Notes

Stereoselective Access to New Half-Sandwich Complexes Containing an Isodicyclopentadienyl Ligand

Sébastien Gentil,[†] Nadine Pirio,[†] Philippe Meunier,*[,†] Judith C. Gallucci,[‡]
Jeffrey D. Schloss,[‡] and Leo A. Paquette[‡]

*Laboratoire de Synthèse et Electrosynthèse Organométalliques Associé au CNRS, UMR 5632,
Université de Bourgogne, BP 138, 21004 Dijon Cedex, France, and Evans Chemicals
Laboratories, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210*

Received June 5, 2000

Summary: The stereoselective synthesis, characterization, and X-ray crystal structure of a new example of a half-sandwich zirconium complex containing a nonplanar cyclopentadienyl ligand are reported. Preliminary ethylene polymerization results reveal catalyst activity that is comparable with related complexes.

Introduction

The development of homogeneous group 4 metallocene/methylalumoxane Ziegler catalysts for ethylene and propylene polymerization continues unabated. The replacement of one cyclopentadienyl ligand by a pendant donor group acting as a bidentate ligand bonded to the metal center introduced by Bercaw[1] has created a new family of polymerization catalysts. Amido-functionalizated complexes (CpA) of titanium and zirconium, which differ from classical bis(cyclopentadienyl) systems by the open nature of their catalytically active site, have shown a remarkable ability to incorporate bulkier olefins such as styrene, 1-hexene, or 1-decene into growing ethylene or propylene chains. In the past decade, intensive industrial investigations have been carried out at Dow and Exxon,[2] and variations of the amido substituents, the nature of the bridge, and the character of the ring substituents have appeared in the literature.[3−27] The most common ligands used in such complexes have planar structures, for example, the η^5-cyclopentadienyl or indenyl systems, and, to the best of our knowledge, nonplanar cyclopentadienyl ligands possessing the ability to discriminate between their two π-surfaces have not been examined. For this reason, so-called half-sandwich metallocenes featuring an isodicyclopentadienyl ligand hold considerable attraction. The isodicyclopentadienyl ligand has already been used in Ziegler−Natta catalysts synthesis, and the combination of bis(isodicyclopentadienyl)titanium and zirconium dichlorides with methylalumoxane exhibits interesting activity.[33]

---

* Correspponding author. Tel: +33(0)380396105. Fax: +33(0)-380396100. E-mail: Philippe.Meunier@u-bourgogne.fr.

[†] Université de Bourgogne.

[‡] The Ohio State University.

(1) (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867−869. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623−4640.

(2) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S.-y. (Dow) Eur. Pat. Appl. 0 416 815 B1, 1991.

(3) Hughes, K. A.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936−1945.

(4) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1994**, *13*, 4140−4142.

(5) Herrmann, W. A.; Morawietz, M. J. A. *J. Organomet. Chem.* **1994**, *482*, 169−181.

(6) Ciruelos, S.; Cuenca, T.; Gomez-Sal, P.; Manzanero, A.; Royo, P. *Organometallics* **1995**, *14*, 177−185.

(7) Okuda, J.; Schattenmann, F. J.; Wocadlo, S.; Massa, W. *Organometallics* **1995**, *14*, 789−795.

(8) Du Plooy K. E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics* **1995**, *14*, 3129−3131.

(9) Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132−3134.

(10) Spence, R. E. v. H.; Piers, W. E. *Organometallics* **1995**, *14*, 4617−4624.

(11) Amor, F.; Okuda, J. *J. Organomet. Chem.* **1996**, *520*, 245−248.

(12) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572−1581.

(13) Ciruelos, S.; Cuenca, T.; Gomez, R.; Gomez-Sal, P.; Manzanero, A.; Royo, P. *Organometallics* **1996**, *15*, 5577−5585.

(14) Okuda, J.; Eberle, T.; Spaniol, T. P. *Chem. Ber.* **1997**, 130, 209−215.

(15) Dias, H. V. R.; Wang, Z. *J. Organomet. Chem.* **1997**, *539*, 77−85.

(16) Gomes, P. T.; Green, M. L. H.; Martins, A. M.; Mountford, P. *J. Organomet. Chem.* **1997**, *541*, 121−125.

(17) McKnight, A. L.; Masood, Md. A.; Waymouth, R. M., Straus, D. A. *Organometallics* **1997**, *16*, 2879−2885.

(18) Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649−3657.

(19) Sinnema, P.-J.; Van der Veen, L.; Spek, A. L., Veldman, N.; Teuben, J. H. *Organometallics* **1997**, *16*, 4245−4247.

(20) Amor, F.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4765−4767.

(21) Sernetz, F. G.; Mülhaupt, R.; Amor, F.; Eberle, T.; Okuda, J. *J. Polym. Sci. A: Polym. Chem.* **1997**, *35*, 1571−1578.

(22) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587−2598.

(23) Brown, S. J.; Gao, X., Harrison, D. G., Koch, L.; Spence, R. E. v. H.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5445−5447.

(24) Amor, F.; Butt, A.; Du Plooy K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836−5849.

(25) Eberle, T.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **1998**, 237−244.

(26) Leung, W.-P.; Song, F.-Q.; Zhou, Z.-Y.; Xue, F.; Mak, T. C. W. *J. Organomet. Chem.* **1999**, *575*, 232−241.

(27) Gomez, R.; Gomez-Sal, P.; Del Real, P. A.; Royo, P. *J. Organomet. Chem.* **1999**, *588*, 22−27.

(28) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1983**, *105*, 3126−3135.

(29) Paquette, L. A.; Moriarty, K. J.; Meunier P.; Gautheron B.; Sornay C.; Rogers R. D.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2159.

(30) Sornay C.; Meunier, P.; Gautheron B.; O'Doherty G. A.; Paquette, L. A. *Organometallics* **1991**, *10*, 2082−2083.

10.1021/om000472m CCC: $19.00
Publication on Web 09/06/2000

In continuation of these studies, we describe in this paper the synthesis and characterization of a zirconium complex containing an amido−isodicyclopentadienyl ligand.

Results and Discussion

CpA catalysts can be obtained according to three different ways. The method introduced by Royo[6] that involves the reaction between LiNHR and the (monocyclopentadienyl)titanium derivative Cp(SiMe$_2$Cl)TiCl$_3$ is exemplary. The method that we have used consists of the stepwise introduction of the silyl bridge followed by the amine group to the cyclopentadienyl ligand. As demonstrated earlier,[12] this strategy leads to very poor yields with unsubstituted cyclopentadienyl ligands but seems to be workable for substituted ones.[7−10] A variation of this route could consist of the introduction of the aminosilyl bridge Me$_2$Si(NHR)Cl, which would be reacted immediately with the Cp fragment.

Isodicyclopentadienide anion **1** was obtained by conventional reaction of isodicyclopentadiene with *n*-butyllithium in ether at −78 °C.[28,29,33] Reaction of **1** at −78 °C with a large excess of dichlorodimethylsilane in THF led to chloro(dimethyl)(isodicyclopentadienyl)silane (**2**) in 81% yield. In related published works,[28−33] the influence of reaction temperature on stereoselectivity was demonstrated. At −78 °C, the endo product is obtained nearly exclusively. The NMR spectra confirmed the presence of the *endo*-chloro(dimethyl)(isodicyclopentadienyl)silane in a large majority, and traces of *exo*-chloro(dimethyl)(isodicyclopentadienyl)silane and *ansa*-bis(isodicyclopentadienyl)dimethylsilane[7,12] have been noted. When a solution of the chloride in diethyl ether at 0 °C was allowed to react with lithium *tert*-butylamide, *tert*-butylamino(dimethyl)(isodicyclopentadienyl)silane (**3**) was obtained. Double deprotonation of **3** with 2 equiv of *n*-butyllithium and subsequent reaction of the dilithium salt with ZrCl$_4$ in diethyl ether afforded only one dichloro zirconocene complex. According to the NMR (^{1}H and ^{13}C) spectra of this complex and precedent results in this field,[29,30] it appeared that the isodicyclopentadienyl ligand was evidently complexed on its exo face in a completely stereoselective manner. When the same reaction was performed in toluene, a yellow precipitate formed slowly over a few days. The precipitation in diethyl ether is slower than in toluene. Unfortunately, no single crystals of complex **5** have been obtained to date. For this reason, reaction of **5** with Me$_3$SiCH$_2$MgCl[7] was conducted in ether, and crystals of **6** suitable for X-ray diffraction were formed by cooling the solution.

Crystal Structure Data. The molecular structure of **6** is illustrated in Figure 1, and selected bond lengths and angle values are listed in Table 1. The Si(3) atom lies 0.854(3) Å out of the least-squares plane through C(1), C(2), C(3), C(4), and C(5) and is obviously on the same side of this plane as the Zr atom. Atoms C(6) and C(9) lie on the opposite side of this five-membered ring.

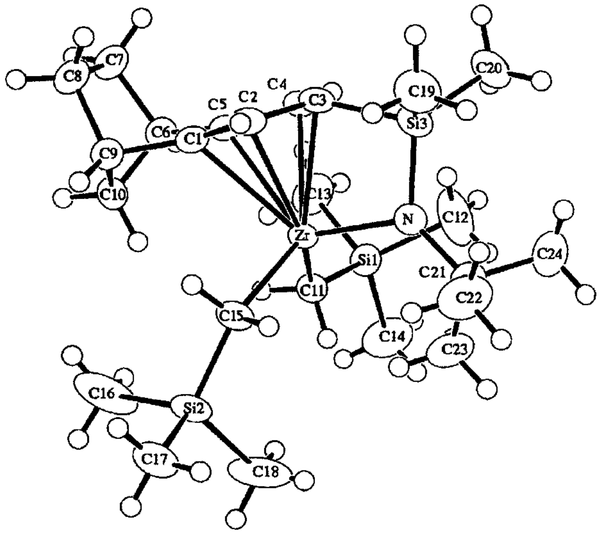


Figure 1. ORTEP view of molecular structure of **6**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 6

Zr−N	2.086(1)	Si(1)−C(11)	1.856(2)
Zr−C(11)	2.241(2)	Si(2)−C(15)	1.854(2)
Zr−C(15)	2.266(2)	Si(3)−N	1.732(2)
Zr−C(1)	2.567(2)	Si(3)−C(3)	1.862(2)
Zr−C(2)	2.493(2)	C(1)−C(5)	1.419(2)
Zr−C(3)	2.440(2)	C(1)−C(2)	1.400(3)
Zr−C(4)	2.516(2)	C(2)−C(3)	1.439(2)
Zr−C(5)	2.585(2)	C(3)−C(4)	1.437(2)
N−C(21)	1.480(2)	C(4)−C(5)	1.404(2)
N−Zr−C(11)	112.65(6)	C(11)−Zr−C(15)	107.68(6)
N−Zr−C(15)	107.79(6)	N−Si(3)−C(3)	94.86(7)
Si(3)−N−Zr	105.14(7)	Si(1)−C(11)−Zr	130.10(9)
C(21)−N−Zr	126.64(11)	Si(2)−C(15)−Zr	130.48(9)

The dihedral angle between the least-squares planes defined by C(6)−C(5)−C(1)−C(9) and C(2)−C(1)−C(5)−C(4) is 9.5(1)°. The structural features of **6** are similar to those reported in the literature. The compound exhibits a pseudotetrahedral geometry of the different ligands and adopts the expected three-legged piano stool configuration. The sum of the angle values at the nitrogen atom is close to 360 °C, which is in agreement with the nitrogen sp^2 hybridization. As a consequence, the zirconium−nitrogen bond length of 2.086(1) Å is in the range of an amido ligand bonded to a d^0 zirconium center with appreciable π-bonding: 2.052 Å in C$_5$Me$_4$SiMe$_2$(N*t*Bu)ZrCl$_2$;[12] 2.018 Å in C$_5$Me$_4$SiMe$_2$(N*t*Bu)Zr(NMe$_2$)$_2$;[12] 2.061 Å in C$_{13}$H$_{18}$SiMe$_2$(N*t*Bu)Zr(CH$_2$SiMe$_3$)$_2$.[7]

The orientation of the two trimethylsilylmethyl groups is influenced by the steric effect of the isodicyclopentadienyl methano bridge. They are both turned away from the zirconium center and from the isodicyclopentadienyl ligand. The angles N−Zr−C(11) and N−Zr−C(15) are 112.65(6)° and 107.79(6)°, respectively, but the groups' orientation differs slightly from that observed with C$_{13}$H$_{18}$SiMe$_2$(N*t*Bu)Zr(CH$_2$SiMe$_3$)$_2$.[7] The two equivalent methylene carbon angle values for Si(2)−C(15)−Zr and Si(1)−C(11)−Zr are not significantly different (Table 1), and thus, no methyl groups are close to the isodicyclopentadienyl ligand.

Similar influence can be expected with complex **5**. The steric repulsion effect of the methano bridge should influence the zirconium α-position substituents and enhance the possibilities for olefin incorporation.

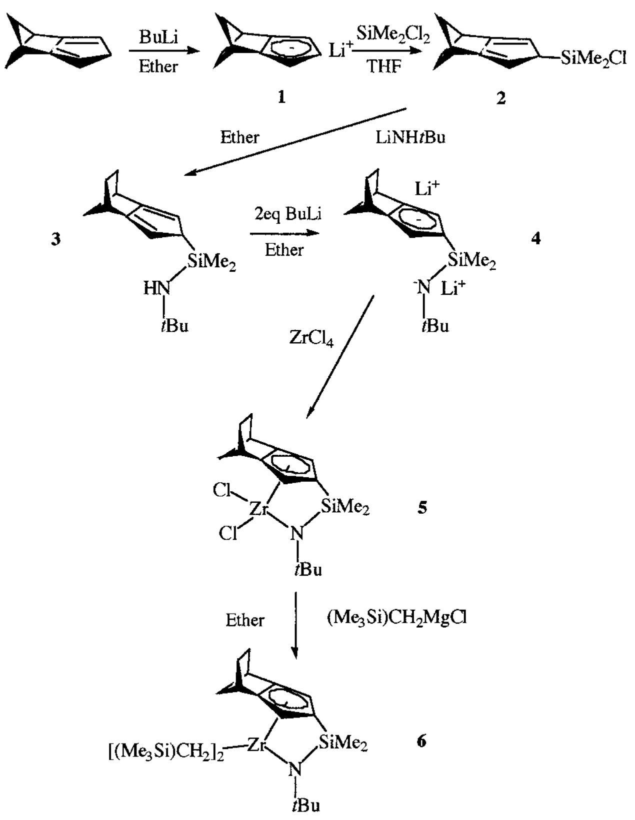
---

(31) Zaegel, F.; Gallucci, J. C.; Meunier, P.; Gautheron B.; Bzowej, E. I.; Paquette, L. A. *Organometallics* **1995**, *14*, 4576−4584.

(32) Gallucci, J. C.; Kozmina, N.; Paquette, L. A.; Zaegel, F.; Meunier, P.; Gautheron B. *Acta Crystallogr.* **1997**, *C53*, 1416−1420.

(33) Gobley, O.; Meunier, P.; Gautheron, B.; Gallucci, J. C.; Erker, G.; Dahlmann, M.; Schloss, J. D.; Paquette, L. A. *Organometallics* **1998**, *17*, 4897−4903.

Scheme 1



Ethylene Polymerization Catalysis. The catalytic properties of the amino complex **5** were first evaluated for ethylene polymerization. The catalyst was activated with MAO in toluene solution at 20 °C under a constant ethylene pressure of 4 bar. The examined catalyst system proved to be very stable during the polymerization reaction and was found to be active toward ethylene monomers. With a Zr:Al ratio of 1:1000, activity values were found to be in agreement with the range of activities obtained with other cyclopentadienyl ligands (131 kg[PE] [mol cat]$^{-1}$ h^{-1}). As expected, because of the lower isodiCp-ring electron density, the amido isodicyclopentadienyl catalyst is less active than the amido tetramethylcyclopentadienyl complex with the same amide function.[25] Steric influence effects of the methano bridge are not readily noted with ethylene polymerization. As mentioned in the literature,[21] the steric hindrance could reduce the bulkier olefin's incorporation during copolymerization and increase the long-term activity of the catalyst.

Conclusion. To expand the isodicyclopentadienyl ligand polymerization catalyst family, we have synthesized the new half-sandwich *tert*-butyl amido(dimethylsilyl)isodicyclopentadienyl dichloro complex of zirconium. Derivation with (Me$_3$Si)CH$_2$MgCl provided crystals that were suitable for X-ray structure determination. As expected, exo complexation to the zirconium resulted. Potentialities for the polymerization of propylene and bulkier olefins are currently under investigation, and isodicyclopentadienyl bridge steric influence has to be studied.

Experimental Section

General Conditions. All manipulations were conducted under an argon atmosphere. The solvents were dried and distilled prior to use. Butyllithium, *tert*-butylamine, ZrCl$_4$, ((trimethylsilyl)methyl)magnesium chloride, and methylalumoxane (MAO) were obtained from Aldrich and used as received. Dichlorodimethylsilane was distilled over copper turnings. Elemental analyses were performed by the Service de microanalyses du L.S.E.O. (Université de Bourgogne), and ^{1}H, ^{13}C NMR spectra were recorded with a Bruker DRX500 spectrometer. Isodicyclopentadienyl methano and ethano bridge NMR chemical assignments were not possible by simple first-order approximation, and the coupling constants could no longer be obtained by simple spacing measurement. For this reason, methano and ethano bridge protons were described as multiplet (m), and additional NMR description will be reported shortly. Mass spectra were determined with a KRATOS concept IS instrument (Centre de Spectroscopie Moléculaire de l'Université de Bourgogne); EI at 70 eV.

Ethylene Polymerization Procedure. Polymerization reactions were carried out in a 250 mL Büchi glass autoclave equipped with a magnetic stirrer. In the autoclave, methylalumoxane (10 wt % in toluene, Al:Zr = 1000:1) was added to 60 mL of dry toluene under argon. The reactor was maintained at the desired temperature and pressurized with ethylene (1 bar) for 30 min. A solution of catalyst (20−50 mg) in toluene (5 mL) was then added via a syringe. After the addition, the autoclave was pressurized with an ethylene pressure of 4 bar, and the reaction mixture was stirred for 1 h. During the polymerization reactions, monomer was fed continuously to maintain the desired pressure. Finally, the autoclave was vented, and the reaction mixture was quenched with 10% HCl in methanol (30 mL) and stirred for 1 h. The precipitated polymer was collected by filtration, washed several times with water and methanol to remove Al residues, and dried under vacuum for 1 day to constant weight.

Chloro(dimethyl)(isodicyclopentadienyl)silane, 2. A solution of (isodicyclopentadienyl)lithium[28,29,33] (**1**, 5.17 mmol, 716 mg) in dry THF (10 mL) was slowly added to a solution of dichlorodimethylsilane (10 mL) in THF (10 mL) cooled to −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent and a large excess of dichlorodimethylsilane were removed under vacuum. Lithium chloride was precipitated with methylene chloride and filtered off. Removal of the solvent gave a pale green-yellow oil (4.16 mmol, 81%). According to the NMR spectra, traces of *exo*-chloro(dimethyl)(isodicyclopentadienyl)silane and *ansa*-bis(isodicyclopentadienyl)dimethylsilane were noted. ^{1}H NMR (C$_6$D$_6$): δ 5.86 (d, J_{HH} = 1.5 Hz, 2H, peripheral), 3.65 (t, J_{HH} = 1.2 Hz, 1H, central), 3.07 (br s, 2H, bridgehead), 1.80−1.74 (m, 3H, exo-ethano bridge, anti-methano bridge), 1.46 (m, 1H, syn-methano bridge), 1.24 (m, 2H, endo-ethano bridge), 0.20 (s, 6H, SiCH_3). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 156.6 (quaternary), 114.7 (peripheral), 54.5 (central), 46.3 (methano bridge), 39.3 (bridgehead), 28.7 (ethano bridge), 0.23 (s, SiCH_3). MS, *m*/*z* (relative intensity): 224 (M$^+$, 78).

(*tert*-Butylamino)(dimethyl)(isodicyclopentadienyl)silane, 3. To a solution of crude Me$_2$Si(isodicyclopentadienyl)Cl (4.16 mmol, 932 mg) in diethyl ether at 0 °C was added solid lithium *tert*-butylamide (4.16 mmol, 329 mg). After the solution was warmed to room temperature and stirred overnight, the solvent was removed under vacuum, and LiCl was precipitated with methylene chloride and filtered off. Methylene chloride was removed from the filtrate, leaving behind a yellow oil (2.95 mmol, 71% yield). ^{1}H NMR (C$_6$D$_6$): δ 5.98 (d, J_{HH} = 1.2 Hz, 2H, peripheral), 3.60 (t, J_{HH} = 1.0 Hz, 1H, central), 3.15 (br s, 2H, bridgehead), 1.87−1.83 (m, 3H, exo-ethano bridge, anti-methano bridge), 1.57 (m, 1H, syn-methano bridge), 1.43 (m, 2H, endo-ethano bridge), 1.21 (s, 9H, NCCH_3), 0.56 (br s, 1H, NH), 0.13 (s, 6H, SiCH_3). ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 154.2 (quaternary), 115.7 (peripheral), 55.2 (central), 49.6 (NCCH$_3$), 47.1 (methano bridge), 39.0 (bridgehead), 33.9 (NCCH$_3$), 28.9 (ethano bridge), 0.16 (s, SiCH_3). MS, *m*/*z* (relative intensity): 261 (M^+, 72), 246 ($M^+ - Me$, 68), 130 ($M^+ -$ isodiCp, 100).

***exo*-[η^1:η^5-*tert*-Butyl(dimethylisodicyclopentadienylsilyl)amido]dichlorozirconium, 5.** To a solution of **3** (2.95 mmol, 770 mg) in 15 mL of diethyl ether at −78 °C was slowly added *n*-butyllithium (5.90 mmol, 3.7 mL of a 1.6 M solution in hexane). The mixture was allowed to warmed to room temperature, refluxed overnight, and filtered. The pale yellow precipitate **4** was washed three times with diethyl ether and dried in a vacuum (745 mg, 97%). After the pale yellow powder **4** was placed in 15 mL of diethyl ether at −78 °C, the suspension was treated gradually with solid zirconium tetrachloride (3.50 mmol, 808 mg). The mixture was warmed to room temperature and stirred for 18 h. The resulting yellow-brown suspension was filtered off. The filtrate was concentrated to ca. 7 mL and was cooled to −20 °C to afford a microcrystalline powder (1.57 mmol, 55% yield). ^{1}H NMR ($CDCl_3$): δ 6.04 (s, 2H, peripheral), 3.47 (br s, 2H, bridgehead), 1.99 (m, 2H, exo-ethano bridge), 1.84 (m, 1H, anti-methano bridge), 1.73 (m, 1H, syn-methano bridge), 1.24 (m, 2H, endo-ethano bridge), 1.43 (s, 9H, $NCCH_3$), 0.55 (s, 6H, $SiCH_3$). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 148.3 (quaternary), 113.3 (peripheral), 107.2 (central), 57.9 ($NCCH_3$), 51.4 (methano bridge), 40.9 (bridgehead), 33.4 ($NCCH_3$), 28.3 (ethano bridge), 1.5 (s, $SiCH_3$). Anal. Calcd for $C_{16}H_{25}NSiZrCl_2$: C, 45.58; H, 5.97; N, 3.32. Found: C, 45.40; H, 6.03; N, 3.57.

***exo*-[η^1:η^5-*tert*-Butyl(dimethylisodicyclopentadienylsilyl)amido]{bis(trimethylsilyl)methyl}zirconium, 6.** A solution of ((trimethylsilyl)methyl)magnesium chloride (3 mL of a 1 M solution in diethyl ether, 3 mmol) was added dropewise to a solution of complex **5** (1.50 mmol, 632 mg) in diethyl ether (10 mL) at −78 °C. The reaction mixture was warmed to 0 °C and stirred for 4 h. The solvent was removed, and the residue was extracted with 30 mL of pentane and filtered. Concentration of the filtrate to ca. 5 mL and cooling to −20 °C for one night afforded colorless crystals (1.10 mmol, 72% yield). ^{1}H NMR (C_6D_6): δ 5.98 (s, 2H, peripheral), 3.40 (br s, 2H, bridgehead), 1.74 (m, 3H, exo-ethano bridge, anti-methano bridge), 1.42 (m, 1H, syn-methano bridge), 1.25 (m, 2H, endo-ethano bridge), 1.53 (s, 9H, $NCCH_3$), 0.59 (d, J_{HH} = 11.4 Hz, 2H, $ZrCH_2$), 0.53 (s, 6H, $SiCH_3$), 0.33 (s, 18H, CH_2-$SiCH_3$), 0.06 (d, J_{HH} = 11.3 Hz, 2H, $ZrCH_2$). ^{13}C {^{1}H} NMR (C6D6) δ 143.5 (quaternary), 110.3 (peripheral), 102.1 (central), 56.3 ($NCCH_3$), 51.3 ($ZrCH_2$), 49.9 (methano bridge), 40.8 (bridgehead), 34.6 ($NCCH_3$), 29.2 (ethano bridge), 4 (CH_2-$SiCH_3$), 2.2 (s, $SiCH_3$). MS, *m*/*z* (relative intensity): 436 ($M^+ - CH_2(SiMe_3)$). Anal. Calcd for $C_{24}H_{47}NSi_3Zr$: C, 54.96; H, 8.96; N, 2.67. Found: C, 54.78; H, 9.07; N, 2.75.

X-ray Structure Determination. The data collection crystal was a clear, colorless rectangular block which had been cut from a large, thick plate. Examination of the diffraction pattern on a Nonius Kappa CCD diffractometer indicated a triclinic crystal system. All work was done at 173 K using an Oxford Cryosystems Cryostream Cooler. A hemisphere of data was measured using the scan method with a frame width of 1.0°. Data integration was done with Denzo,[34] and scaling and merging of the data was done with Scalepack.[34] Merging the data and averaging the symmetry equivalent reflections resulted in an R_{int} value of 0.027.

The Zr atom was located in P1 by the Patterson method using SHELXS-86.[35] Phasing on the Zr in DIRDIF[36] revealed the positions of most of the other non-hydrogen atoms. Full-matrix least-squares refinements based on F^2 were performed in SHELXL-93.[37]

The hydrogen atoms were included in the model at calculated positions using a riding model with $U(H) = 1.2U_{eq}$ (attached atom). For a methyl group, the torsion angle that defines its orientation was allowed to refine, and these hydrogen atoms were assigned $U(H) = 1.5U_{eq}$ (attached carbon atom). The final refinement cycle was based on all the 6720 intensities and 273 variables and resulted in agreement factors of $R1(F) = 0.033$ and $wR2(F^2) = 0.072$. For the subset of data with $I > 2(I)$, the R1(*F*) value is 0.028 for 6072 reflections. One reflection (−10 −6 8) was excluded from the refinement because it had a substantial negative intensity value. The final difference electron density map contains maximum and minimum peak heights of 0.40 and −0.45 e/Å^3. Neutral atom scattering factors were used and include terms for anomalous dispersion.[38]

Acknowledgment. The French group thanks MERT, CNRS, and Conseil Régional de Bourgogne for financial support. S.G. thanks CNRS and Conseil Régional de Bourgogne for the award of a thesis grant. The American group is indebted to the National Science Foundation for financial support.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM000472M

---

[34] DENZO: Otwinowski, Z.; Minor, W. *Methods in Enzymology, Vol 276*; *Macromolecular Crystallography, Part A*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; pp 307−326.

[35] SHELXS-86: Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

[36] DIRDIF: Parthasarathi, V.; Beursken, P. T.; Slot, H. J. B. *Acta Crystallogr.* **1983**, *A39*, 860−864.

[37] Sheldrick, G. M. *SHELXL-93*; Universität Gottingen: Germany, 1993.

[38] *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.