# Synthesis, Stereochemistry, and Reactivity of Group 4 Metal Complexes That Contain a Chiral Tetradentate Diamine-Diamide Ligand

Jean-François Carpentier,[†,‡] Alfredo Martin,[‡] Dale C. Swenson,[‡] and Richard F. Jordan*[,§]

*Department of Chemistry, The University of Chicago, 5735 S. Ellis Avenue, Chicago, Illinois 60637, and Department of Chemistry, The University of Iowa, Iowa City, Iowa 52242*

*Received July 16, 2003*

Ti and Zr complexes of the new chiral tetradentate diamine-diamide ligand $(Me_2PMEN)^{2-}$ are described ($H_2(Me_2PMEN)$, **1** = *N*,*N*′-dimethyl-*N*,*N*′-bis[(*S*)-2-methylpyrrolidine]ethylenediamine). The reaction of **1** with $Zr(NMe_2)_4$ affords $(Me_2PMEN)Zr(NMe_2)_2$ ($C_2$-**2**) which is shown by NMR to have effective $C_2$-symmetry in solution. Addition of excess $ClSiMe_3$ to $C_2$-**2** gives $(Me_2PMEN)ZrCl_2$ (**3**) as a mixture of two isomers, $C_2$-**3** (kinetic product) and $C_1$-**3** (thermodynamic product). An X-ray diffraction study of $C_1$-**3** revealed a distorted octahedral structure with a cis-amide/cis-chloride arrangement of ligands. Reaction of $C_1/C_2$-**3** with MeLi yields $(Me_2PMEN)ZrMe_2$ ($C_2$-**4**), which exists as a single $C_2$-symmetric isomer in solution. The reaction of **1** and $Zr(CH_2Ph)_4$ affords $(Me_2PMEN)Zr(CH_2Ph)_2$ (**5**), which can be isolated as a mixture of two isomers, $C_1$-**5** (kinetic product) and $C_2$-**5** (thermodynamic product). The Ti derivative $(Me_2PMEN)Ti(CH_2Ph)_2$ ($C_2$-**6**) was prepared similarly from **1** and $Ti(CH_2Ph)_4$. Compound **6** shows effective $C_2$-symmetry in solution. An X-ray study of **6** revealed a $C_2$-symmetric distorted octahedral structure with a trans-amide/cis-benzyl arrangement of ligands. Iodinolysis of $C_2$-**6** followed by alkylation with MeMgCl leads to the unstable dimethyl derivative $(Me_2PMEN)TiMe_2$ ($C_2$-**7**). Alkyl abstraction from $C_2$-**4**, $C_1/C_2$-**5**, and $C_2$-**6** using $[Ph_3C][B(C_6F_5)_4]$, $[HNMe_2Ph][B(C_6F_5)_4]$, $[HNMePh_2][B(C_6F_5)_4]$, or $B(C_6F_5)_3$ affords cationic alkyl complexes, of which $[(Me_2PMEN)M(CH_2Ph)][B(C_6F_5)_4]$ (M = Ti, **8**; M = Zr, **9**) were isolated. In situ-generated **8** and **9** are moderately active ethylene polymerization catalysts.



## Introduction

Group 4 metal complexes that contain tetradentate nitrogen donor ligands, including porphyrins, tetraaza-[14]-annulenes, and other tetradentate *N*-based macrocycles,[1] have been studied extensively in the last decade.[2] One driving force for this work is the interest in the design of nonmetallocene single-site catalysts for the polymerization of α-olefins.[3] An attractive goal in this area is to develop chiral metal complexes that incorporate readily available chiral amide ligands for exploitation in stereoselective catalysis.[4] Here we describe Zr and Ti complexes that incorporate the new tetradentate diamine-diamide ligand $Me_2PMEN^{2-}$, derived by double deprotonation of the parent tetraamine *N*,*N*′-dimethyl-*N*,*N*′-bis[(*S*)-2-methylpyrrolidine]ethylenediamine ($H_2(Me_2PMEN)$, **1**, Chart 1).

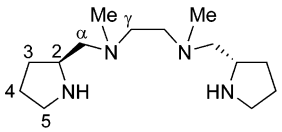
The coordination of linear tetradentate *N*-based ligands to a hexacoordinate metal center can produce many geometrical and optical isomers.[5] However, tetradentate ligands that incorporate defined chiral centers may coordinate in a more selective manner. Several chiral tetraamines that contain two pyrrolidine groups, including $H_4(PMEN)$ and $H_4(PPM)$ (Chart 1), have been prepared previously, and Mn(III), Co(III), Rh(I), Ir(I), Ni(II), and Cu(II) complexes of these ligands have been characterized.[6]

* To whom correspondence should be addressed. Fax: (+1)773-702-0805. E-mail: rfjordan@uchicago.edu.
† Present address: UMR 6509 CNRS−Université de Rennes 1, Institut de Chimie, 35042 Rennes Cedex, France.
‡ The University of Iowa.
§ The University of Chicago.

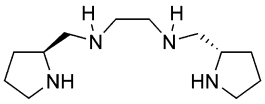
(1) (a) Martin, A.; Uhrhammer, R.; Gardner, T. G.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1998**, *17*, 382. (b) Black, D. G.; Swenson, D. C.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3539. (c) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493. (d) Giannini, L.; Solari, E.; De Angelis, S.; Ward, T. R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 5801. (e) De Angelis, S.; Solari, E.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 2520. (f) Floriani, C.; Ciurli, S.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 70. (g) Cotton, F. A.; Czuchajowska, J. *Polyhedron* **1990**, *9*, 2553. (h) Oberthür, M.; Arndt, P.; Kempe, R. *Chem. Ber.* **1996**, *129*, 1087. (i) Fuhrmann, H.; Brenner, S.; Arndt, P.; Kempe, R. *Inorg. Chem.* **1996**, *35*, 6742. (j) Housmekerides, C. E.; Ramage, D. L.; Kritz, C. M.; Shontz, J. T.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *3*, 4453. (k) Hagadorn, J. R.; Arnold, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1729. (l) Scott, M. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 3411. (m) Brand, H.; Arnold, J. *Coord. Chem. Rev.* **1995**, *140*, 137. (n) Brand, H.; Capriotti, J. A.; Arnold, J. *Organometallics* **1994**, *13*, 4469. (o) Morton, C.; Gillepsie, K. M.; Sanders, C. J.; Scott, P. *J. Organomet. Chem.* **2000**, *606*, 141. (p) O'Shaughnessy, P. N.; Gillepsie, K. M.; Morton, C.; Westmoreland, I.; Scott, P. *Organometallics* **2002**, *21*, 4496. (q) Westmoreland, I.; Munslow, I. J.; O'Shaughnessy, P. N.; Scott, P. *Organometallics* **2003**, *22*, 2972. (r) Male, N. A. H.; Skinner, M. E. G.; Bylikin, S. Y.; Wilson, P. J.; Mountford, P., Schröder, M. *Inorg. Chem.* **2000**, *39*, 5483. (s) Skinner, M. E. G.; Li, Y.; Mountford, P. *Inorg. Chem.* **2002**, *41*, 1110.

10.1021/om0340443 CCC: $25.00 
Publication on Web 10/28/2003

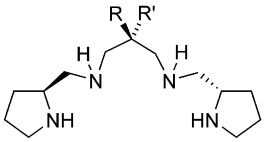
**Chart 1**




$H_2(Me_2PMEN)$ (**1**)




$H_4(PMEN)$




$H_4(PPM)$

R, R' = H, Me, $NO_2$, $NH_2$

The new ligand $(Me_2PMEN)^{2-}$ was designed by modification of $H_4(PMEN)$[7] considering the following features: (i) $H_2(Me_2PMEN)$ is readily prepared in enantiomerically pure form starting from commercially available (*S*)-(2-hydroxymethyl)pyrrolidine; (ii) the $(Me_2PMEN)^{2-}$ ligand is flexible and therefore should be able to coordinate to a variety of metals; and (iii) $H_2(Me_2PMEN)$ has $C_2$-symmetry, which may lead to $C_2$-symmetric structures for $(Me_2PMEN)MX_2$ complexes. Assuming an ideal octahedral arrangement, 12 $(Me_2PMEN)MX_2$ isomeric structures are possible (**A**−**L**, Chart 2), of which four have $C_2$-symmetry. These structures differ in the arrangement (cis vs trans) of the pairs of amide and X ligands and in the configuration of the amine nitrogens.

## Results and Discussion

**Ligand Synthesis.** The tetraamine (*S*,*S*)-$H_2(Me_2$-PMEN) (**1**) was prepared from (*S*)-(2-hydroxymethyl)-pyrrolidine as shown in Scheme 1. The reaction of 2 equiv of (*S*)-(2-iodomethyl)pyrrolidine with *N*,*N*′-dimethylethylenediamine affords the ditosyl derivative $Ts_2(Me_2PMEN)$, contaminated by ca. 30% of the mono-(pyrrolidinyl)ethylenediamine alkylation product.[8] Reduction of this crude mixture by excess $LiAlH_4$ affords **1** as a colorless oil in overall 32% yield after workup.[8]

**Synthesis of $(Me_2PMEN)ZrX_2$ Complexes.** The amine elimination reaction of **1** and $Zr(NMe_2)_4$ yields $(Me_2PMEN)Zr(NMe_2)_2$ ($C_2$-**2**) in 61% isolated yield as a white solid (Scheme 2).[9] $^1H$ NMR data indicate that the yield of $C_2$-**2** is essentially quantitative, but the high solubility of $C_2$-**2** in hydrocarbons and chlorinated solvents reduces the isolated yield. $^1H$ and $^{13}C$ NMR data establish that **2** has $C_2$-symmetry on the NMR time scale between −60 and 100 °C in toluene-$d_8$ solution. The assignment of the $^1H$ NMR spectrum of $C_2$-**2** (see Chart 1 for the $Me_2PMEN^{2-}$ numbering scheme) was made on the basis of a COSY experiment. The H-5 resonances appear at $\delta$ 4.3 (ddd) and 3.3 (m), the latter overlapping with the H-2 resonance, the H-$\gamma$ resonances appear as two doublets at $\delta$ 2.62 and 1.70, and the H-$\alpha$ resonances comprise two doublets of doublets at $\delta$ 2.25 and 2.20. A single $Me_2PMEN$ N-$CH_3$ resonance is observed at $\delta$ 2.13 (6H). The $^{13}C$ NMR spectrum contains seven resonances for the $Me_2PMEN^{2-}$ ligand, consistent with $C_2$-symmetry.

Addition of excess $ClSiMe_3$ to $C_2$-**2** gives $(Me_2PMEN)$-$ZrCl_2$ (**3**), which was isolated in 61% yield as pale yellow crystals (Scheme 2). The yield of **3** is essentially quantitative according to NMR data,[10] but again isolation is hampered by the high solubility of this complex. $^1H$ NMR monitoring experiments show that the reaction proceeds via a monochloro intermediate, $(Me_2PMEN)$-$ZrCl(NMe_2)$, which is transformed to a $C_2$-symmetric dichloride complex ($C_2$-**3**). $C_2$-**3** is slowly transformed to a $C_1$-symmetric isomer. The equilibrium ratio [$C_2$-**3**]/[$C_1$-**3**] = 13/87 is reached after 2 days in $C_6D_6$ at 23 °C.[11] The two isomers of **3** are easily differentiated by $^1H$ NMR spectroscopy. The pattern of H-5, H-2, H-$\gamma$, and

(2) For related $(R_2N)_2MX_2$ chemistry, see: (a) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 2928. (b) Andersen, R. A. *J. Organomet. Chem.* **1980**, *192*, 189. (c) Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, *2*, 16. (d) Bürger, V. H.; Wiegl, K. *Z. Anorg. Allg. Chem.* **1973**, *398*, 257. (e) Bürger, V. H.; Neese, H. J. *Z. Anorg. Allg. Chem.* **1969**, *370*, 275. (f) Bürger, V. H.; Kluess, C.; Neese, H. J. *Z. Anorg. Allg. Chem.* **1971**, *381*, 198. (g) Minhas, R. K.; Scoles, L.; Wong, S.; Gambarotta, S. *Organometallics* **1996**, *15*, 1113. (h) Herrmann, W. A.; Huber, N. W.; Behm, J. *Chem. Ber.* **1992**, *125*, 1405. (i) Horton, A. D.; de With, J. *J. Chem. Soc., Chem. Commun.* **1996**, 1375. (j) Canich, J. M.; Turner, H.; W. World Patent 92/12162, 1992. (k) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273. (l) Shah, S. A. A.; Dorn, H.; Voigt, A.; Roesky, H. W.; Parisini, E.; Schmidt, H. G.; Noltemeyer, M. *Organometallics* **1996**, *15*, 3176.

(3) For recent reviews on olefin polymerization catalyzed by group 4 nonmetallocene complexes, see: (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (c) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236.

(4) For representative examples of group 4 metal complexes containing chiral *bidentate* diamido ligands, see: (a) Cloke, F. G. N.; Geldbach, T. J.; Hitchcock, P. B.; Love, J. B. *J. Organomet. Chem.* **1996**, *506*, 343. (b) Pritchett, S.; Gantzel, P.; Walsh, P. J. *Organometallics* **1997**, *16*, 5130. (c) Pritchett, S.; Woodmansee, D. H.; Gantzel, P.; Walsh, P. J. *J. Am. Chem. Soc.* **1998**, *120*, 6423. (d) Armistead, L. T.; White, P. S.; Gagné, M. R. *Organometallics* **1998**, *17*, 216. (e) Tsuie, B.; Swenson, D. C.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1997**, *16*, 1392. (f) Male, N. A. H.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487. (g) Flora, M. A.; Manzoni, M. R.; Baumann, R.; Davis, W. M.; Schrock, R. R. *Organometallics* **1998**, *18*, 3220.

(5) For example, see the coordination chemistry of triethylenetetramine (triene): (a) Basolo, F. *J. Am. Chem. Soc.* **1948**, *70*, 2634. (b) Buckimgham, D. A.; Marzilli, P. A.; Sargeson, A. M. *Inorg. Chem.* **1967**, *6*, 1032. (c) Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1967**, *6*, 787.

(6) $H_4$(PMEN), *N*,*N*′-bis[(*S*)-2-methylpyrrolidine]ethane-1,2-diamine; $H_4$(PPM), *N*,*N*′-bis[(*S*)-2-methylpyrrolidine]propane-1,3-diamine. (a) Kitagawa, S.; Murakami, T.; Hatano, M. *Inorg. Chem.* **1975**, *14*, 2347. (b) Comba, P.; Hambley, T. W.; Lawrence, G. A.; Martin, L. L.; Renold, P.; Varnagy, K. *J. Chem. Soc., Dalton Trans.* **1991**, 277. (c) Bernhardt, P. V.; Comba, P.; Hambley, T. W.; Martin, L. L.; Varnagy, K.; Zipper, L. *Helv. Chim. Acta* **1992**, *75*, 145. (d) Bernhardt, P. V.; Comba, P.; Gyr, T.; Varnagy, K. *Inorg. Chem.* **1992**, *31*, 1220. (e) Bernhardt, P. V.; Comba, P.; Hambley, T. W.; Sovago, I.; Varnagy, K. *J. Chem. Soc., Dalton Trans.* **1993**, 2023. (f) Kim, D.-Y.; Lee, D.-J.; Heo, N. H.; Jung, M.-J.; Lee, B.-W.; Oh, C.-E.; Doh, M.-K. *Inorg. Chim. Acta* **1998**, *267*, 127. (g) Alcon, M. J.; Gutierrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Sanchez, F. *Inorg. Chim. Acta* **2000**, *306*, 117. (h) Alcon, M. J.; Iglesias, M.; Sanchez, F.; Viani, I. *J. Organomet. Chem.* **2000**, *601*, 284. (i) Alcon, M. J.; Corma, A.; Iglesias, M.; Sanchez, F. *J. Mol. Catal. A: Chem.* **2002**, *178*, 253.

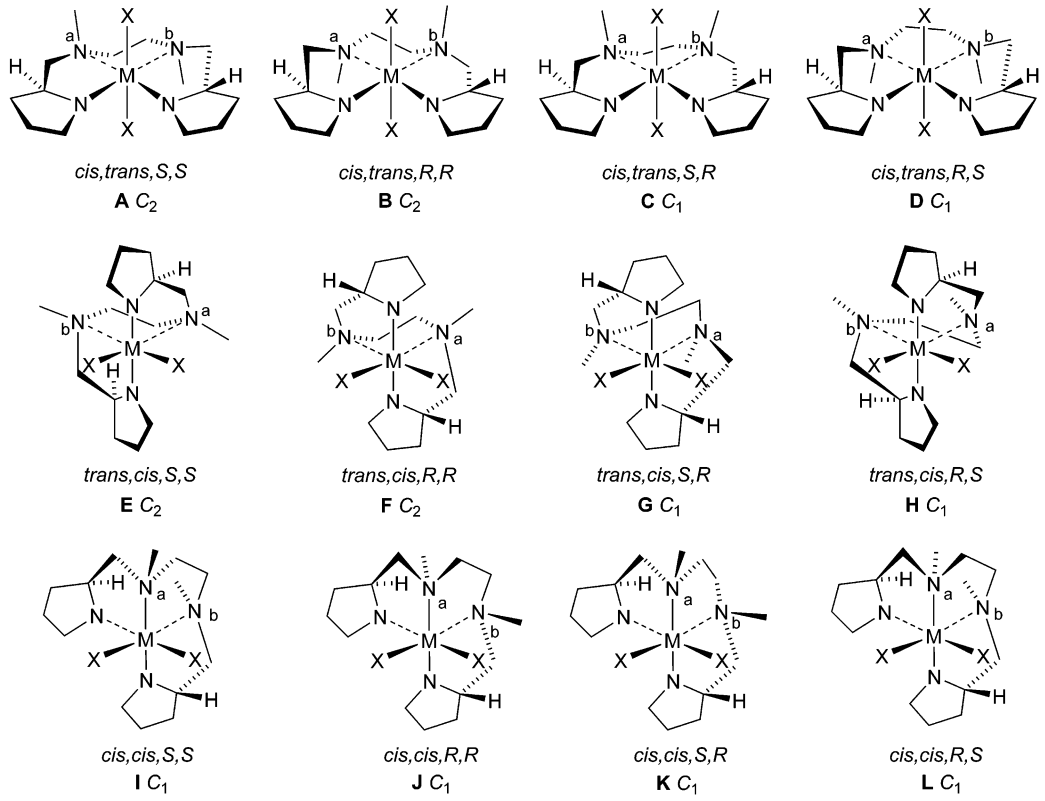
(7) The nomenclature adopted for **1** follows that used for $H_4$-(PMEN)[6a] and accounts for the substitution of the two exocyclic N*H* residues by N*Me* groups.

(8) For a similar alkylation reaction and the subsequent reduction of the *N*-tosylamine see: Tuladhar, S. M., D'Silva, C. *Tetrahedron Lett.* **1992**, *33*, 2203.

(9) (a) Bradley, D. C.; Thomas, I. M. *Proc. Chem. Soc., London* **1959**, 225. (b) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857. (c) Chisholm, M. H.; Hammond, C. E.; Hoffman, J. C. *Polyhedron* **1988**, *7*, 2515. (d) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024.

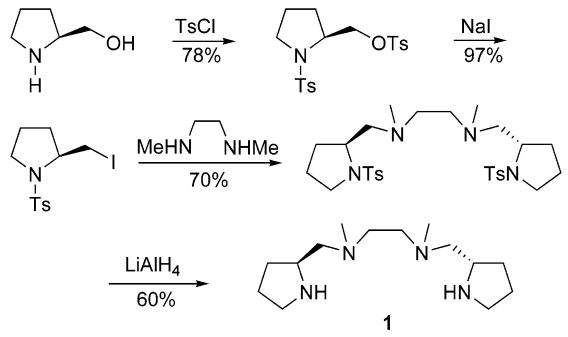
(10) The fact that **3** is formed quantitatively in the reaction of $C_2$-**2** and excess $ClSiMe_3$ shows that the $Me_2PMEN$ amide groups are much less reactive than the $NMe_2$ groups.

**Chart 2. Possible Isomers for Octahedral ($Me_2$PMEN)$MX_2$ Complexes[a]**




[a] The four entries in the descriptor refer to the arrangement of amide ligands, the arrangement of X ligands, the configuration of $N^a$, and the configuration of $N^b$, respectively. Note that the amine ligands must be cis.

**Scheme 1**




H-α resonances observed for $C_2$-**3** is very similar to that for $C_2$-**2**. $C_2$-**3** exhibits one N−$CH_3$ $^1$H NMR resonance, while $C_1$-**3** exhibits two. The $^{13}$C NMR spectra of $C_2$-**3** and $C_1$-**3** exhibit seven and 14 $Me_2PMEN^{2-}$ resonances, respectively.

**Molecular Structure of $C_1$-($Me_2$PMEN)$ZrCl_2$ ($C_1$-3).** The solid state structure of $C_1$-**3** was determined by X-ray crystallography and is shown in Figure 1. Selected bond distances and angles are given in Table 1. $C_1$-**3** has a highly distorted octahedral structure with a cis-amide/cis-chloride ligand arrangement (structure **K**, Chart 2). The N−Zr−N angles in the five-membered chelate rings (N(1)−Zr−N(7) 72.1(2)°, N(16)−Zr−N(10) 74.5(2)°, N(7)−Zr−N(10) 73.8(2)°) are much smaller than the ideal octahedral value due to the chelation, while the N(amide)−Zr−Cl angles are correspondingly larger (N(16)−Zr−Cl(1) 104.7(2)°, N(7)−Zr−Cl(2) 113.2-(2)°, N(16)−Zr−Cl(2) 99.0(2)°, N(1)−Zr−Cl(2) 96.9(2)°). The Cl(1)−Zr−Cl(2) angle is 91.04(9)°. The geometry at the amide nitrogens is planar (Σ(angles): N(1) 359.6°, N(16) 358.9°). The Zr−N(amide) distances (2.039(6) and 2.038(6) Å) are similar to those in other zirconium-amide complexes,[4f,12] and the Zr−N(amine) distances are ca. 0.4 Å longer than those values. The Zr−Cl(2) bond (2.457(2) Å) is slightly shorter than the Zr−Cl(1) bond (2.510(2) Å), as expected from the difference in trans influence of the N(10) amino and N(1) amido groups.

**Synthesis of ($Me_2$PMEN)$ZrR_2$ Complexes.** The addition of 2 equiv of MeLi to a benzene solution of $C_1$-**3** or a mixture of $C_1$-**3**/$C_2$-**3** cleanly affords ($Me_2$PMEN)-$ZrMe_2$ ($C_2$-**4**), which can be isolated in moderate yield as colorless crystals (Scheme 2). The most convenient synthesis of $C_2$-**4** (overall yield 67%) is a one-pot synthesis directly from $C_2$-**2** without isolation of **3**. Regardless of the isomer ratio of the starting material **3**, only one $C_2$-symmetric isomer of **4** is observed by NMR spectroscopy in benzene-$d_6$ solution. The $^1$H NMR spectrum of $C_2$-**4** was assigned on the basis of COSY and NOESY experiments. The NOESY spectrum in-

(11) Rate constants for the isomerization of $C_2$-**3** to $C_1$-**3** ($k$ = 0.087-(2) $h^{-1}$, $k'$ = 0.013(2) $h^{-1}$; $r$ = 0.99; determined in the presence of 2 equiv of $Me_2NSiMe_3$) and $C_1$-**5** to $C_2$-**5** ($k$ = 0.0261(3) $h^{-1}$, $k'$ = 0.0046-(3) $h^{-1}$; $r$ = 0.996) were determined from $^1$H NMR spectra assuming a reversible first-order reaction and using the relation $\ln(([A]_0 - [A]_\infty)/([A]_t - [A]_\infty)) = (k + k')(t)$, where $[A]_0$, $[A]_t$, and $[A]_\infty$ are respectively the concentration of the kinetic product ($C_2$-**3** or $C_1$-**5**) at the beginning of the reaction, at time $t$, and at equilibrium, $k$ and $k'$ are the forward and reverse rate constants, and $r$ is the correlation coefficient. Emanuel, N. M.; Knorre, D. G. In *Chemical Kinetics, Homogeneous Reactions*; Wiley: New York, 1973; pp 165−168.

(12) (a) Warren, T. H.; Schrock, R. R.; Davis, W, M. *Organometallics* **1998**, *17*, 308. (b) Gibson, V. C.; Kimberley, B. S.; White, A. J. P.; Williams, D. J.; Howard, P. *J. Chem. Soc., Chem. Commun.* **1998**, 313. (c) Aoyagi, K.; Gantzel, P. K.; Kalai, K.; Tilley, T. D. *Organometallics* **1996**, *15*, 923. (d) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1996**, *15*, 5586.

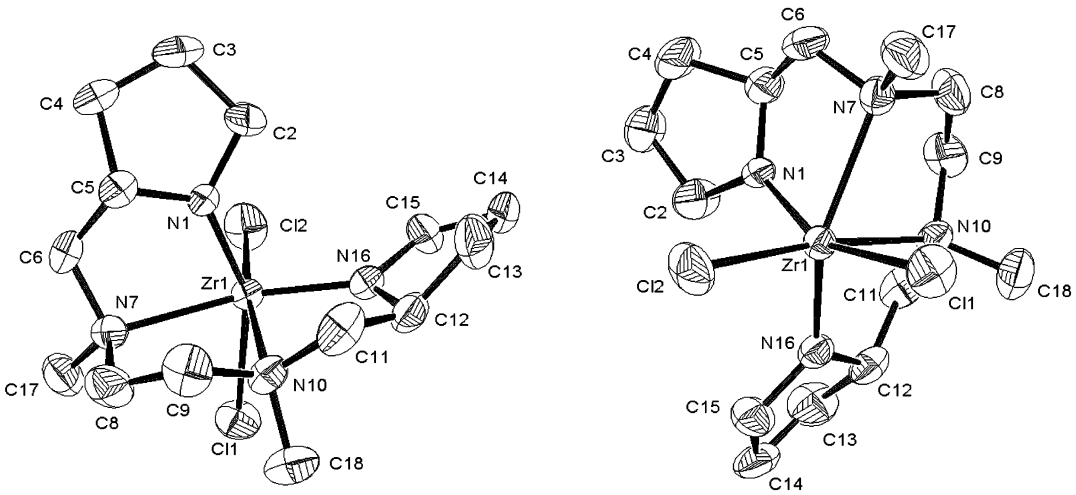



**Figure 1.** Two views of the molecular structure of $C_1$-($Me_2$PMEN)$ZrCl_2$ ($C_1$-**3**). The right view corresponds to structure **K** in Chart 2. Hydrogen atoms and disordered C(13′) and C(14′) are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

**Scheme 2**

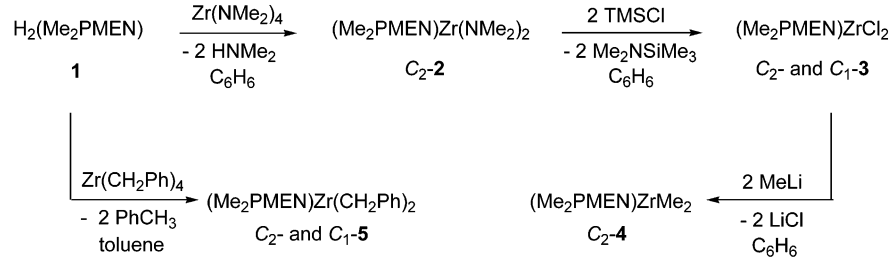



**Table 1. Selected Bond Lengths (Å) and Angles (deg) for $C_1$-3**

| | | | |
|---|---|---|---|
| Zr(1)−N(1) | 2.039(6) | Zr(1)−N(10) | 2.415(6) |
| Zr(1)−N(16) | 2.038(6) | Zr(1)−Cl(1) | 2.510(2) |
| Zr(1)−N(7) | 2.464(6) | Zr(1)−Cl(2) | 2.457(2) |
| N(16)−Zr(1)−N(1) | 97.7(2) | N(1)−Zr(1)−N(7) | 72.1(2) |
| N(16)−Zr(1)−N(10) | 74.5(2) | N(10)−Zr(1)−N(7) | 73.8(2) |
| N(1)−Zr(1)−N(10) | 87.5(2) | Cl(2)−Zr(1)−N(7) | 113.2(2) |
| N(16)−Zr(1)−Cl(2) | 99.0(2) | N(16)−Zr(1)−Cl(1) | 104.7(2) |
| N(1)−Zr(1)−Cl(2) | 96.9(2) | N(1)−Zr(1)−Cl(1) | 154.7(2) |
| N(10)−Zr(1)−Cl(2) | 172.6(2) | N(10)−Zr(1)−Cl(1) | 87.3(2) |
| N(16)−Zr(1)−N(7) | 147.0(2) | Cl(2)−Zr(1)−Cl(1) | 91.04(9) |
| N(7)−Zr(1)−Cl(1) | 82.7(2) | | |

cludes a correlation between the multiplet at $\delta$ 3.41−3.34 that corresponds to H-2 and one H-5, and one H-$\gamma$ resonance ($\delta$ 2.78), which is consistent with either a type **E** structure (close H-2···H-$\gamma$ contact) or a type **F** structure (close H-5···H-$\gamma$ contact), but not with structure **A** or **B** (Chart 2). The $^1$H and $^{13}$C NMR Zr−$CH_3$ resonances of $C_2$-**4** appear at $\delta$ 0.39 and 35.1, respectively.

The reaction of **1** and $Zr(CH_2Ph)_4$ in toluene affords ($Me_2$PMEN)$Zr(CH_2Ph)_2$ (**5**), which was isolated in 76% yield as a pale beige powder (Scheme 2).[13] A $^1$H NMR monitoring experiment established that the reaction proceeds quantitatively within 15 min at room temperature in benzene-$d_6$ with release of 2 equiv of toluene. The kinetic product is a $C_1$-symmetric complex, which is slowly and partially transformed to a $C_2$-symmetric isomer. The equilibrium ratio [$C_1$-**5**]/[$C_2$-**5**] = 15/85 is reached after 5 days in $C_6D_6$ at 23 °C.[11]

The Zr−$CH_2$Ph $^1$H NMR resonances of $C_2$-**5** appear as two doublets at $\delta$ 2.45 and 2.11 ($^2J_{H-H}$ = 10.1 Hz), and the *ortho*-Ph resonance appears as a low-field doublet at $\delta$ 7.1. The Zr−$CH_2$Ph $^{13}$C NMR resonance is observed at $\delta$ 67.1 with $^1J_{C-H}$ = 117 Hz. These data are consistent with normal $\eta^1$-bonding of the benzyl ligands.[14] The $^{13}$C NMR spectrum of $C_1$-**5** displays two Zr−$CH_2$Ph resonances each with $^1J_{C-H}$ = 117 Hz, also consistent with $\eta^1$-bonding of the benzyl groups.

**Synthesis of ($Me_2$PMEN)$TiX_2$ Complexes.** Halide displacement and amine elimination routes did not prove useful for the synthesis of ($Me_2$PMEN)$TiX_2$ complexes. The amine elimination reaction of $Ti(NMe_2)_4$ and **1** in toluene at room temperature is complete within 3 h but gives a mixture of several products, of which the expected product ($Me_2$PMEN)$Ti(NMe_2)_2$ accounts for only ca. 30% according to $^1$H NMR.[15] As a result, this species could be isolated only in very low (<5%) yield. The reaction of $TiCl_4(THF)_2$ with in situ-generated dilithium or magnesium salts[16] of $Me_2PMEN^{2-}$ yielded

(13) (a) Collier, M. R.; Lappert, M. F.; Pearce, R. *J. Chem. Soc., Dalton Trans.* **1973**, 445. (b) Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. G. *Organometallics* **1984**, *3*, 977. (c) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P. *Organometallics* **1985**, *4*, 902. (d) Chestnut, R. W.; Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1987**, *6*, 2019. (e) Crowther, D. J.; Baezinger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455. (f) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1995**, *14*, 371.

(14) (a) Guram, A. S.; Jordan, R. F. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Lappert, M. F., Ed.; Pergamon: Oxford, U.K., 1995; Vol. 4, pp 589−625. (b) Crowther, D. J.; Borkowsky, S. L.; Swenson, D.; Meyer, T. Y.; Jordan, R. F. *Organometallics* **1993**, *12*, 2897. (c) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (c) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902.

(15) For examples of amine elimination from $Ti(NR_2)_4$ see refs 4b−d and: (a) Bowen, D.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3630. (b) Kim, I.; Nishihara, Y.; Jordan, R. F.; Rogers, R. D.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1997**, *16*, 3314.

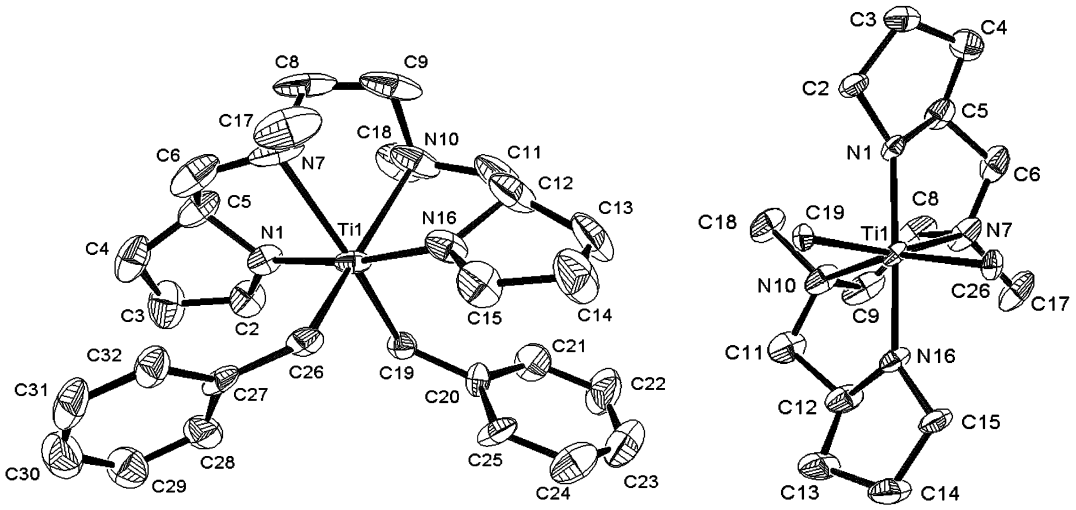



**Figure 2.** Two views of the molecular structure of $C_2$-(Me$_2$PMEN)Ti(CH$_2$Ph)$_2$ ($C_2$-**6**). In the right view, which corresponds to structure **E** in Chart 2, the phenyl groups are removed; note that C19 and C26 are cis. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

**Scheme 3**

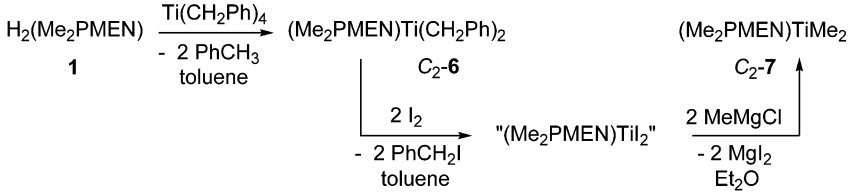



**Table 2. Selected Bond Lengths (Å) and Angles (deg) for $C_2$-6**

| | | | |
|---|---|---|---|
| Ti(1)−N(1) | 1.984(7) | Ti(1)−N(10) | 2.290(7) |
| Ti(1)−N(16) | 1.944(8) | Ti(1)−C(26) | 2.190(7) |
| Ti(1)−N(7) | 2.343(7) | Ti(1)−C(19) | 2.210(7) |
| N(16)−Ti(1)−N(1) | 170.9(3) | N(1)−Ti(1)−N(7) | 75.3(3) |
| N(16)−Ti(1)−N(10) | 76.3(3) | N(10)−Ti(1)−N(7) | 77.4(3) |
| N(1)−Ti(1)−N(10) | 96.1(3) | C(19)−Ti(1)−N(7) | 159.3(3) |
| N(16)−Ti(1)−C(26) | 85.7(3) | N(16)−Ti(1)−C(19) | 98.4(3) |
| N(1)−Ti(1)−C(26) | 100.5(3) | N(1)−Ti(1)−C(19) | 86.9(3) |
| N(10)−Ti(1)−C(26) | 157.9(3) | N(10)−Ti(1)−C(19) | 94.3(3) |
| N(16)−Ti(1)−N(7) | 98.0(3) | C(26)−Ti(1)−C(19) | 101.0(3) |
| N(7)−Ti(1)−C(26) | 92.8(3) | Ti(1)−C(19)−C(20) | 122.9(5) |

mixtures of unidentified products. However, alkane elimination provides an entry to (Me$_2$PMEN)TiX$_2$ systems. The reaction of **1** and Ti(CH$_2$Ph)$_4$ in toluene yields the dibenzyl derivative (Me$_2$PMEN)Ti(CH$_2$Ph)$_2$ ($C_2$-**6**) cleanly (Scheme 3). This reaction proceeds rapidly at room temperature, as evidenced by the precipitation of **6** after 10 min, and is complete within 3 h. Analytically pure $C_2$-**6** was isolated in 85% yield as a brick red solid by precipitation from toluene/pentane.

**Molecular Structure of $C_2$-(Me$_2$PMEN)Ti(CH$_2$Ph)$_2$ ($C_2$-6).** Deep red crystals of $C_2$-**6** suitable for X-ray analysis were grown from a saturated toluene solution at −30 °C. The molecular structure of $C_2$-**6** is shown in Figure 2, and selected bond distances and angles are given in Table 2. $C_2$-**6** has a type **E** structure. The N−Ti−N angles in the five-membered chelate rings (N(1)−Ti−N(7) 75.3(3)°, N(10)−Ti−N(16) 76.3(3)°, N(7)−Ti−N(10) 77.4(3)°) are much smaller than the ideal octahedral value, but to a lesser extent than in $C_1$-**3** since Ti−N bonds are ca. 0.05−0.1 Å shorter than corresponding Zr−N bonds. This difference also results in larger N(amide)−Ti−C(benzyl) angles (N(16)−Ti−C(19) 98.4(3)°, N(1)−Ti−C(26) 100.5(3)°) and a larger C(benzyl)−Ti−C(benzyl) angle (C(19)−Ti−C(26) 101.0(3)°) compared to the corresponding angles in $C_1$-**3**. The benzyl ligands are bonded in a normal $\eta^1$-mode, and the amide nitrogens are planar (sum of the angles around N(1) = 360.0°, N(16) = 359.9°). A $C_2$ axis (noncrystallographic) passes through the Ti atom and bisects the benzyl−Ti−benzyl angle. The Ti−N(amide) distances are comparable to those found in other Ti(IV)-amido complexes.[16,17]

$^1$H and $^{13}$C NMR spectroscopy establish that $C_2$-**6** retains its $C_2$-symmetry on the NMR time scale between −80 and 30 °C in CD$_2$Cl$_2$, toluene-$d_8$, and benzene-$d_6$ solutions. The $^1$H NMR spectrum was assigned on the basis of COSY and NOESY experiments (CD$_2$Cl$_2$, 25 °C). The NOESY spectrum includes a correlation between H-2 ($\delta$ 3.85) and a H-$\gamma$ ($\delta$ 3.26), which is consistent with a type **E** structure (as found in the solid state) but not with the other $C_2$-symmetric structures **A**, **B**, or **F**

(16) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562.

(17) (a) Scollard, J. D.; McConville *J. Am. Chem. Soc.* **1996**, *118*, 10008. (b) Scollard, J. D.; McConville, Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241. (c) Scollard, J. D.; McConville, D. H.; Vittal, J. J.; Payne, N. C. *J. Mol. Catal. A: Chem.* **1998**, *128*, 201. (d) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 5478. (e) Guérin, F.; McConville, D. H.; Payne, N. C. *Organometallics* **1996**, *15*, 5085. (f) Aoyagi, K.; Gantzel, P. K.; Kalai, K.; Tilley, T. D. *Organometallics* **1996**, *15*, 923. (g) Jones, R. A.; Seeberger, M. H.; Atwood, J. L.; Hunter, W. E.; *J. Organomet. Chem.* **1983**, *247*, 1. (h) Friedrich, S.; Gade, L. H.; Edwards, A. J.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1993**, *32*, 1959. (i) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452. (j) Johnson, A. R.; Davis, W. M.; Cummins, C. C. *Organometallics* **1996**, *15*, 3825. (k) Scoles, L.; Minhas, R.; Duchateau, R.; Jubb, J.; Gambarotta, S. *Organometallics* **1994**, *13*, 4978. (l) Herrmann, W. A.; Denk, M.; Albach, R. W.; Behm, J.; Herdweck, E. *Chem. Ber.* **1991**, *124*, 683. (m) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333.

(Chart 2). Additionally, one of the H-3 resonances appears at very high field ($\delta$ 0.23), consistent with the anisotropic shielding by a phenyl ring. Therefore we conclude that $C_2$-**6** has the same structure (type **E**) in the solid state and solution.

The $\eta^1$-bonding of the benzyl ligands observed in the solid state was confirmed in solution by normal $^2J_{H-H}$ (10.1 Hz) and $^1J_{C-H}$ (120 Hz) values for the Ti−$CH_2$Ph unit.[14]

**Synthesis of (Me$_2$PMEN)TiMe$_2$ ($C_2$-7).** Compound $C_2$-**6** was evaluated as a precursor to (Me$_2$PMEN)TiMe$_2$ through the intermediacy of the diiodide (Scheme 3). The reaction of $C_2$-**6** with 2 equiv of $I_2$ in toluene generates benzyl iodide (identified by $^1$H and $^{13}$C NMR and GC−MS) and a brown precipitate, which was isolated in 78% yield. This material is insoluble in aliphatic and aromatic solvents and sparingly soluble in $CD_2Cl_2$. The $^1$H NMR spectrum in $CD_2Cl_2$ contained many resonances and was not informative about the structure. However, the mass spectrum contained a high-intensity peak envelope assigned by isotopic analysis to (Me$_2$PMEN)TiI$^+$, which suggests that the brown material is (Me$_2$PMEN)TiI$_2$. The loss of one X group from the parent ion is a major mass spectral fragmentation process for the other (Me$_2$PMEN)MX$_2$ complexes described here (see Experimental Section). The addition of 2 equiv of MeMgCl to an ether suspension of crude (Me$_2$PMEN)TiI$_2$ at −78 °C affords (Me$_2$PMEN)-TiMe$_2$ ($C_2$-**7**) in 49% yield as a bright red gummy solid, which is ca. 90% pure by NMR. Compound $C_2$-**7** is thermally sensitive and decomposes within several hours at 23 °C, either neat or in benzene solution, which precluded further purification. Titanium dimethyl complexes bearing amide ligands are known to form methylidene species by α-elimination.[17e,k] **7** exists as a single $C_2$-symmetric isomer in benzene-$d_6$ solution. The $^1$H NMR spectrum contains resonances for the Me$_2$PMEN ligand that are similar to those of $C_2$-**6**. The $^1$H and $^{13}$C NMR spectra of $C_2$-**7** display Ti−$CH_3$ resonances at $\delta$ 0.81 and 47.9, respectively.

**Stereoselectivity of Me$_2$PMEN$^{2-}$ Coordination.** An interesting aspect of this study is the stereoselectivity of coordination of Me$_2$PMEN$^{2-}$ to group 4 metal centers. It is remarkable that for each (Me$_2$PMEN)MX$_2$ compound described here only a single $C_2$-symmetric isomer (**2**, **4**, **6**, **7**) or a mixture of a single $C_2$-symmetric and a single $C_1$-symmetric isomer (**3**, **5**) is formed, out of the 12 possible isomers (Chart 2). It appears that $C_2$-symmetric structures are generally favored. Only for (Me$_2$PMEN)ZrCl$_2$ (**3**) is a $C_1$-symmetric isomer thermodynamically favored (structure **K**).

These structural trends reflect the donor properties of the X$^-$ ligands and the conformational preferences of the Me$_2$PMEN$^{2-}$ ligand. In structures **E**−**H**, the X$^-$ ligands are trans to the weak donor amine groups, which is expected to be favorable for cases with strong donor X$^-$ ligands, i.e., dialkyl complexes **4**−**7**. As noted above, X-ray structural data, NOESY data (correlation between H-2 and a H-$\gamma$), and NMR chemical shift data (anisotropic shielding of a H-3 by Ti−$CH_2$*Ph*) establish that $C_2$-**6** adopts structure **E** in the solid state and in solution. Additionally, as summarized in Tables 3 and 4, the $^1$H and $^{13}$C NMR data for the Me$_2$PMEN$^{2-}$ ligand of (Me$_2$PMEN)TiMe$_2$ ($C_2$-**7**) are very similar to those of

**Table 3. Selected $^1$H NMR Data ($C_6D_6$) for $C_2$-(Me$_2$PMEN)MX$_2$ Complexes 2−7**

| compound | $\delta$ H-α | | $\delta$ H-$\gamma$ | | $\delta$ H-5 | | $\delta$ H-2 | $\delta$ NCH$_3$ |
|---|---|---|---|---|---|---|---|---|
| $C_2$-**2** | 2.20 | 2.25 | 1.70 | 2.62 | 3.30 | 4.30 | 3.35 | 2.13 |
| $C_2$-**3** | 2.35 | 2.78 | 1.95 | 2.93 | 3.22 | 4.75 | 3.28 | 2.34 |
| $C_2$-**4** | 2.16 | 2.43 | 1.23 | 2.78 | 3.35 | 4.61 | 3.37 | 1.93 |
| $C_2$-**5** | 1.95 | 2.26 | 1.10 | 2.61 | 3.20 | 4.35 | 3.25 | 1.83 |
| $C_2$-**6** | 2.02 | 2.55 | 1.16 | 2.58 | 3.60 | 4.83 | 3.55 | 1.81 |
| $C_2$-**7** | 2.15 | 2.50 | 1.20 | 2.73 | 3.80 | 5.04 | 3.65 | 1.78 |

**Table 4. Selected $^{13}$C NMR Data ($C_6D_6$) for $C_2$-(Me$_2$PMEN)MX$_2$ Complexes 2−7**

| compound | $\delta$ C-α | $\delta$ C-$\gamma$ | $\delta$ C-5 | $\delta$ C-2 | $\delta$ N-CH$_3$ |
|---|---|---|---|---|---|
| $C_2$-**2** | 53.6 | 55.1 | 67.5 | 64.3 | 47.2 |
| $C_2$-**3** | 54.3 | 54.4 | 65.2 | 64.6 | 47.6 |
| $C_2$-**4** | 52.2 | 53.0 | 64.9 | 64.7 | 45.2 |
| $C_2$-**5** | 52.5 | 53.2 | 63.4 | 65.1 | 44.9 |
| $C_2$-**6** | 52.8 | 55.0 | 62.0 | 67.6 | 45.8 |
| $C_2$-**7** | 52.3 | 55.0 | 63.4 | 67.4 | 45.7 |

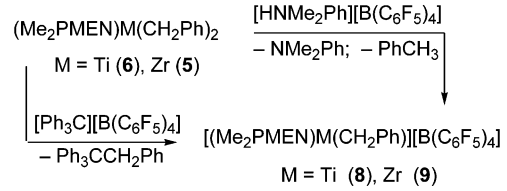
$C_2$-**6**, which suggests that this species also has a type **E** structure in solution.[18] $C_2$-**4** and $C_2$-**5** likely adopt structure **E** or **F**, because the other $C_2$ structures **A** and **B** feature mutually trans alkyl groups. Indeed, NOESY data for $C_2$-**4** (correlation between a H-$\gamma$ and H-2 or a H-5) are consistent with type **E** or **F** structures but inconsistent with structure **A** or **B** (vide supra). Conversely, structures **I**−**L** have one X$^-$ ligand trans to a strong donor amido group, which is expected to be favorable for weak donor X$^-$ ligands. This may account for the conversion of the kinetic product $C_2$-(Me$_2$PMEN)-ZrCl$_2$ ($C_2$-**3**) to the thermodynamic product $C_1$-(Me$_2$-PMEN)ZrCl$_2$ ($C_1$-**3**). It is striking that of the four possible **I**−**L** isomers, only one, structure **K**, is observed for $C_1$-**3**. Further studies will be required to unambiguously establish the structures of the $C_2$-symmetric isomers of **2**−**5**.

**Synthesis of (Me$_2$PMEN)MR$^+$ Complexes.** The reaction of the Ti-dibenzyl complex $C_2$-**6** with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$][19] in $CD_2Cl_2$ at −78 °C proceeds rapidly (<10 min) and cleanly to afford a soluble product, [(Me$_2$PMEN)Ti(CH$_2$Ph)][B(C$_6$F$_5$)$_4$] (**8**), with release of 1 equiv of toluene and NMe$_2$Ph (Scheme 4). The corresponding reaction of the Zr-dibenzyl complex $C_2/C_1$-**5** similarly affords [(Me$_2$PMEN)Zr(CH$_2$Ph)]-[B(C$_6$F$_5$)$_4$] (**9**). The $^1$H and $^{13}$C NMR data for **8** and **9** establish that the NMe$_2$Ph coproduct does not coordinate to these cations between −80 and 25 °C, indicating that **8** and **9** are rather poor Lewis acids. When the reactions are performed in benzene at 23 °C, **8** and **9** are deposited as orange oils and can be isolated in 85%

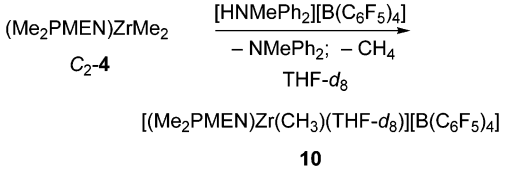
(18) For a similar use of $^{13}$C NMR spectroscopy in the structural analysis of geometrical isomers of coordination complexes with related ligands, see: Strasak, M.; Bachraty, F. *J. Coord. Chem.* **1984**, *13*, 105.

(19) For the use of HNR$_3^+$ reagents with B(C$_6$F$_5$)$_4^-$ type counterions in the generation of L$_n$M(R)$^+$ species, see: (a) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. (b) Lin, Z.; Le Marechal, J.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127. (c) Turner, H. W.; Hlatky, G. G. Eur. Pat. Appl. 0 277 003, 1988. (d) Turner, H. W. Eur. Pat. Appl. 0 277 004, 1988. (e) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413. (f) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362. (g) Amorose, D. M.; Lee, R. P.; Petersen, J. L. *Organometallics* **1991**, *10*, 2191. (h) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910. (i) Bochmann, M.; Jagger, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780. (j) Horton, A. G.; Frijins, J. H. G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1152. (k) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501. (l) Bochmann, M.; Lancaster, S. *J. Organomet. Chem.* **1992**, *434*, C1. (m) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424.

**Scheme 4**




**Scheme 5**




and 92% yield, respectively, as orange powders by separation from the supernatants, trituration with pentane, and drying under vacuum. Compound **8** is stable in $CD_2Cl_2$ for hours at room temperature and for days at −40 °C, while **9** decomposes above −40 °C in this solvent. These compounds were characterized by elemental analysis and low-temperature NMR spectroscopy.

The room-temperature $^1$H and $^{13}$C NMR spectra of **8** and the $^1$H NMR spectrum of **9** exhibit broad resonances due to fluxionality. The low-temperature (−60 °C) $^{13}$C NMR spectra of **8** and **9** each display 14 resonances for the $Me_2$PMEN backbone and five resonances for the benzyl ligand. Also, the low-temperature (−40 °C) $^1$H NMR spectra of **8** and **9** each contain two N−C$H_3$ singlets, an AB pattern for the MC$H_2$Ph unit, and one *ortho*-Ph and one *meta*-Ph resonance. These data are consistent with $C_1$-symmetric structures with free rotation around the Zr$CH_2$−Ph bond.[20] A weak $\eta^2$-benzyl interaction is suggested for both compounds by reduced $^2J_{H-H}$ values (**8**, 9.0 Hz; **9**, 8.3 Hz) and increased $^1J_{C-H}$ values (**8**, 127 Hz;[21] **9**, 136 Hz) of the M−$CH_2$Ph unit[14] and by high-field *ortho*-Ph $^1$H resonances (**8**, $\delta$ 6.77; **9**, $\delta$ 6.82) and *ipso*-Ph $^{13}$C resonances (**8**, $\delta$ 146.8; **9**, $\delta$ 142.3), compared to the corresponding data for neutral dibenzyl complexes $C_2$-**6** and $C_2/C_1$-**5**. The $^{19}$F and $^{11}$B NMR spectra show no evidence for $B(C_6F_5)_4^-$ coordination. In parallel NMR scale reactions, complexes **8** and **9** were generated by the reaction of $C_2$-**6** and $C_2/C_1$-**5**, respectively, with $[Ph_3C][B(C_6F_5)_4]$[22] in chlorobenzene-$d_5$ (Scheme 4). The formation of $Ph_3CCH_2Ph$ as a coproduct was established by $^1$H and $^{13}$C NMR spectroscopy.

NMR scale reactions of the dimethyl-Zr derivative $C_2$-**4** with $[HNMePh_2][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$, or $B(C_6F_5)_3$,[23] in $CD_2Cl_2$, $C_2D_4Cl_2$, or benzene-$d_6$, led to complex mixtures of products. The formation of free $NMePh_2$ and $CH_4$ as coproducts in the first case and $Ph_3CMe$ in the second case was confirmed by $^1$H and $^{13}$C NMR spectroscopy and suggests that $(Me_2PMEN)Zr(CH_3)^+$ species are generated initially. The reaction of $C_2$-**4** and $[HNMePh_2][B(C_6F_5)_4]$ in THF-$d_8$ at room temperature proceeds rapidly (<10 min) with $CH_4$ evolution (Scheme 5). $^1$H NMR monitoring established that several complexes are present in the first stage of the reaction, but after 4 days at 23 °C, only one species, assigned as THF-$d_8$ complex **10**, is observed. The $^1$H and $^{13}$C NMR data establish that this species has $C_1$-symmetry. The $^1$H and $^{13}$C Zr−Me resonances appear at $\delta$ −0.22 and $\delta$ 33.7, respectively, slightly upfield of the corresponding resonances of $C_2$-**4**.

**Olefin Polymerization Studies.** The ethylene and 1-hexene polymerization behavior of several cationic species was briefly investigated. The $(Me_2PMEN)MR^+$ cations were generated in situ by reaction of $C_2$-**4**, $C_1/C_2$-**5**, and $C_2$-**6** with different activators in various solvents, and their ethylene and 1-hexene polymerization activities were compared under similar conditions. As summarized in Table 5, $(Me_2PMEN)MR^+$ cations exhibit poor to moderate ethylene polymerization activity, the activity order being $(Me_2PMEN)Zr(CH_2Ph)^+$ (**9**) > "$(Me_2PMEN)Zr(CH_3)^+$" > $(Me_2PMEN)Ti(CH_2Ph)^+$ (**8**). None of these systems are active for 1-hexene polymerization under the conditions studied (0−23 °C, toluene or chlorobenzene solvent, or neat 1-hexene).

Exposure of a toluene solution of $C_2$-**4** and $[Ph_3C][B(C_6F_5)_4]$ (to generate $(Me_2PMEN)Zr(CH_3)^+$) to 1.4 atm of ethylene at 23 °C (entry 1) results in an exothermic reaction, rapid (ca. 2 min) formation of solid polymer, and discoloration of the initially orange-yellow reaction mixture. These observations suggest that polymerization is rapid but that rapid catalyst deactivation also occurs; the average activity calculated over the whole experiment time is therefore a lower limit. The polymer produced under these conditions has a high molecular weight with a very broad multimodal molecular weight distribution, which may reflect the apparent complexity of the reaction of $C_2$-**4** and the activator (vide supra) and/or the changes in the reaction conditions during polymerization.

Activation of **5** with $[Ph_3C][B(C_6F_5)_4]$ or $[HNMePh_2][B(C_6F_5)_4]$ in toluene produces catalysts that display similar ethylene polymerization activity and produce polyethylene with similar properties (entries 3 and 5). These results suggest that the same active species, i.e., **9**, is generated in both cases. In contrast, the catalyst generated by the reaction of **5** with $B(C_6F_5)_3$, presumed to be $[(Me_2PMEN)Zr(CH_2Ph)][PhCH_2B(C_6F_5)_3]$, is less active than **9** (entries 3 and 5 vs 6). When the polymerization temperature is raised to 100 °C (entry 7), the activity of **9** increases and a polymer with a lower molecular weight and a narrower polydispersity ($M_w/M_n = 3.1$, monomodal) is formed. When polymerizations are carried out in chlorobenzene in place of toluene, the activities of both **9** and "$(Me_2PMEN)Zr(CH_3)^+$" decrease (entries 2 and 4). Visual observations (discoloration of reaction mixtures) suggest that catalyst deactivation is faster in chlorobenzene than toluene for zirconium species.

(20) Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282, and references therein.

(21) The $^1J_{C-H}$ coupling constant of 127 Hz for the Ti$CH_2$ group is in the lower limit for an $\eta^2$-benzyl character ($^1J_{C-H}$ > 125 Hz).[14] It has been proposed for closely related benzyl Ti-diamide complexes that the steric bulk of the ligand could prevent the close approach of the *ipso* carbon to Ti, thus lowering the observed C−H coupling constant.[17d]

(22) For use of $[Ph_3C][B(C_6F_5)_4]$ in the generation of $L_nM(R)^+$ species, see: (a) Chien, J. C. W.; Tsai, W.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570. (b) Ewen, J. A.; Elder, M. J. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 179. (c) Bochmann, M.; Lancaster, S. *J. Organomet. Chem.* **1993**, *12*, 633. (d) Razavi, A.; Thewalt, U. *J. Organomet. Chem.* **1993**, *445*, 111. (e) Straus, D. A.; Zhang, C.; Tilley, T. D. *J. Organomet. Chem.* **1989**, *369*, C13.

(23) For use of $B(C_6F_5)_3$ in the generation of $L_nM(R)^+$ species, see ref 5 and: Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015, and references therein.

**Table 5. Ethylene Polymerization Data[a]**

| entry | catalyst precursor | activator | solvent | time (min) | yield (mg) | activity[b] | $M_w$[f] ($10^3$) | $M_w/M_n$[f] | $T_m$ (°C)[g] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $ZrMe_2[Me_2PMEN]$ ($C_2$-**4**) | $[Ph_3C][B(C_6F_5)_4]$ | toluene | 90 | 295 | 3240 | 546 | 148 | 132 |
| 2[c] | $ZrMe_2[Me_2PMEN]$ ($C_2$-**4**) | $[Ph_3C][B(C_6F_5)_4]$ | $C_6H_5Cl$ | 120 | 20 | 150 | nd | nd | nd |
| 3 | $Zr(CH_2Ph)_2[Me_2PMEN]$ (**5**)[d] | $[Ph_3C][B(C_6F_5)_4]$ | toluene | 90 | 495 | 5430 | 65.8 | 5.6 | 136 |
| 4 | $Zr(CH_2Ph)_2[Me_2PMEN]$ (**5**)[d] | $[Ph_3C][B(C_6F_5)_4]$ | $C_6H_5Cl$ | 90 | <5 | <50 | nd | nd | nd |
| 5 | $Zr(CH_2Ph)_2[Me_2PMEN]$ (**5**)[d] | $[HNMe_2Ph][B(C_6F_5)_4]$ | toluene | 90 | 625 | 6850 | 67.8 | 6.3 | 134 |
| 6 | $Zr(CH_2Ph)_2[Me_2PMEN]$ (**5**)[d] | $B(C_6F_5)_3$ | toluene | 90 | 117 | 1280 | nd | nd | nd |
| 7[e] | $Zr(CH_2Ph)_2[Me_2PMEN]$ (**5**)[d] | $[HNMe_2Ph][B(C_6F_5)_4]$ | toluene | 15 | 305 | 20100 | 27.9 | 3.1 | 131 |
| 8 | $Ti(CH_2Ph)_2[Me_2PMEN]$ ($C_2$-**6**) | $[Ph_3C][B(C_6F_5)_4]$ | toluene | 60 | 50 | 825 | nd | nd | nd |
| 9 | $Ti(CH_2Ph)_2[Me_2PMEN]$ ($C_2$-**6**) | $[Ph_3C][B(C_6F_5)_4]$ | $C_6H_5Cl$ | 150 | 170 | 1120 | 25.0 | 1.7 | 139 |

[a] Unless otherwise stated, polymerization experiments were conducted at 23 °C under 20 psi (1.4 atm) of ethylene using 47.7 μmol of catalyst precursor and 43.3 μmol of activator in 13 mL of solvent (see Experimental Section). [b] Average activity calculated over the whole polymerization time and expressed in (g of PE)·(mol of activated catalyst)$^{-1}$·atm$^{-1}$·h$^{-1}$. [c] 50.8 μmol of catalyst precursor and 46.6 μmol of activator were used. [d] 77/23 mixture of $C_1$ and $C_2$ isomers. [e] $T$ = 100 °C. [f] Determined by GPC. [g] Determined by DSC.

The activity of $(Me_2PMEN)Ti(CH_2Ph)^+$ (**8**), generated in situ by the reaction of $C_2$-**6** with $[Ph_3C][B(C_6F_5)_4]$ in toluene, is significantly lower than that of **9** (entries 8 vs 3). In contrast to the Zr catalysts, the activity of **8** slightly increases when the polymerization is carried out in chlorobenzene (entry 9). The polyethylene produced under these conditions has a relatively low molecular weight with a narrow monomodal molecular weight distribution, characteristic of a single-site catalyst.

**Conclusions.** Alkane and amine elimination reactions of the new chiral tetraamine $H_2(Me_2PMEN)$ with $M(CH_2Ph)_4$ (M = Zr, Ti) and $Zr(NMe_2)_4$ provide efficient access to $(Me_2PMEN)MX_2$ (X = $NMe_2$, Cl, $CH_2Ph$, Me) complexes. The coordination of the $Me_2PMEN^{2-}$ ligand to group 4 metals is highly stereoselective. For each $(Me_2PMEN)MX_2$ compound prepared, only a single $C_2$-symmetric isomer (**2**, **4**, **6**, **7**) or a mixture of a single $C_2$-symmetric and a single $C_1$-symmetric isomer (**3**, **5**) is formed, out of the 12 possible isomers. It appears that the structure of $(Me_2PMEN)MX_2$ complexes is controlled by the donor properties of the $X^-$ ligands and the conformational preferences of the $Me_2PMEN^{2-}$ ligand. Cationic $(Me_2PMEN)MR^+$ species are generated by protonolysis or alkyl abstraction reactions of $(Me_2PMEN)MR_2$ complexes, of which $(Me_2PMEN)M(\eta^2\text{-}CH_2Ph)^+$ (**8**, M = Ti; **9**, M = Zr) were isolated in good yields. Cations **8** and **9** catalyze ethylene polymerization under mild conditions, but are inactive for 1-hexene polymerization. Neither **8** nor **9** coordinates $NMe_2Ph$, which suggests that these species may be insufficiently electrophilic to efficiently bind and activate α-olefins for insertion.

## Experimental Section

**General Procedures.** All manipulations involving organometallic complexes were performed under a purified $N_2$ atmosphere using standard high-vacuum, Schlenk, or glovebox techniques. Solvents were distilled from Na/benzophenone ketyl (THF, hexanes, pentane, diethyl ether, benzene, toluene) or $CaH_2$ (dichloromethane). (*S*)-(+)-2-(Hydroxymethyl)pyrrolidine (Aldrich, 99%) and the other reagents used for the synthesis of $H_2(Me_2PMEN)$ were purchased from ACROS or Aldrich and used as received. The commercial reagents *n*-butyllithium, methyllithium, methylmagnesium chloride, and trimethylsilyl chloride (99%+, Aldrich) were used as received. $[Ph_3C][B(C_6F_5)_4]$ (Asahi Glass) and $[HNMe_2Ph][B(C_6F_5)_4]$ (Boulder Scientific) were used as received. $B(C_6F_5)_3$ (Boulder Scientific) was sublimed before use. The following compounds were prepared by literature methods: $[HNMePh_2][B(C_6F_5)_4]$,[24] $Zr(NMe_2)_4$,[9] $Ti(NMe_2)_4$,[9] $Zr(CH_2Ph)_4$,[25] and $Ti(CH_2Ph)_4$.[25]

$^1H$, $^{13}C$, and $^{11}B$ NMR spectra were recorded on a Bruker AMX-360 spectrometer at ambient probe temperature (23 °C) unless otherwise indicated. $^{19}F$ NMR spectra were recorded on a Bruker AC-300 spectrometer at ambient probe temperature. $^1H$ and $^{13}C$ chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual $^1H$ and $^{13}C$ solvent peaks. $^{11}B$ and $^{19}F$ NMR spectra were referenced externally to neat $CFCl_3$ and $BF_3{\cdot}Et_2O$, respectively. All coupling constants are given in Hz. Optical rotations were recorded at room temperature using a 1 cm cell on a JASCO DIP-1000 polarimeter. Mass spectra were recorded on a VG Analytical ZAB-HF instrument. Elemental analyses were performed by Desert Analytics Laboratory (Tucson, AZ).

***N,O*-Ditosyl-(*S*)-2-(hydroxymethyl)pyrrolidine.**[26] A solution of *p*-toluenesulfonyl chloride (39.7 g, 208 mmol) in dry pyridine (130 mL) was placed under nitrogen and cooled to −5 °C. A solution of (*S*)-2-(hydroxymethyl)pyrrolidine (9.62 g, 95.0 mmol) in pyridine (15 mL) was added over 3 min. The mixture was stirred for 4 h at −5 °C and then allowed to warm to room temperature. The reaction mixture was further stirred for 0.5 h and poured into ca. 1.5 kg of ice. The gummy orange-brown product was triturated, leading to the progressive formation of a yellow-green solid. When all of the ice was melted, the precipitate was collected by filtration, washed thoroughly with water, and dried under vacuum overnight (30.3 g, 78%). Anal. Calcd for $C_{19}H_{23}NO_5S_2$: C, 55.73; H, 5.66; N, 3.42. Found: C, 55.60; H, 5.57; N, 3.48. $^1H$ NMR ($CDCl_3$): δ 7.76 (d, $J$ = 8.3, 2H, *o*-Ph), 7.59 (d, $J$ = 8.2, 2H, *o*-Ph), 7.32 (d, $J$ = 8.1, 2H, *m*-Ph), 7.25 (d, $J$ = 8.0, 2H, *m*-Ph), 4.20 (dd, $J$ = 9.9 and 3.6, 1H, C*H*HO), 3.91 (dd, $J$ = 9.9 and 8.1, 1H, CH*H*O), 3.68 (m, 1H, C*H*N), 3.32 (m, 1H, CH*H*N), 2.97 (m, 1H, C*H*HN), 2.41 (s, 3H, $CH_3$), 2.37 (s, 3H, $CH_3$), 1.85−1.69 (m, 2H, $CH_2$), 1.60−1.45 (m, 2H, $CH_2$). $^{13}C$ NMR ($CDCl_3$): δ 144.9 (m, *i*-Ph), 143.7 (m, *i*-Ph), 133.3 (m, *p*-Ph), 132.4 (m, *p*-Ph), 129.8 (d, $J_{C-H}$ = 160, *o*-Ph), 129.6 (d, $J_{C-H}$ = 160, *o*-Ph), 127.8 (d, $J_{C-H}$ = 165, *m*-Ph), 127.3 (d, $J_{C-H}$ = 163, *m*-Ph), 71.3 (t, $J_{C-H}$ = 150, $CH_2O$), 57.5 (d, $J_{C-H}$ = 141, CHN), 49.1 (t, $J_{C-H}$ = 142, $CH_2N$), 28.3 (t, $J_{C-H}$ = 134, $CH_2$), 23.5 (t, $J_{C-H}$ = 139, $CH_2$), 21.4 (q, $J_{C-H}$ = 126, $CH_3$), 21.3 (q, $J_{C-H}$ = 126, $CH_3$). $[\alpha]^{25}_D$ (*c* 0.65, acetone) = −121. Mp: 96−98 °C. EI-MS: 254 (3), 237 (15), 224 (100), 155 (60), 91 (100), 65 (25).

***N*-Tosyl-(*S*)-2-(iodomethyl)pyrrolidine.**[27] A slurry of *N*,*O*-ditosyl-(*S*)-2-(hydroxymethyl)pyrrolidine (30.3 g, 74.0 mmol) and NaI (13.3 g, 89.0 mmol) in dry acetone (160 mL) was refluxed under nitrogen, protected from light with aluminum

(24) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1995**, *14*, 371.
(25) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.
(26) Kostyanovsky, R. G.; Gella, I. M., Markov, V. I.; Samojlova, Z. E. *Tetrahedron* **1974**, *30*, 39.
(27) Yamashita, T.; Mitsui, H.; Watanabe, H.; Nakamura, N. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 961.

foil, for 4 days. The mixture was cooled to room temperature and poured into ca. 2 kg of ice. A yellow precipitate immediately formed. When all of the ice was melted, the precipitate was collected by filtration, washed thoroughly with water, and dried under vacuum overnight (26.4 g, 98%). Anal. Calcd for $C_{12}H_{16}INO_2S$: C, 39.46; H, 4.42; N, 3.84. Found: C, 39.63; H, 4.43; N, 3.93. $^1$H NMR ($CDCl_3$): $\delta$ 7.67 (d, $J$ = 8.2, 2H, *o*-Ph), 7.29 (d, $J$ = 8.2, 2H, *m*-Ph), 3.67 (m, 1H, C*H*N), 3.56 (dd, $J$ = 9.7 and 3.0, 1H, C*H*HI), 3.45 (m, 1H, CH*H*N), 3.18 (t, $J$ = 9.7, 1H, CH*H*I), 3.13 (m, 1H, CH*H*N), 2.39 (s, 3H, C$H_3$), 1.86−1.68 (m, 3H, C*H*H and C$H_2$), 1.50−1.42 (m, 2H, CH*H*). $^{13}$C NMR ($CDCl_3$): $\delta$ 143.6 (m, *i*-Ph), 133.9 (m, *p*-Ph), 129.7 (d, $J_{C-H}$ = 160, *o*-Ph), 127.3 (d, $J_{C-H}$ = 164, *m*-Ph), 60.5 (d, $J_{C-H}$ = 141, *C*HN), 49.9 (t, $J_{C-H}$ = 142, *C*H$_2$N), 31.8 (t, $J_{C-H}$ = 132, *C*H$_2$), 23.7 (t, $J_{C-H}$ = 133, *C*H$_2$), 21.4 (q, $J_{C-H}$ = 126, *C*H$_3$), 11.5 (t, $J_{C-H}$ = 152, *C*H$_2$I). $[\alpha]_D^{25}$ (*c* 1.025, $CH_2Cl_2$) = −154. Mp: 94−96 °C. EI-MS: 365 ($M^+$, 0.1), 238 (5), 224 (100), 155 (45), 91 (85), 65 (15).

***N,N′*-Dimethyl-*N,N′*-bis[(*S*)-2-methylpyrrolidine]ethylenediamine ($H_2$(Me$_2$PMEN), 1).** A slurry of *N*-tosyl-(*S*)-2-(iodomethyl)pyrrolidine (32.8 g, 89.9 mmol), *N,N′*-dimethylethylenediamine (4.78 mL, 45.0 mmol), and anhydrous $K_2CO_3$ (31.1 g, 225 mmol) in dry acetonitrile (150 mL) was refluxed under nitrogen, protected from light with aluminum foil, for 16 h. The mixture was cooled to room temperature and filtered. The filtrate was concentrated under vacuum, dissolved in ethyl acetate (150 mL), and filtered to remove remaining solid. The filtrate was concentrated under vacuum, and residual ethyl acetate was removed by dissolving the oil in THF (100 mL) and further concentrating under vacuum, to afford an orange oil (25.8 g). $^1$H and $^{13}$C NMR and MS analysis of this oil established that it is a ca. 2:1 mixture of the desired bis(pyrrolidinyl)ethylediamine coupling product *N,N′*-ditosyl-Me$_2$PMEN ($^{13}$C{$^1$H} NMR ($CD_2Cl_2$) $\delta$ 143.8 (*i*-Ph), 134.8 (*p*-Ph), 130.0 (*o*-Ph), 127.8 (*m*-Ph), 63.0, 59.0, 56.6, 49.4, 43.6 (N*C*H$_3$), 29.8 (*C*H$_2$ pyr), 24.1 (*C*H$_2$ pyr), 21.4 (*C*H$_3$); FAB-HRMS calcd for $C_{28}H_{43}N_4O_4S_2$ ($MH^+$), 563.2725; found, 563.2710; EI-MS 338 (M − PyrTos, 80), 281 (M/2, 100), 238 (PyrTos, 30), 155 (50), 91 (95)) and the mono(pyrrolidinyl)ethylenediamine coupling product 2-($C_4H_8$N)CH$_2$N(Me)CH$_2$CH$_2$NHMe (FAB-MS 326 ($MH^+$); EI-MS 281 (M − CH$_2$NHMe, 30), 238 (15), 155 (35), 101 (M − PyrTos, 100), 91 (85)).

This crude oil was dissolved in dry 1,2-dimethoxyethane (DME, 75 mL) and added under nitrogen over 1.5 h to a refluxing slurry of $LiAlH_4$ (25.3 g, 668 mmol) in DME (150 mL). The reaction mixture was refluxed for 24 h, cooled to room temperature, and carefully hydrolyzed (ice bath) with 3 N NaOH until $H_2$ evolution ceased. The resulting gel was filtered on a frit and washed with toluene (200 mL), THF (200 mL), and finally hexane (200 mL). The filtrate was concentrated under vacuum to give a yellow oil, which was dissolved in diethyl ether (50 mL) and dried overnight over KOH pellets. After filtration and removal of ether, the oil was distilled under vacuum (0.05 mmHg). The second fraction (bp 100 °C) was collected and redistilled to afford pure **1** as a colorless oil, which rapidly became pale yellow in air (5.27 g, 40% based on *N*-tosyl-(*S*)-2-(iodomethyl)pyrrolidine). Anal. Calcd for $C_{14}H_{30}N_4$: C, 66.09; H, 11.89; N, 22.02. Found: C, 66.33; H, 11.85; N, 21.83. $^1$H NMR ($CDCl_3$): $\delta$ 3.20 (m, 2H), 3.0 (s br, 2H, N*H*), 2.90 (m, 2H), 2.80 (m, 2H), 2.45 (m, 2H), 2.40−2.35 (m, 4H), 2.18 (s, 6H, NC$H_3$), 2.17 (m, 2H), 1.77 (m, 2H), 1.68−1.56 (m, 4H), 1.22 (m, 2H). $^{13}$C NMR ($CDCl_3$): $\delta$ 63.3 (t, $J_{C-H}$ = 128), 55.8 (d, $J_{C-H}$ = 133, N*C*H), 55.8 (t, $J_{C-H}$ = 134), 45.7 (t, $J_{C-H}$ = 136), 43.0 (q, $J_{C-H}$ = 133, N*C*H$_3$), 29.5 (t, $J_{C-H}$ = 132, *C*H$_2$ pyr), 24.7 (t, $J_{C-H}$ = 128, *C*H$_2$ pyr). $[\alpha]_D^{25}$ (*c* 0.78, $CHCl_3$) = +23. EI-MS: 205 (2), 184 (3), 160 (20), 127 (85), 116 (25), 84 (90), 70 (pyr, 75), 58 (100).

**(Me$_2$PMEN)Zr(NMe$_2$)$_2$ (*C*$_2$-2).** Compound **1** (0.767 g, 3.02 mmol) was added to a solution of Zr(NMe$_2$)$_4$ (0.807 g, 3.02 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 3 h, and the volatiles were removed under vacuum to afford a gummy off-white solid. A $^1$H NMR spectrum indicated that this material was $C_2$-**2** in more than 95% purity. The crude material was dissolved in a minimum amount of hexane and cooled at −40 °C. A white solid precipitated after 1 day. The mixture was filtered, and the filtrate was concentrated to half of the initial volume and stored at −40 °C to afford a second crop. The combined solids were dried under vacuum (0.79 g, 61%). Anal. Calcd for $C_{18}H_{40}N_6Zr$: C, 50.07; H, 9.34; N, 19.46. Found: C, 50.22; H, 9.10; N, 19.26. $^1$H NMR ($C_6D_6$): $\delta$ 4.30 (m, 2H, H-5), 3.43−3.23 (m, 4H, H-2 and H-5), 3.23 (s, 12H, ZrN(C$H_3$)$_2$), 2.62 (d, $J$ = 9.2, 2H, H-$\gamma$), 2.25 (q, $J$ = 10.3, 2H, H-$\alpha$), 2.20 (dd, $J$ = 11.0 and 4.6, 2H, H-$\alpha$), 2.13 (s, 6H, NC$H_3$), 1.85−1.75 (m, 4H, 2 H-4), 1.75−1.65 (m, 4H, H-$\gamma$ + H-3), 1.05 (m, 2H, H-3). $^{13}$C NMR ($C_6D_6$): $\delta$ 67.5 (t, $J_{C-H}$ = 140), 64.3 (d, $J_{C-H}$ = 133, N*C*H), 55.1 (t, $J_{C-H}$ = 132), 53.6 (t, $J_{C-H}$ = 130), 47.2 (q, $J_{C-H}$ = 130, N*C*H$_3$), 45.8 (q, $J_{C-H}$ = 129, N(*C*H$_3$)$_2$), 32.2 (t, $J_{C-H}$ = 128), 27.8 (t, $J_{C-H}$ = 138). $[\alpha]_D^{25}$ (*c* 0.645, toluene) = +75. EI-MS: 430 ($M^+$, 1), 386 (M − NMe$_2$, 70), 369 (10), 341 (20), 317 (45), 248 (40), 127 (80), 44 (NMe$_2$, 100).

**(Me$_2$PMEN)ZrCl$_2$ (*C*$_1$-3 and *C*$_2$-3). NMR Scale.** An NMR tube was charged with $C_2$-**2** (20.1 mg, 0.0465 mmol) and $C_6D_6$ (ca. 0.5 mL), and then $SiMe_3Cl$ (12 $\mu$L, 0.093 mmol) was added by syringe. The tube was shaken vigorously, and $^1$H NMR spectra were recorded periodically. After 2 h at room temperature, the spectrum established the presence of unreacted $C_2$-**2** (32%), an intermediate assigned as (Me$_2$PMEN)Zr(NMe$_2$)Cl (36%), as well as $C_2$-**3** (27%) and $C_1$-**3** (5%). After 8 h, all the starting material was consumed, and the solution contained $C_2$-**3** (79%) and $C_1$-**3** (21%). Subsequently, $C_2$-**3** was progressively transformed into $C_1$-**3**, and the [$C_2$-**3**]/[$C_1$-**3**] ratio reached a final value of 13/87 after 2 days.

**Preparative Scale.** A solution of $SiMe_3Cl$ (1.0 mL, 7.9 mmol) in benzene (10 mL) was added by cannula to a solution of $C_2$-**2** (1.28 g, 3.00 mmol) in benzene (10 mL). The clear yellow mixture was stirred at room temperature for 21 h, and then pentane (50 mL) was added. A white solid formed immediately. The solid was collected by filtration and dried under vacuum (0.48 g, 39%). $^1$H NMR analysis established that this material was pure **3**, as a 38/62 mixture of $C_1$ and $C_2$ isomers. The filtrate was concentrated under vacuum to give a yellow oil, which was dissolved in toluene (1 mL). Crystallization of this solution at −30 °C (3 days) afforded pale yellow crystals of pure $C_1$-**3**, which proved to be suitable for X-ray crystallography (0.28 g, 22%). Combined yield: 0.76 g, 61%. Anal. Calcd for $C_{14}H_{28}N_4Cl_2Zr$: C, 40.56; H, 6.81; N, 13.52. Found: C, 40.88; H, 6.88; N, 13.11. $C_2$-**3**: $^1$H NMR ($C_6D_6$): $\delta$ 4.75 (ddd, $J$ = 11.3, 8.2, and 2.8, 2H, H-5), 3.32−3.22 (m, 4H, H-2 and H-5), 2.93 (d, $J$ = 10.1, 2H, H-$\gamma$), 2.78 (t, $J$ = 11.1, 2H, H-$\alpha$), 2.34 (s, 6H, NC$H_3$), 2.35 (m, 2H, H-$\alpha$), 1.95 (d, $J$ = 9.4, 2H, H-$\gamma$), 1.85 (m, 2H), 1.65−1.53 (m, 4H), 1.15 (m, 2H). $^{13}$C NMR ($C_6D_6$): $\delta$ 65.2 (t, $J_{C-H}$ = 138), 64.6 (d, $J_{C-H}$ = 135, N*C*H), 54.4 (t, $J_{C-H}$ = 137), 54.3 (t, $J_{C-H}$ = 137), 47.6 (q, $J_{C-H}$ = 138, N*C*H$_3$), 30.8, 26.6 (t, $J_{C-H}$ = 129). $C_1$-**3**: $^1$H NMR ($C_6D_6$): $\delta$ 4.50 (ddd, $J$ = 3.8, 7.6, and 11.7, 1H, H-5), 4.08 (ddd, $J$ = 3.4, 8.3, and 11.3, 1H, H-5), 3.80−3.65 (m, 2H), 3.30 (m, 1H), 3.10 (m, 1H), 2.57 (s, 3H, NC$H_3$), 2.65−2.50 (m, 3H), 2.46 (s, 3H, NC$H_3$), 2.46 (m, 1H), 2.40−2.30 (m, 2H), 2.26 (dd, $J$ = 3.9 and 11.1, 1H, H-$\alpha$), 2.10−1.90 (m, 2H), 1.71 (m, 1H), 1.65−1.40 (m, 4H), 1.02−0.90 (m, 2H). $^1$H NMR ($CD_2Cl_2$): $\delta$ 4.21 (m, 1H), 4.03 (m, 1H), 3.94 (m, 1H), 3.68 (m, 1H), 3.61 (m, 1H), 3.28 (m, 1H), 3.18−2.84 (m, 5H), 2.79 (s, 3H, NC$H_3$), 2.69 (s, 3H, NC$H_3$), 2.60 (m, 1H), 1.89−1.70 (m, 8H), 1.19−1.09 (m, 2H). $^{13}$C NMR ($C_6D_6$): $\delta$ 69.1 (t, $J_{C-H}$ = 136), 67.3 (t, $J_{C-H}$ = 136), 66.2 (d, $J_{C-H}$ = 138, N*C*H), 64.6 (d, $J_{C-H}$ = 133, N*C*H), 60.6 (t, $J_{C-H}$ = 137), 58.0 (t, $J_{C-H}$ = 138), 56.2 (t, $J_{C-H}$ = 140), 54.1 (t, $J_{C-H}$ = 136), 53.2 (q, $J_{C-H}$ = 138, N*C*H$_3$), 45.5 (q, $J_{C-H}$ = 137, N′*C*H$_3$), 32.0 (t, $J_{C-H}$ = 130), 30.9 (t, $J_{C-H}$ = 130), 27.6 (t, $J_{C-H}$ = 130), 27.0 (t, $J_{C-H}$ = 131). EI-MS: 412 ($M^+$, 7), 377 (M − Cl, 3), 330 (30), 274 (17), 160 (17), 127 (64), 84 (73), 70 (93), 58 (100).

**(Me$_2$PMEN)ZrMe$_2$ (*C*$_2$-4).** Neat $SiMe_3Cl$ (0.300 mL, 2.38 mmol) was added by syringe to a solution of *C*$_2$-**2** (0.490 g, 1.13 mmol) in benzene (7 mL). The mixture was stirred at room temperature for 5 days. The volatiles were removed under vacuum to yield a yellow solid, which was dried under vacuum for 3 h. This material was dissolved in toluene (20 mL), and MeLi (1.4 M in $Et_2O$, 1.7 mL, 2.4 mmol) was added at room temperature over a period of 3 min. The yellow slurry was stirred for 5 h and filtered through a pad of Celite, which was then washed with toluene (10 mL). The combined filtrate and wash was concentrated under vacuum to yield a yellow-brown solid. A $^1$H NMR spectrum indicated that this material was *C*$_2$-**4** in more than 95% purity. This material was recrystallized from pentane at −40 °C (3 days), affording *C*$_2$-**4** as colorless crystals (0.283 g, 67%). Anal. Calcd for $C_{16}H_{34}N_4Zr$: C, 51.43; H, 9.17; N, 14.99. Found: C, 50.64; H, 9.29; N, 14.13.[28] $^1$H NMR ($C_6D_6$): $\delta$ 4.61 (ddd, $J$ = 10.8, 8.2, and 2.8, 2H, H-5), 3.41−3.34 (m, 4H, H-2 and H-5), 2.78 (d, $J$ = 9.4, 2H, H-$\gamma$), 2.43 (t, $J$ = 10.9, 2H, H-α), 2.16 (dd, $J$ = 10.9 and 4.2, 2H, H-α), 2.01 (m, 2H, H-4), 1.93 (s, 6H, NC$H_3$), 1.80−1.66 (m, 4H, H-3 and H-4), 1.23 (d, $J$ = 9.4, 2H, H-$\gamma$), 1.23 (m, 2H, H-3), 0.39 (s, 6H, ZrC$H_3$). $^{13}$C NMR ($C_6D_6$): $\delta$ 64.9 (d, $J_{C-H}$ = 133), 64.7 (t, $J_{C-H}$ = 131), 53.0 (t, $J_{C-H}$ = 132), 52.2 (t, $J_{C-H}$ = 129), 45.2 (q, $J_{C-H}$ = 135, N$CH_3$), 35.1 (q, $J_{C-H}$ = 100, Zr$CH_3$), 31.4 (t, $J_{C-H}$ = 128), 27.4 (t, $J_{C-H}$ = 130). EI-MS: 357 ($M^+ - CH_3$, 85), 339 (85), 288 (39), 272 (100). $[\alpha]^{25}_D$ (*c* 0.47, toluene) = +85.

**(Me$_2$PMEN)Zr(CH$_2$Ph)$_2$ (*C*$_1$-5 and *C*$_2$-5). NMR Scale.** A Teflon-valved NMR tube was charged with $Zr(CH_2Ph)_4$ (90.0 mg, 0.197 mmol) and $C_6D_6$ (ca. 1 mL), and **1** (50.0 mg, 0.197 mmol) was added. The tube was shaken vigorously, and a clear yellow solution formed. A $^1$H NMR spectrum was recorded after 15 min and revealed complete conversion to **5** as a 85/15 mixture of *C*$_1$-**5** and *C*$_2$-**5**. The tube was allowed to stand at room temperature, and $^1$H NMR spectra were periodically recorded. After 5 days, the [*C*$_1$-**5**]/[*C*$_2$-**5**] ratio reached a constant value of 15/85.

**Preparative Scale.** A solution of **1** (0.400 g, 1.57 mmol) in toluene (10 mL) was added by cannula to a solution of $Zr(CH_2Ph)_4$ (0.720 g, 1.57 mmol) in toluene (10 mL) in a Schlenk tube. The tube was protected from light with aluminum foil, and the clear yellow solution was stirred at room temperature for 2 h. Toluene was removed under vacuum to give a yellow oil, which was dried for 3 h. Pentane (10 mL) was added, which resulted in the immediate precipitation of an off-white solid, which was triturated, collected by filtration, and dried under vacuum overnight (0.63 g, 76%). $^1$H NMR analysis established that this material was pure **5** as a 77/23 mixture of *C*$_1$ and *C*$_2$ isomers. Anal. Calcd for $C_{28}H_{42}N_4Zr$: C, 63.95; H, 8.05; N, 10.65. Found: C, 63.58; H, 8.41; N, 10.44. EI-MS: 433 ($M^+ - CH_2Ph$, 40), 339 (25), 272 (25), 91 (100). *C*$_2$-**5**: $^1$H NMR ($C_6D_6$): $\delta$ 7.20−7.08 (m, 8H, Ph), 6.85 (t, $J$ = 7.6, 2H, *p*-Ph), 4.35 (ddd, $J$ = 11.3, 8.4 and 3.2, 2H, H-5), 3.30−3.15 (m, 4H, H-2 and H-5), 2.61 (d, $J$ = 9.7, 2H, H-$\gamma$), 2.45 (d, $J$ = 10.1, 2H, C*H*HPh), 2.26 (t, $J$ = 10.8, 2H, H-α), 2.11 (d, $J$ = 10.1, 2H, CH*H*Ph), 1.95 (m, 2H, H-α), 1.83 (s, 6H, NC$H_3$), 1.79 (m, 2H), 1.60 (m, 2H), 1.45 (m, 2H), 1.10 (d, $J$ = 9.4, 2H, H-$\gamma$), 0.70 (m, 2H). $^{13}$C NMR ($C_6D_6$): $\delta$ 152.4 (s, *i*-Ph), 128.3 (d, $J_{C-H}$ = 155, *C*H Ph), 126.3 (d, $J_{C-H}$ = 153, *C*H Ph), 119.7 (d, $J_{C-H}$ = 158, *p*-Ph), 67.1 (t, $J_{C-H}$ = 117, *C*H$_2$Ph), 65.1 (d, $J_{C-H}$ = 129, N*C*H), 63.4 (t, $J_{C-H}$ = 135), 53.2 (t, $J_{C-H}$ = 137), 52.5 (t, $J_{C-H}$ = 137), 44.9 (q, $J_{C-H}$ = 136, N$CH_3$), 30.2 (t, $J_{C-H}$ = 128), 27.1 (t, $J_{C-H}$ = 127). *C*$_1$-**5**: $^1$H NMR ($C_6D_6$): $\delta$ 7.42−7.32 (m, 2H, Ph), 7.20−7.05 (m, 6H, Ph), 6.98 (m, 1H, *p*-Ph), 6.90 (m, 1H, *p*-Ph), 3.92 (ddd, $J$ = 11.5, 8.0, and 3.6, 1H, H-5), 3.85 (ddd, $J$ = 11.5, 8.6, and 3.6, 1H, H-5), 3.50 (m, 1H), 3.08 (m, 1H), 2.96 (m, 1H), 2.88 (m, 1H), 2.66 (d, $J$ = 9.4, 1H, H-$\gamma$), 2.20−2.12 (m, 2H), 2.10 (d, $J$ = 9.0, 1H, H-$\gamma$), 2.02−1.93 (m, 4H), 1.96 (s, 3H, NC$H_3$), 1.94 (s, 3H, NC$H_3$), 1.70 (d, $J$ = 10.4, 1H), 1.70−1.55 (m, 4H), 1.55−1.40 (m, 3H), 1.32 (m, 1H), 1.12 (d, $J$ = 9.0, 1H), 1.05 (m, 1H), 0.87 (m, 1H). $^{13}$C NMR ($C_6D_6$): $\delta$ 154.4 (s, *i*-Ph), 148.7 (s, *i*-Ph), 127.9, 127.4, 126.2, 119.3 (d, $J_{C-H}$ = 159, *p*-Ph), 118.9 (d, $J_{C-H}$ = 158, *p*-Ph), 70.0 (t, $J_{C-H}$ = 133), 67.0 (t, $J_{C-H}$ = 132), 66.8 (d, $J_{C-H}$ = 136, N*C*H), 66.4 (t, $J_{C-H}$ = 122), 64.8 (d, $J_{C-H}$ = 128, N*C*H), 60.3 (t, $J_{C-H}$ = 117), 59.0 (t, $J_{C-H}$ = 117), 58.9 (t, $J_{C-H}$ = 117), 53.8 (t, $J_{C-H}$ = 138), 52.2 (t, $J_{C-H}$ = 136), 52.1 (q, $J_{C-H}$ = 137, N*C*H$_3$), 43.3 (q, $J_{C-H}$ = 135, N*C*H$_3$), 31.1 (t, $J_{C-H}$ = 131), 31.0 (t, $J_{C-H}$ = 132), 27.6 (t, $J_{C-H}$ = 131), 27.2 (t, $J_{C-H}$ = 137).

**(Me$_2$PMEN)Ti(CH$_2$Ph)$_2$ (*C*$_2$-6).** $H_2$(Me$_2$PMEN) (**1**) (0.400 g, 1.57 mmol) was added to a stirred solution of $Ti(CH_2Ph)_4$ (0.650 g, 1.57 mmol) in toluene (10 mL). A red precipitate formed immediately. Stirring was continued for 4 h at room temperature. The mixture was then concentrated under vacuum to ca. 2 mL, and pentane (20 mL) was added. The resulting precipitate was collected by filtration, washed with pentane, and dried under vacuum overnight to give a brick red powder (0.65 g, 85%). Crystals for X-ray diffraction were obtained by crystallization from toluene at −30 °C. Anal. Calcd for $C_{28}H_{42}N_4Ti$: C, 69.69; H, 8.77; N, 11.61. Found: C, 69.34; H, 8.68; N, 11.52. EI-MS: 427 (3), 391 ($M^+ - CH_2Ph$, 6), 319 (6), 299 (11), 250 (3), 230 (8), 91 (100). $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.01 (t, $J$ = 7.6, 4H, *m*-Ph), 6.92 (d, $J$ = 6.8, 4H, *o*-Ph), 6.66 (t, $J$ = 7.2, 2H, *p*-Ph), 4.59 (ddd, $J \approx$ 13, 8, and 4, 2H, H-5), 3.85 (m, 2H, H-2), 3.55 (m, 2H, H-5), 3.26 (d, $J$ = 9.0, 2H, H-$\gamma$), 2.61 (t, $J$ = 10.6, 2H, H-α), 2.51 (dd, $J$ = 4.5 and 15.8, 2H, H-α), 2.33 (d, $J$ = 10.1, 2H, C*H*HPh), 2.26 (s, 6H, NC$H_3$), 2.09 (d, $J$ = 10.1, 2H, CH*H*Ph), 2.02 (d, $J$ = 8.7, 2H, H-$\gamma$), 1.56−1.43 (m, 4H, H-4), 1.37 (m, 2H, H-3), 0.23 (ddd, 2H, H-3). $^1$H NMR ($C_6D_6$, low solubility): $\delta$ 7.28 (t, $J$ = 7.9, 4H, *m*-Ph), 7.20 (d, overlap with solvent, 4H, *o*-Ph), 6.97 (t, $J$ = 6.8, 2H, *p*-Ph), 4.83 (ddd, $J \approx$ 13, 9, and 5, 2H, H-5), 3.64−3.52 (m, 4H, H-2 and H-5), 2.62−2.50 (m, 8H, H-α + H-$\gamma$ + others), 2.02 (dd, $J$ = 11.2 and 4.3, 2H, H-α), 1.81 (s, 6H, NC$H_3$), 1.61 (m, 2H), 1.43 (m, 2H), 1.16 (d, $J$ = 9.0, 2H, H-$\gamma$), 0.45 (m, 2H, H-3). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 157.4 (s, *i*-Ph), 127.7 (d, $J_{C-H}$ = 155, Ph), 125.4 (d, $J_{C-H}$ = 155, Ph), 119.2 (d, $J_{C-H}$ = 158, *p*-Ph), 81.9 (t, $J_{C-H}$ = 120, *C*H$_2$Ph), 67.9 (d, $J_{C-H}$ = 130, N*C*H), 62.3 (t, $J_{C-H}$ = 136), 54.9 (t, $J_{C-H}$ = 129), 53.5 (t, $J_{C-H}$ = 136), 46.5 (q, $J_{C-H}$ = 136, N*C*H$_3$), 29.2 (t, $J_{C-H}$ = 130), 26.6 (t, $J_{C-H}$ = 130). $^{13}$C{$^1$H} NMR ($C_6D_6$, low solubility): $\delta$ 157.3 (*i*-Ph), 127.9 (Ph), 125.8 (Ph), 119.8 (*p*-Ph), 83.7 (*C*H$_2$Ph), 67.6 (N*C*H), 62.0, 55.0, 52.8, 45.9 (N*C*H$_3$), 29.2, 26.8. $[\alpha]^{25}_D$ (*c* 0.42, toluene) = −3733.

**(Me$_2$PMEN)TiMe$_2$ (*C*$_2$-7).** A flask was charged with $Ti(CH_2Ph)_4$ (0.325 g, 0.790 mmol) and toluene (20 mL), and **1** (0.200 g, 0.790 mmol) was added dropwise at room temperature. The mixture was stirred for 4 h, at which point the $^1$H NMR spectrum of an aliquot ($C_6D_6$) revealed total conversion to (Me$_2$PMEN)Ti(CH$_2$Ph)$_2$ (**6**). The mixture was cooled to −78 °C, and a solution of $I_2$ (0.400 g, 1.57 mmol) in toluene (10 mL) was added by cannula. A brown precipitate immediately formed. The mixture was warmed to room temperature and stirred for 3 h. The volatiles were removed under vacuum to leave a dark brown oily solid, which was dried under vacuum overnight. The residue was dissolved in $CH_2Cl_2$ (10 mL), and hexanes (10 mL) were added. An orange-brown solid immediately formed and was isolated by removing the supernatant by cannula. The solid was dried under vacuum overnight ("(Me$_2$PMEN)TiI$_2$", 0.34 g, 78%; EI-MS: 427 ($M^+ - I$, 30), 358 (6), 128 (100), 84 (45), 70 (55)). A portion of this solid (0.27 g, 0.49 mmol) was slurried in $Et_2O$ (40 mL) and cooled to −78 °C, and MeMgCl (0.33 mL, 3.0 M in $Et_2O$, 0.98 mmol) was added by syringe. The mixture was warmed to room temperature and stirred for 7 h. A clear orange solution formed. Dioxane (0.2 mL, 2.3 mmol) was added by syringe, resulting in the immediate formation of a precipitate. The mixture was filtered, and the volatiles were removed under vacuum to leave a red gummy solid, which was dried overnight (0.080 g, 49%). NMR analysis indicated that this material is ca. 90% pure (Me$_2$PMEN)TiMe$_2$. This material is thermally unstable as

(28) Low C and N analyses for *C*$_2$-**4** and **8** were consistently obtained for spectroscopically pure samples.

described in the text. EI-MS: 315 ($M^+ - CH_3$, 40), 297 (45), 230 (35), 228 (40), 127 (82), 58 (100). $^1$H NMR ($C_6D_6$): $\delta$ 5.04 (ddd, $J$ = 4.0, 7.9, and 11.9, 2H, H-5), 3.80−3.65 (m, 4H, H-2 and H-5), 2.73 (d, $J$ = 9.0, 2H, H-$\gamma$), 2.50 (t, $J$ = 10.4, 2H, H-$\alpha$), 2.20−2.10 (m, 6H), 1.85−1.75 (m, 4H), 1.78 (s, 6H, NC$H_3$), 1.20 (d, $J$ = 9.0, 2H, H-$\gamma$), 0.81 (s, 6H, TiC$H_3$). $^{13}$C NMR ($C_6D_6$): $\delta$ 67.4 (d, $J_{C-H}$ = 131, NCH), 63.4 (t, $J_{C-H}$ = 135), 55.0 (t, $J_{C-H}$ = 131), 52.3 (t, $J_{C-H}$ = 132), 47.9 (q, $J_{C-H}$ = 116, Ti$CH_3$), 45.7 (q, $J_{C-H}$ = 137, N$CH_3$), 31.2 (t, $J_{C-H}$ = 129), 27.4 (t, $J_{C-H}$ = 129).

**(Me$_2$PMEN)Ti(NMe$_2$)$_2$.** Neat H$_2$(Me$_2$PMEN) (**1**) (0.200 g, 0.786 mmol) was added to a solution of Ti(NMe$_2$)$_4$ (0.176 g, 0.786 mmol) in toluene (4 mL). The reaction mixture was stirred at room temperature for 18 h, and the volatiles were removed under vacuum to leave a red oil. A $^1$H NMR spectrum indicated that this material contained ca. 30% of $C_2$-(Me$_2$PMEN)Ti(NMe$_2$)$_2$ along with unidentified products. The crude material was dissolved in a minimum amount of pentane and cooled at −40 °C. After 2 months, a small amount of red crystals was recovered by filtration (10 mg) and identified as $C_2$-(Me$_2$PMEN)Ti(NMe$_2$)$_2$ by $^1$H NMR ($C_6D_6$): $\delta$ 4.44 (m, $J$ = 8.9, 2H, H-5), 3.46 (s, 12H, Ti−N(C$H_3$)$_2$), 3.30−3.20 (m, 4H), 2.47 (d, $J$ = 9.0, 2H, H-$\gamma$), 2.33 (t, $J$ = 10.9, 2H, H-$\alpha$), 2.17 (dd, $J$ = 11.1 and 4.6, 2H, H-$\alpha$), 2.12 (s, 6H, N-C$H_3$), 2.03 (d, $J$ = 8.7, 2H, H-$\gamma$), 1.85−1.60 (m, 6H, H-4 + H-3), 1.20−1.10 (m, 2H, H-3).

**[(Me$_2$PMEN)Ti(CH$_2$Ph)][B(C$_6$F$_5$)$_4$] (8). Preparative Scale.** Benzene (10 mL) was added to a mixture of $C_2$-**6** (0.150 g, 0.311 mmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (0.249 g, 0.311 mmol). An orange-red oil separated immediately. The mixture was stirred at room temperature for 15 min. The yellow upper layer was removed with a pipet, benzene (10 mL) was added to the remaining oil, and the mixture was stirred for 5 min. The upper benzene layer was removed with a pipet. This procedure was repeated twice. The final oily lower phase was dried under vacuum. The resulting brown residue was triturated with pentane (5 mL) to leave an orange-brown powder, which was collected by filtration, washed with pentane, and dried under vacuum overnight (0.284 g, 85%). Anal. Calcd for $C_{45}H_{35}N_4BF_{20}Ti$: C, 50.49; H, 3.30; N, 5.23. Found: C, 48.92; H, 2.89; N, 5.02.[28] $^1$H NMR ($CD_2Cl_2$, 233 K): $\delta$ 7.20 (t, $J$ = 7.9, 2H, *m*-Ph), 6.83 (t, $J$ = 7.2, 1H, *p*-Ph), 6.77 (d, $J$ = 7.6, 2H, *o*-Ph), 4.18 (m, 1H), 4.09 (m, 1H), 4.00 (m, 1H), 3.77 (dd, $J$ = 8.1 and 13.4, 1H), 3.70 (m, 1H), 3.67−3.55 (m, 2H), 3.50−3.42 (m, 2H), 3.29 (d, $J$ = 9.0, 1H, C$H$HPh), 3.18 (m, 1H), 2.91 (d, $J$ = 9.4, 1H), 2.85 (dd, $J$ = 2.7 and 13.6, 1H), 2.74 (m, 1H), 2.70 (s, 3H, NC$H_3$), 2.67−2.57 (m, 2H), 2.31 (s, 3H, N′C$H_3$), 2.03 (d, $J$ = 9.0, 1H, CH$H$Ph), 2.00−1.89 (m, 2H), 1.87−1.45 (m, 5H). $^{13}$C NMR ($CD_2Cl_2$, 213 K): $\delta$ 146.8 (s, *i*-Ph), 128.1 (d, $J_{C-H}$ = 157), 126.5 (d, $J_{C-H}$ = 157), 121.5 (d, $J_{C-H}$ = 153, *p*-Ph), 73.4 (t, $J_{C-H}$ = 127, $C$H$_2$Ph), 65.6 (d, $J_{C-H}$ = 144, N$C$H), 63.2 (t, $J_{C-H}$ = 140), 62.7 (t, $J_{C-H}$ = 140), 60.4 (d, $J_{C-H}$ = 139, N′$C$H), 57.5 (t, $J_{C-H}$ = 139), 55.0 (t, $J_{C-H}$ = 137), 54.5 (overlap with solvent), 54.2 (t, $J_{C-H}$ = 140), 46.6 (q, $J_{C-H}$ = 138, N$C$H$_3$), 44.3 (q, $J_{C-H}$ = 137, N′$C$H$_3$), 30.5 (t, $J_{C-H}$ = 132), 30.4 (t, $J_{C-H}$ = 132), 25.9 (t, $J_{C-H}$ = 133), 25.8 (t, $J_{C-H}$ = 133). Resonances for B(C$_6$F$_5$)$_4^-$ were also observed: $\delta$ 147.4 (d, $J_{C-F}$ = 241), 137.7 (d, $J_{C-F}$ = 239), 135.7 (d, $J_{C-F}$ = 243), 123.0 (m br). $^{19}$F NMR ($CD_2Cl_2$): $\delta$ −132.5 (d, $J_{F-F}$ = 11.0, 2F, *o*-F), −163.1 (t, $J_{F-F}$ = 20.5, 1F, *p*-F), −167.0 (t, $J_{F-F}$ = 18, 2F, *m*-F). $^{11}$B NMR ($CD_2Cl_2$): $\delta$ −15.0 (s).

**NMR Scale Generation of 8 from $C_2$-6 and [Ph$_3$C][B(C$_6$F$_5$)$_4$].** An NMR tube was charged with $C_2$-**6** (50.0 mg, 0.103 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (96.0 mg, 0.103 mmol). Chlorobenzene-$d_5$ was vacuum transferred in at −80 °C, and the tube was allowed to warm to room temperature. The resulting yellow solution was immediately analyzed by NMR, which established the formation of Ph$_3$CCH$_2$Ph ($^1$H NMR $\delta$ 3.95 (s, 2H, Ph$_3$CC$H_2$Ph); $^{13}$C NMR $\delta$ 46.2 (t, $J$ = 128, Ph$_3$C$C$H$_2$Ph)). $^1$H NMR (25 °C): Most of the $^1$H NMR signals for **8** were broad at 25 °C except: $\delta$ 2.75 (d, 1H, $J$ = 9.3, C$H$HPh) and 2.05 (d, 1H, $J$ = 9.3, CH$H$Ph). $^{13}$C NMR (25 °C): $\delta$ 146.8 (s, *i*-Ph), 122.5 (d, $J_{C-H}$ = 153, *p*-Ph), 74.9 (t, $J_{C-H}$ = 127, $C$H$_2$Ph), 65.6 (br), 64.1 (br), 62.4 (br), 60.5 (br), 57.5 (br), 55.0 (br), 54.5 (t, $J_{C-H}$ = 140), 46.6 (br), 43.7 (br), 30.4 (br), 25.9 (t, $J_{C-H}$ = 133). Resonances for B(C$_6$F$_5$)$_4^-$ were also observed: $\delta$ 147.8 (d, $J_{C-F}$ = 241), 138.0 (d, $J_{C-F}$ = 249), 135.7 (d, $J_{C-F}$ = 251), $C_{ipso}$ not observed.

**[(Me$_2$PMEN)Zr(CH$_2$Ph)][B(C$_6$F$_5$)$_4$] (9). Preparative Scale.** Benzene (10 mL) was added to a mixture of **5** (0.118 g, 0.224 mmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (0.179 g, 0.224 mmol), and the mixture was stirred at room temperature for 15 min. An orange oil separated. The yellow upper layer was removed with a pipet, benzene (5 mL) was added, and the mixture was stirred for 5 min. The upper benzene layer was removed with a pipet, pentane (5 mL) was added, and the mixture was stirred for 5 min. The supernatant was decanted off, and the solid was dried under vacuum to yield a pale orange solid (0.230 g, 92%). Anal. Calcd for $C_{45}H_{35}N_4BF_{20}Zr$: C, 48.53; H, 3.17; N, 5.03. Found: C, 48.38; H, 3.39; N, 4.69. $^1$H NMR ($CD_2Cl_2$, −40 °C) (assignments were made on the basis of a COSY and a $^{13}$C-detected $^{13}$C−$^1$H HETCOR experiment at −40 °C): $\delta$ 7.37 (t, $J$ = 7.2, 2H, *m*-Ph), 7.06 (t, $J$ = 7.2, 1H, *p*-Ph), 6.82 (d, $J$ = 7.2, 2H, *o*-Ph), 4.02−3.87 (m, 2H, H-5 and H′-5), 3.84 (m, 1H, H-2), 3.70 (m, 1H, H′-2), 3.38−3.25 (m, 2H, H-5 and H-$\gamma$), 3.15 (m, 1H, H′-5), 3.00 (dd, $J$ = 4.1 and 12.4, 1H, H-$\alpha$), 2.73 (d, $J$ = 8.3, 1H, C$H$HPh), 2.80−2.60 (m, 5H, 3H-$\alpha$ and 2H-$\gamma$), 2.57 (s, 3H, NC$H_3$), 2.17 (d, $J$ = 8.3, 1H, CH$H$Ph), 2.12 (dd, $J$ = 2.7 and 14.2, 1H, H-$\gamma$), 1.90−1.70 (m, 6H, 4H-4 + H-3 + H′-3), 1.76 (s, 3H, N′C$H_3$), 1.25−1.05 (m, 2H, H-3 and H′-3). $^{13}$C NMR ($CD_2Cl_2$, −80 °C): $\delta$ 142.3 (s, *i*-Ph), 133.0 (d, $J_{C-H} \approx$ 160, *m*-Ph), 124.8 (d, $J_{C-H}$ = 157, *p*-Ph), 119.6 (d, $J_{C-H}$ = 152, *o*-Ph), 64.3 (t, $J_{C-H}$ = 135, N$C$H$_2$), 63.5 (t, $J_{C-H}$ = 136, N′$C$H$_2$), 61.8 (d, $J_{C-H}$ = 144, N$C$H), 61.0 (d, $J_{C-H}$ = 137, N′$C$H), 60.7 (t, $J_{C-H}$ = 138, $C$H$_2$Ph), 56.2 (t, $J_{C-H}$ = 136), 50.9 (t, $J_{C-H}$ = 139), 49.9 (t, $J_{C-H}$ = 138), 47.1 (q, $J_{C-H}$ = 138, N$C$H$_3$), 42.7 (q, $J_{C-H}$ = 138, N′$C$H$_3$), 30.1 (t, $J_{C-H}$ = 131), 29.6 (t, $J_{C-H}$ = 131), 27.2 (t, $J_{C-H}$ = 131), 26.2 (t, $J_{C-H}$ = 132); one resonance is obscured by the solvent signals. Resonances for B(C$_6$F$_5$)$_4^-$ were also observed: $\delta$ 147.2 (d, $J_{C-F}$ = 240), 137.4 (d, $J_{C-F}$ = 243), 135.5 (d, $J_{C-F}$ = 243), 123.0 (m br). $^{19}$F NMR ($CD_2Cl_2$): $\delta$ −132.5 (d, $J_{F-F}$ = 11.0, 2F, *o*-F), −163.1 (t, $J_{F-F}$ = 20.5, 1F, *p*-F), −167.0 (t, $J_{F-F}$ = 18, 2F, *m*-F). $^{11}$B NMR ($CD_2Cl_2$, 193 K): $\delta$ −15.6 (s).

**Generation of [(Me$_2$PMEN)Zr(CH$_3$)(THF-$d_8$)][B(C$_6$F$_5$)$_4$] (10).** A NMR tube was charged with **5** (29 mg, 0.078 mmol) and [HNMePh$_2$][B(C$_6$F$_5$)$_4$] (67 mg, 0.078 mmol). THF-$d_8$ was vacuum transferred in at −80 °C, and the tube was allowed to warm to room temperature. Vigorous gas evolution was observed. A $^1$H NMR analysis of the resulting yellow solution after 15 min established the presence of methane ($\delta$ 0.17), free NMePh$_2$ ($\delta$ 7.20 (tm, $J$ = 7.6, 4H, *m*-H), 6.98 (dd, $J$ = 7.6 and 1.1, 4H, *o*-H), 6.87 (tt, $J$ = 7.3 and 1.1, 2H, *p*-H), 3.27 (s, 3H, NC$H_3$)), and three zirconium complexes, of which the major one has $C_2$-symmetry (key data: $\delta$ 2.54 (s, 6H, NC$H_3$), 0.08 (s, 3H, ZrC$H_3$)). After 4 days at room temperature, only one $C_1$-symmetric species, assigned as **10**, was observed. $^1$H NMR (THF-$d_8$): $\delta$ 4.07 (td, $J$ = 10.8 and 6.3, 1H), 3.97 (m, 1H), 3.84 (ddd, $J$ = 10.7, 7.6, and 2.7, 1H), 3.66 (m, 1H), 3.47−3.34 (m, 2H), 3.19 (dd, $J$ = 12.3 and 4.5, 1H), 3.12−3.02 (m, 2H), 2.84 (m, 1H), 2.78 (t, $J$ = 4.9, 1H), 2.74 (s, 3H, NC$H_3$), 2.72 (s, 3H, N′C$H_3$), 1.80−1.70 (m, 9H), 1.23−1.13 (m, 2H), −0.22 (s, 3H, ZrC$H_3$). $^{13}$C NMR (THF-$d_8$): $\delta$ 67.2 (t, $J_{C-H}$ = 135), 66.7 (t, $J_{C-H}$ = 136), 64.7 (d, $J_{C-H}$ = 139, N$C$H), 64.2 (d, $J_{C-H}$ = 139, N′$C$H), 59.5 (t, $J_{C-H}$ = 137), 55.7 (t, $J_{C-H}$ = 136), 53.7 (t, $J_{C-H}$ = 136), 52.2 (t, $J_{C-H}$ = 136), 49.1 (q, $J_{C-H}$ = 137, N$C$H$_3$), 45.3 (q, $J_{C-H}$ = 137, N′$C$H$_3$), 33.7 (q, $J_{C-H}$ = 110, Zr$C$H$_3$), 31.6 (t, $J_{C-H}$ = 131), 30.9 (t, $J_{C-H}$ = 128), 28.0 (t, $J_{C-H}$ = 131), 27.6 (t, $J_{C-H}$ = 130). Resonances for free NMePh$_2$ ($\delta$ 129.8 (dm, $J_{C-H}$ = 155), 121.9 (dt, $J_{C-H}$ = 159), 121.2 (dm, $J_{C-H}$ = 157), $C_{ipso}$ not observed, 40.4 (q, $J_{C-H}$ = 135, N$C$H$_3$)) and

**Table 6. Summary of Crystal Data for Compounds $C_1$-3 and $C_2$-6**

| | $C_1$-**3** | $C_2$-**6** |
|---|---|---|
| formula | $C_{14}H_{28}Cl_2N_4Zr$ | $C_{28}H_{42}N_4Ti$ |
| cryst syst | orthorombic | hexagonal |
| space group | $P2_12_12_1$ | $P6_1$ |
| $a$ (Å) | 12.739(4) | 8.436(2) |
| $b$ (Å) | 15.984(6) | 8.436(2) |
| $c$ (Å) | 8.960(3) | 65.57(2) |
| $V$ (Å$^3$) | 1824(1) | 4041(1) |
| $Z$ | 4 | 6 |
| $D_c$ (g cm$^{-3}$) | 1.509 | 1.190 |
| $\mu$ (mm$^{-1}$) | 0.895 | 0.339 |
| cryst size (mm) | 0.39 × 0.09 × 0.08 | 0.13 × 0.13 × 0.09 |
| cryst color, habit | pale yellow needle | red block |
| $T$ (K) | 213 | 213 |
| diffractometer | Enraf-Nonius CAD4 | Enraf-Nonius CAD4 |
| radiation, $\lambda$ (Å) | Mo Kα, 0.710 73 | Mo Kα, 0.710 73 |
| $F$(000) | 856 | 1560 |
| $\theta$ range (deg) | 2.0−25.0 | 2.0−25.0 |
| data collected: $h;k;l$ | ±15; −1,18; −10,3 | −1,10; −10,4; −77,53 |
| no. of reflns | 3870 | 7497 |
| no. of indep reflns ($R_{int}$) | 2882 (0.0922) | 3089 (0.1158) |
| no. of obsd reflns ($I > 2\sigma(I)$) | 2021 | 1861 |
| structure solution | direct methods[a] | direct methods[a] |
| GOF on $F^2$ | 1.032 | 0.998 |
| $R_1$ ($I > 2\sigma(I)$)[b] | 0.0483 | 0.0535 |
| $wR_2$[c] | 0.0834 | 0.0846 |
| max. resid density (e Å$^{-3}$) | 0.42 | 0.22 |

[a] SHELXTL-Plus Version 5, Siemens Industrial Automation, Inc., Madison, WI. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

$B(C_6F_5)_4^-$ ($\delta$ 149.1 (d, $J_{C-F} = 226$), 139.2 (d, $J_{C-F} = 229$), 137.1 (d, $J_{C-F} = 243$), 125.0 (m br)) were also observed.

**X-ray Structural Determinations.** Data collection, solution, and refinement procedures and parameters are summarized in Table 6, and details are provided in the Supporting Information. The data processing, solution, and refinement were done using SHELXTL v5.0 programs.

A pale yellow needle of $C_1$-**3** was selected, and a total of 3870 data were collected using $\theta/2\theta$ scans. On the basis of preliminary examination of the crystal, the space group $P2_12_12_1$ was assigned. Intensity standards were measured at 2 h intervals and showed no decay. Lorentz and polarization corrections, as well as a Gaussian absorption correction based on crystal dimensions, were applied. The C12−C13−C14−C15−N16 ring has two conformations; C12, C15, and N16 are common to both. Two positions of partial occupancy were included for C13 and C14 (C13′ and C14′ are the alternate sites; occupancy fraction = 0.46(2) for C13 and C14, occupancy fraction = 0.54(2) for C13′ and C14′). The C12−C13, C13−C14, and C14−C15 distances were restrained to be the same as the C12′−C13′, C13′−C14′, and C14′−C15′ distances, respectively. The rigid bond restraint was applied to the anisotropic thermal parameters of the atoms of this ring. Additionally, because of near coincidence (C13−C13′ = 0.270 Å), the thermal parameters for C13 and C13′ were constrained to be the same. The thermal parameters of C14 and C14′ were restrained to be similar due to their close proximity (C14−C14′ = 0.681 Å). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included with the riding model using program default values.

A red hexagonal plate of $C_2$-**6** was selected, and a total of 7497 data were collected using $\theta/2\theta$ scans. Based on preliminary examination of the crystal, the space group $P6_1$ was assigned. Intensity standards were measured at 2 h intervals and showed no decay. Lorentz and polarization corrections and an empirical absorption correction based on three $\varphi$ scans measured at 10° intervals were applied. The rigid bond restraint was imposed on the anisotropic thermal parameters of the ligand atoms. The crystal is merohedrally twinned (twin law = 0 1 0, 1 0 0, 0 0 −1) and the fraction of twinning refined to 0.470(2). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included with the riding model using program default values.

**Ethylene Polymerization.** Polymerization experiments were performed in a 250 mL Fischer−Porter bottle equipped with a magnetic stirring bar and externally heated with an oil bath as desired. In a typical experiment (Table 5, entry 3), the Fischer−Porter bottle was charged with the activator $[Ph_3C][B(C_6F_5)_4]$ (40 mg, 43 $\mu$mol) and placed under 1 atm of ethylene (99.99%). A solution of **5** (25 mg, 48 $\mu$mol) in toluene (13 mL) was introduced via cannula. The ethylene pressure was increased to 1.4 atm (20 psi, maintained constant during the experiment), and the solution was stirred for 1.5 h. Ethylene was vented, the Fischer−Porter bottle was opened to air, and 5% solution of HCl in ethanol (60 mL) was added. The mixture was stirred for 30 min. The polymer was collected by filtration, washed with 5% aqueous HCl (60 mL) and acetone (2 × 10 mL), and dried under vacuum overnight (0.495 g; activity = 5430 g PE/mol of activated Zr·h·atm). Gel permeation chromatography (GPC) analyses were performed on a Waters 150C chromatograph equipped with differential refractometer and viscometer detectors using a PL gel mixed-bed column, and at 145 °C in 1,2,4-trichlorobenzene. DSC analyses were conducted on a Perkin-Elmer DSC-2 model calibrated using indium metal with a sweep rate of 10 °C/min from 25 to 200 °C.

**Acknowledgment.** This work was supported by the Department of Energy (DE-FG02-00ER15036) and Total Co. J.F.C. thanks the Centre National de la Recherche Scientifique for a sabbatical leave.

**Supporting Information Available:** Tables of crystallographic data (positional and thermal parameters and bond distances and angles) for $C_1$-**3** and $C_2$-**6**; data are also available for these compounds in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0340443