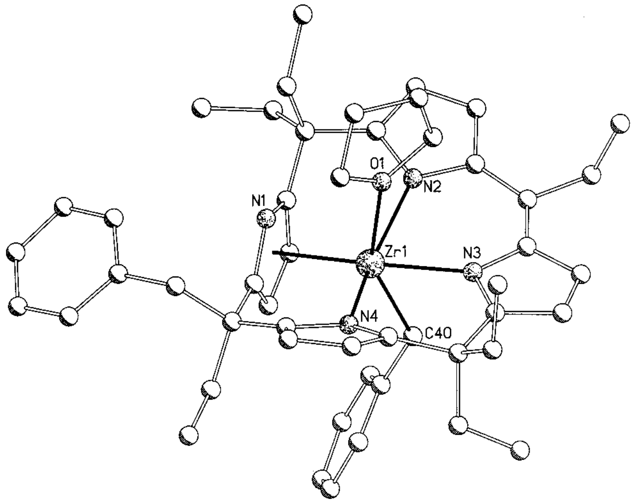

Figure 1. View of compound **6** (hydrogens omitted for clarity). Selected bond lengths (Å) and angles (deg): Zr1−η^5(Pyr), 2.219(4); Zr1−N2, 2.257(7); Zr1−N3, 2.290(6); Zr1−N4, 2.188(7); Zr1−C40, 2.312(8); Zr1−O1, 2.453(5); C41−C40−Zr1, 129.8(6). η^5(Pyr) indicates the centroid.

The chemical evolution of **3** upon heating is completely different from that of **4**. The reaction produced methane and led to the formation of Zr−C bonds with the α-carbons of the two meso-ethyl groups, as shown in complex **8**.[14] In the case of **3**, we assume, as for the structure of **2**, that the close geometrical proximity

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(5) For metal−porphyrinogen: (a) Floriani, C. *Pure Appl. Chem.* **1996**, *68*, 1. (b) Jacoby, D.; Isoz, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 2805. (c) Isoz, S.; Floriani, C.; Schenk, K.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1996**, *15*, 337. (d) Jacoby, D.; Isoz, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 2793. (e) De Angelis, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1092. (f) Jacoby, D.; Isoz, S.; Floriani, C.; Schenk, K.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 4816. (g) Solari, G.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1997**, *16*, 508. (h) Jacoby, D.; Isoz, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 2793.

(6) For porphyrins, see: (a) Brand, H.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 95. (b) Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655. (c) Kim, H.-J.; Whang, D.; Kim, K.; Do, Y. *Inorg. Chem.* **1993**, *32*, 360. (d) Arnold, J.; Johnson, S. E.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 3996. (e) Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 2266. (f) Brand, H.; Arnold, J. *Coord. Chem. Rev.* **1995**, *140*, 137. (g) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39. (h) Kim, H.-J.; Jung, S.; Jeon, Y.-M.; Whang, D.; Kim, K. *Chem. Commun.* **1999**, 1033. (i) Ryu, S.; Whang, D.; Kim, H.-J.; Kim, K.; Yoshida, M.; Hashimoto, K.; Tatsumi, K. *Inorg. Chem.* **1997**, *36*, 4607. (d) Kim, H.-J.; Jung, S.; Jeon, Y.-M.; Whang, D.; Kim, K. *Chem. Commun.* **1997**, 2201.

(7) Benech, J.-M.; Bonomo, L.; Solari, E.; Scopelliti, R.; Floriani, C. *Angew. Chem., Int. Ed.* **1999**, *38*, 1957, and references therein.

(8) Procedure for **2.** Solid $ZrCl_4 \cdot THF_2$ (5.57 g, 14.8 mmol) was added to a solution of **1** (9.41 g, 14.8 mmol) in toluene (600 mL) under argon atmosphere. The resulting solution was stirred at room temperature for 1 day. The undissolved white solid, LiCl, was filtered off, and the solution was evaporated to dryness. The residue was triturated with *n*-pentane to give a red powder (6.8 g, 72%), which was collected and dried in vacuo. Crystals suitable for X-ray analysis were obtained by recrystallization in THF. Anal. Calcd for **2**, $C_{32}H_{38}N_4Cl_2$: C, 59.98; H, 5.98; N, 8.74. Found: C, 59.73; H, 6.16; N, 8.45. ^{1}H NMR (C_6D_6, 200 MHz, 298 K): δ 7.07 (d, J = 4.4 Hz, 4H, C_4H_2N); 6.26 (d, J = 4.4 Hz, 4H, C_4H_2N); 2.66 (q, J = 7.32 Hz, 4H, CH_2); 2.43 (q, J = 7.32 Hz, 4H, CH_2); 1.92 (q, J = 7.32 Hz, 4H, CH_2); 1.15 (t, J = 7.32 Hz, 6H, CH_3); 0.90 (t, J = 7.32 Hz, 12H, CH_3).

(9) Unpublished results.

(10) Procedure for **3**. MeLi (42.9 mL, 1.51 M in Et_2O, 64.8 mmol) was added dropwise to a solution of **2** (20.82 g, 32.4 mmol) in toluene (600 mL) cooled to −30 °C. The resulting dark orange solution was warmed to room temperature, and the undissolved white solid, LiCl, was filtered off. The solution was evaporated to dryness, and *n*-pentane was added to give a brown powder (13.6 g, 70%), which was collected and dried in vacuo. Anal. Calcd for $C_{34}H_{44}N_4Zr$: C, 68.06; H, 7.39; N, 9.34. Found: C, 68.51; H, 6.89; N, 9.73. ^{1}H NMR (C_6D_6, 400 MHz, 298 K, ppm): δ 7.14 (d, J = 4.4 Hz, 4H, C_4H_2N); 6.44 (d, J = 4.4 Hz, 4H, C_4H_2N); 2.73 (q, J = 7.3 Hz, 4H, CH_2); 2.27 (q, J = 7.3 Hz, 4H, CH_2); 2.03 (q, J = 7.3 Hz, 4H, CH_2); 1.18 (t, J = 7.3 Hz, 6H, CH_3); 0.94 (t, J = 7.3 Hz, 6H, CH_3); 0.9 (s, 6H, CH_3); 0.88 (t, J = 7.3 Hz, 6H, CH_3).

(11) Migration of the alkyl group from the metal to an electron-deficient imino group is known both for tmtaa (see ref 2) and for Schiff-base complexes: (a) Floriani, C.; Solari, E.; Corazza, F.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 64. (b) Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1992**, 367. (c) Solari, E.; Maltese, C.; Latronico, M.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1998**, 2395.

(12) Procedure for **6**. $(PhCH_2)_2Mg$ (29.9 mL, 0.44 M in THF, 13.0 mmol) was added to a solution of **2** (8.35 g, 13.0 mmol) in toluene (350 mL) cooled to −30 °C. The reaction mixture was stirred at room temperature for 1 h and then was evaporated to dryness. Toluene (300 mL) was added, and the undissolved white solid, $MgCl_2$, was filtered off. The solution was evaporated to dryness, and the residue was treated with *n*-pentane to give a pink powder, which was collected and dried in vacuo (6.5 g, 61%). Crystals suitable for X-ray analysis were obtained by recrystallisation in THF/Et_2O. Anal. Calcd for **6**, $C_{50}H_{60}N_4OZr$: C, 72.86; H, 7.34; N, 6.80. Found: C, 72.45; H, 7.05; N, 6.34. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.28 (d, J = 4.4 Hz, 1H, C_4H_2N); 7.14 (m, 4H, ArH); 7.01 (d, J = 4.4 Hz, 1H, C_4H_2N overlapping with m, 2H, ArH); 6.75 (m, 1H, ArH); 6.53 (d, J = 4.4 Hz, 1H, C_4H_2N); 6.51 (d, J = 2.93 Hz, 1H, C_4H_2N); 6.50 (m, 3H, ArH); 6.40 (d, J = 2.93, 1H, C_4H_2N); 6.23 (d, J = 2.93 Hz, 1H, C_4H_2N); 6.22 (d, J = 4.4 Hz, 2H, C_4H_2N); 5.79 (d, J = 2.93, 1H, C_4H_2N); 4.13 (d, J = 13.2, 1H, CH_2Ph); 3.17 (s broad, 4H, THF); 3.49 (d, J = 13.2, 1H, CH_2Ph); 2.70 (q, J = 7.34 Hz, 2H, CH2); 2.40 (dq, J_{gem} = 13.6 Hz, J_{vic} = 7.34 Hz, 1H, CH_2); 2.18 (dq, J_{gem} = 13.2 Hz, J_{vic} = 7.34 Hz, 1H, CH_2); 2.03(m, 4H, CH2); 1.95−1.7 (m, 6H, CH2); 1.23 (t, J = 7.34 Hz, 3H, CH_3 overlapping with s broad, 4H, THF); 1.11 (t, J = 7.34 Hz, 3H, CH_3); 0.8 (t, J = 7.34 Hz, 3H, CH_3 overlapping with t, J = 7.34 Hz, 3H, CH_3); 0.75 (t, J = 7.34 Hz, 3H, CH_3); 0.68 (t, J = 7.34 Hz, 3H, CH_3).

(13) Crystal data for **6**: $C_{50}H_{60}N_4OZr$, M = 824.24, monoclinic, space group $P2_1/n$, a = 18.880(2) Å, b = 11.940(2) Å, c = 19.253(2) Å, β = 103.259(11)°, V = 4224.6(11) Å^3, Z = 4, ρ_{calcd} = 1.296 g/mL, F(000) = 1744, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 0.302 mm^{-1}; crystal dimensions 0.24 × 0.16 × 0.10. Diffraction data were collected on a KUMA CCD at 143 K. The structure was solved with direct methods and refined using full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. For 3071 observed reflections [$I > 2\sigma(I)$] and 505 parameters, the conventional R is 0.0819 ($wR2$ = 0.2340 for 6996 independent reflections). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (England). See the Supporting Information for more details.

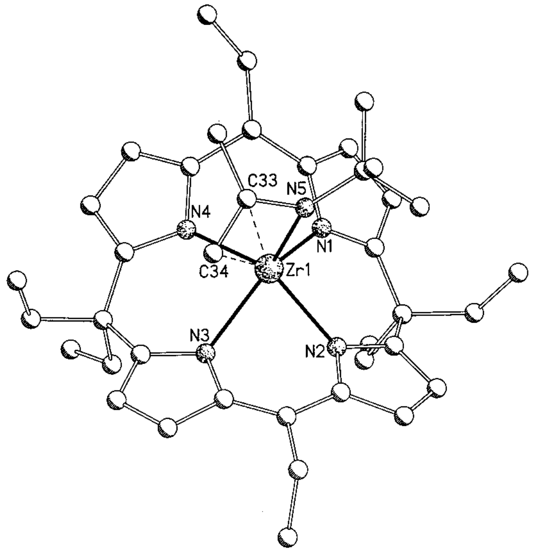

Figure 2. View of compound **9** (hydrogens omitted for clarity). Selected bond lengths (Å): Zr1−N1, 2.152(4); Zr1−N2, 2.194(4); Zr1−N3, 2.217(4); Zr1−N4, 2.152(4); Zr1−N5, 2.095(4); Zr1⋯C33, 2.624(5); Zr1⋯C34, 2.721(5); Zr1−η^3(N5, C33, C34), 2.280(4); N5−C33, 1.387(6); C33−C34, 1.363(7). η^3(N5, C33, C34) indicates the centroid.

between the methyl group and the CH_2 from two meso-ethyl groups is crucial for the concerted elimination of CH_4 and the consequent metalation of the lateral ethyl chains. Unlike in the case of zirconium−porphyrinogen chemistry,[5b] the metalation of the aliphatic chain is regiochemically selective; not only is the reaction occurring only at the α-carbon but also it produces a single stereoisomer. The absence of Zr⋯CH_2 (meso-ethyl) interactions prevented by the sterically more demanding benzyl subtituents in **4** opens the pathway of the nucleophilic attack by the benzylic carbanions to the meso-positions of the porphodimethene skeleton. The characterization of **8** included a quite preliminary X-ray analysis.[9] The synthetic relevance of **8** has to be emphasized; it can be used as an intermediate in the functionalization of the meso aliphatic chain of the porphodimethene skeleton, due to the easy demetalation, upon hydrolysis, of complexes of this type.[5h] An additional interest in complex **8** comes from its potential use in the intermolecular C−H bond activation of hydrocarbons, as already reported for the Zr−porphyrinogen complexes.[5a,b] The Zr−Me functionality in **3** has been engaged in other migration processes, exemplified by its reaction with Bu^tNC,[15] which has some unusual peculiarities. The reaction led to the migration of both methyls to the isocyanide functionality and the intermediate formation of η^2-C,N imine[2f,3c] (see complex **A** in Scheme 1), which underwent a C−H (Me) deprotonation followed by a hydrogen transfer to one of the meso-positions. On the basis of the structural parameters, the deprotonated imine behaves more as an *N*-methylated enamine than as an azaallyl ligand (see complex **9** in Scheme 1[16] and Figure 2[17]), while the resulting porphomethene macrocycle displays an η^1:η^1:η^1:η^1 bonding mode proven by the X-ray structure of **9** and the NMR spectra in solution.

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Supporting Information Available: ORTEP drawings and tables giving crystal data and details of the structure determination, atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **6** and **9**. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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(14) Procedure for **8**. MeLi (11.4 mL, 1.82 M in Et_2O, 20.8 mmol) was added dropwise to a solution of **2** (6.9 g, 10.4 mmol) in toluene (300 mL) at −30 °C. The resulting dark orange solution was stirred at room temperature for 1 h. The ^1H NMR showed that **2** was entirely converted into **3**. The solution was then heated at 110 °C for 2 h, and the undissolved white solid, LiCl, was filtered off. The solution was evaporated to dryness and the solid residue collected with *n*-pentane, yielding a brown powder (3.2 g, 55%). Anal. Calcd for **8**, $C_{32}H_{36}N_4Zr$: C, 67.68; H, 6.39, N, 9.86. Found: C, 68.08; H, 6.82, N, 9.55. ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 6.45 (d, $J = 3.91$ Hz, 2H, C_4H_2N); 6.38 (d, $J = 3.91$ Hz, 2H, C_4H_2N); 5.95 (d, $J = 3.91$ Hz, 2H, C_4H_2N); 5.90 (d, $J = 3.91$ Hz, 2H, C_4H_2N); 2.18 (m, 4H, CH_2); 2.06 (q, $J = 2.85$ Hz, 2H, CH_2); 1.86 (q, $J = 7.34$ Hz, 4H, CH_2); 1.68 (d, $J = 2.85$ Hz, 6H, CH_3); 1.00 (t, $J = 7.34$ Hz, 6H, CH_3); 1.37 (s, 3H, CH_3); 0.88 (t, $J = 7.34$ Hz, 3H, CH_3). Crystal suitable for X-ray analysis were obtained from THF/Et_2O.

(15) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

(16) Procedure for **9**. A solution of Bu^tNC (0.71 g, 8.5 mmol) in benzene (60 mL) was added dropwise to a dark orange solution of **3** (5.1 g, 8.5 mmol) in benzene (90 mL) cooled to −30 °C. The resulting dark violet solution was stirred at room temperature for 1 day and then evaporated to dryness. The residue was triturated with *n*-pentane to give a red powder (4.5 g, 77%), which was collected and dried in vacuo. Anal. Calcd for **9**, $C_{39}H_{53}N_5Zr$: C, 68.57; H, 7.82; N, 10.25. Found: C, 68.12; H, 7.35; N, 9.82. ^1H NMR (C_6D_6, 400 MHz, 298 K, ppm): δ 7.01 (d, $J = 4.4$ Hz, 2H, C_4H_2N); 6.39 (d, $J = 3.4$ Hz, 2H, C_4H_2N); 6.32 (d, $J = 4.4$ Hz, 2H, C_4H_2N); 6.13 (d, $J = 3.4$ Hz, 2H, C_4H_2N); 4.04 (s, 3H, CH_3); 2.51 (m, 4H, CH_2); 2.17 (q, $J = 7.34$ Hz, 4H, CH_2); 1.91 (m, 2H, CH_2); 1.70 (m, 6H, CH_2); 1.37 (s, 3H, CH_3); 1.36 (t, $J = 7.34$, 3H, CH_3); 1.11 (t, $J = 7.34$ Hz, 3H, CH_3), 1.07 (t, $J = 7.34$ Hz, 6H, CH3); 0.89 (s, 9H, Bu^t); 0.61 (t, $J = 7.34$ Hz, 6H, CH_3). Crystal suitable for X-ray analysis were obtained from toluene/*n*-hexane.

(17) Crystal data for **9**. $C_{39}H_{53}N_5Zr$, $M = 683.08$, triclinic, space group $P\bar{1}$, $a = 9.1942(8)$ Å, $b = 10.9092(18)$ Å, $c = 17.887(3)$ Å, $\alpha = 89.771(14)°$, $\beta = 87.736(12)°$, $\gamma = 71.089(13)°$, $V = 1695.9(4)$ Å^3, $Z = 2$, $D_{calcd} = 1.338$ g/cm^3, $F(000) = 724$, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 0.360 mm^{-1}; crystal dimensions 0.28 × 0.20 × 0.15. Diffraction data were collected on a KUMA CCD at 143 K. The structure was solved with direct methods and refined using full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. For 4681 observed reflections [$I > 2\sigma(I)$] and 406 parameters, the conventional R is 0.0720 ($wR2 = 0.1451$ for 5140 indipendent reflections).