1652 *Organometallics* **1998,** *17,* 1652−1654

Titanium Hydrocarbyl Complexes with a Linked Cyclopentadienyl−Alkoxide Ancillary Ligand; Participation of the Ligand in an Unusual Activation of a (Trimethylsilyl)methyl Group[†]

Esther E. C. G. Gielens, Johan Y. Tiesnitsch, Bart Hessen,* and Jan H. Teuben

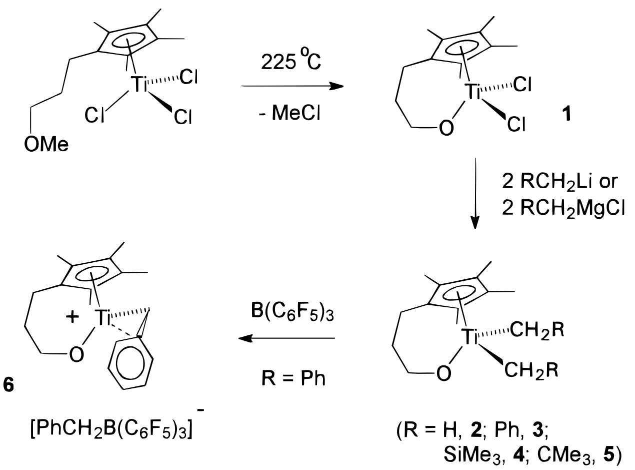
Center for Catalytic Olefin Polymerization, Department of Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received October 6, 1997

Summary: The titanium complexes [η^5:η^1-$C_5Me_4(CH_2)_3O$]-TiR_2 (R = Cl, Me, CH_2Ph, CH_2CMe_3, CH_2SiMe_3), with a linked Cp−alkoxide ancillary ligand, have been prepared in good yield. Cationic [$C_5Me_4(CH_2)_3O$]Ti(η^2-CH_2-Ph)$^+$ catalyzes the polymerization of propene to atactic polypropene. $B(C_6F_5)_3$ reacts with [$C_5Me_4(CH_2)_3O$]Ti(CH_2-$SiMe_3$)$_2$ by Me abstraction from one of the CH_2SiMe_3 groups accompanied by an attack of the ligand alkoxide functionality on the Si atom of this group.

There is considerable interest in early-transition-metal organometallic species with η^5:η^1-ancillary ligands that consist of a Cp group covalently linked to another anionic moiety. Usually this anionic moiety is an alkyl/aryl−amido group, and these so-called "constrained geometry" complexes (of the group 4 metals) have been highly successful as catalysts for the copolymerization of ethene with α-olefins,[1] especially using the C_5Me_4-$SiMe_2N$*t*-Bu ligand.[2,3] These ligands are considered to be inert ancillary ligands, but they have more reactive possibilities than, e.g., the *ansa*-metallocene framework. For example, Herrmann et al. reported photochemical cleavage of the Si−N bond in η^5:η^1-$C_5H_4SiMe_2NPh$ complexes of Nb and Ta.[4] Here, we report the synthesis and reactivity of neutral and cationic organotitanium complexes with a linked Cp−alkoxide ancillary ligand. In this system we observed that the alkoxide functionality of the Cp−alkoxide ligand participates in an unexpected Lewis-acid-induced fragmentation of a (trimethylsilyl)methyl group bound to titanium.

Scheme 1



Reaction of the cyclopentadienyl−alkoxide titanium dichloride complex [η^5:η^1-$C_5Me_4(CH_2)_3O$]$TiCl_2$ (**1**)[5,6] with the appropriate alkyllithium or Grignard reagents produces the corresponding bis(hydrocarbyl) derivatives [η^5:η^1-$C_5Me_4(CH_2)_3O$]TiR_2 (R = Me, **2**; CH_2Ph, **3**; CH_2-$SiMe_3$, **4**; CH_2CMe_3, **5**) that are readily obtained as crystalline solids in 60−80% yield (Scheme 1). These compounds show the expected NMR spectroscopic features for C_s-symmetric dialkyls, such as diastereotopic alkyl methylene protons for **3**−**5**.[7] For the benzyl complex **3**, the downfield shift of the benzyl *ipso* carbon (δ 149.60) and the $^1J_{CH}$ of 121.3 Hz for the methylene group is normal for an η^1-benzyl group attached to an electropositive metal center.[8]

The dibenzyl complex **3** reacts cleanly with the Lewis-acidic borane $B(C_6F_5)_3$ in bromobenzene solvent to give

---

[†] This contribution is dedicated to Prof. P. Royo on the occasion of his 60th birthday.

* Author to whom correspondence should be addressed. E-mail: hessen@chem.rug.nl.

[1] (a) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Eur. Pat. Appl. EP 416815, 1991. (b) Canich, J. M. Eur. Pat. Appl. EP 420436, 1991. Canich, J. M. U.S. Pat. Appl. 5026798, 1991. Canich, J. M.; Hlatky, G. G.; Turner, H. W. PCT Appl. WO92-00333, 1992.

[2] (a) Shapiro, P. J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, *2*, 74.

[3] Other recent papers dealing with Cp−amide titanium alkyl species: (a) Okuda, J.; Eberle, T.; Spaniol, T. P. *Chem. Ber./Recl.* **1997**, *130*, 209. (b) Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649. (c) Sinnema, P.-J.; van der Veen, L.; Spek, A. L.; Veldman, N.; Teuben, J. H. *Organometallics* **1997**, *16*, 4245.

[4] Herrmann, W. A.; Baratta, W. *J. Organomet. Chem.* **1996**, *506*, 357.

[5] Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 59.

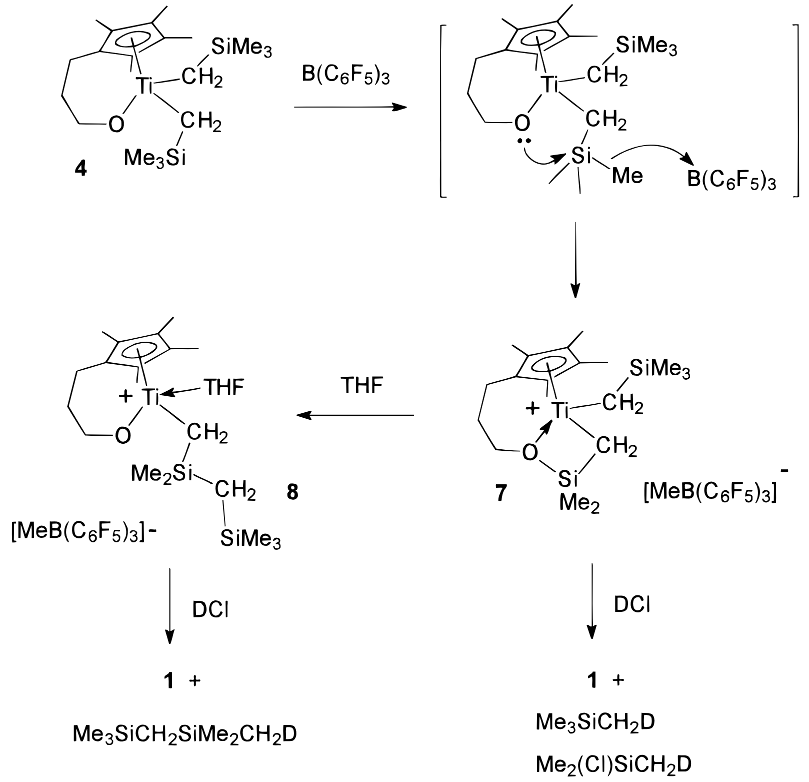
[6] An improved preparation of **1** over that in ref 5 involves the elimination of MeCl from [$C_5Me_4(CH_2)_3OMe$]$TiCl_3$ under thermolysis conditions. A solution of [$C_5Me_4(CH_2)_3OMe$]$TiCl_3$ (3.00 g, 8.63 mmol)[5] in 60 mL of toluene was heated to 225 °C for 16 h in a 250 mL stainless steel autoclave, during which the pressure increased to 15 bar. After the autoclave was cooled to room temperature, it was vented and the solvent removed in vacuo. The residual solid was sublimed at 112 °C and 0.005 mmHg. After the solid was rinsed with cold pentane and dried, 2.19 g (7.37 mmol, 86%) of orange crystalline **1** was obtained, with satisfactory elemental analysis.

[7] Selected NMR data (C_6D_5Br, 25 °C). ^{1}H NMR: **2** δ 0.27 (s, $TiCH_3$); **3** δ 2.22, 1.92 (d, $^2J_{HH}$ = 10.3 Hz, $TiCH_2$); **4** δ 0.81, −0.06 (d, $^2J_{HH}$ = 11.7 Hz, $TiCH_2$); **5** δ 1.36, 0.29 (d, $^2J_{HH}$ = 12.2 Hz, $TiCH_2$). ^{13}C NMR: **2** δ 47.63 (q, J_{CH} = 112.0 Hz, $TiCH_3$); **3** δ 78.35 (t, J_{CH} = 121.2 Hz, $TiCH_2$), 149.60 (s, Ph *ipso* C); **4** 63.74 (dd, J_{CH} = 104.5, 113.8 Hz, $TiCH_2$); **5** 90.05 (t, J_{CH} = 111.9 Hz, $TiCH_2$).

[8] For some recent examples of η^1- and η^2-benzyl groups, see: (a) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672. (b) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235 and references therein.

S0276-7333(97)00867-4 CCC: $15.00

Scheme 2



a deep red solution of the ionic complex $\{[\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)_3O]Ti(\eta^2\text{-}CH_2Ph)\}[PhCH_2B(C_6F_5)_3]$ (**6**, Scheme 1).[9] Various NMR spectroscopic features of the anion (^{19}F NMR $\Delta\delta(p-m) = 2.77$ ppm; ^{13}C NMR BCH_2C_{ipso} δ 148.47 ppm) show that it is not coordinated to the metal center.[10] The bonding of the benzyl ligand in **6** is fluxional. At 50 °C, ^{1}H NMR shows a symmetrically averaged spectrum, but at −35 °C, an asymmetric structure is evident. The strong upfield shift of the benzyl *o*-H nucleus and the large $^1J_{CH}$ and small $^2J_{HH}$ coupling constants for the benzylic methylene group are indicative of a significant amount of η^2-character in the bonding of this fragment.[8] In C_6D_5Br solution, **6** is stable at ambient temperature for days. Complex **6** is active in the catalytic polymerization of olefins and polymerizes propene (4 bar, ambient temperature, benzene solvent, 18 min run time) with a productivity of 263 kg of PP (mol of Ti)$^{-1}$ h^{-1}. The polypropene formed is atactic with a noticeable amount of 2,1-misinsertions,[11] $M_w = 41\,000$, and $M_n = 19\,600$ ($M_w/M_n = 2.1$, indicative of a single active species).

The bis(neopentyl) complex **5** does not react with $B(C_6F_5)_3$ in bromobenzene solvent at ambient temperature. This is likely to be due to the steric bulk of the neopentyl groups that prevents attack of the borane on the nucleophilic neopentyl methylene carbons. In contrast, the bis(trimethylsilylmethyl) complex **4** reacts readily with $B(C_6F_5)_3$ in bromobenzene, but the product is not a simple $[\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)_3O]Ti(alkyl)$ cation. Instead, in a clean reaction an ionic complex is produced, which we formulate as $\{[\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4(CH_2)_3\text{-}OSiMe_2CH_2]Ti(CH_2SiMe_3)\}[MeB(C_6F_5)_3]$ (**7**, Scheme 2). In the formation of this complex, one methyl group has been removed from one of the (trimethylsilyl)methyl groups and the ligand alkoxide oxygen is now bound to both Ti and Si. One could consider this as a silyl ether moiety attached to the Cp ligand via the $(CH_2)_3$ bridge and coordinated to the electrophilic Ti center. The compound could not be crystallized, and the identification of **7** was performed through ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR. The NMR characteristics[12] of the four-membered Ti−CH$_2$−Si−O ring in **7** show strong resemblance with those of related M−CH$_2$−Si−N rings obtained by cyclometalation of trimethylsilyl amide ligands.[13] The metallacycle methylene group in **7** has characteristically large $^2J_{HH}$ (14.2 Hz) and $^1J_{CH}$ (136.2, 124.9 Hz) coupling constants, and in the ^{13}C NMR spectrum, its chemical shift of δ 80.58 ppm is considerably upfield from that

---

[9] **6**. Selected NMR data. ^{1}H NMR (500 MHz, C_6D_5Br, −35 °C): δ 2.43, 2.90 (d, $^2J_{HH} = 5.4$ Hz, $TiCH_2$), 5.65 (d, $^3J_{HH} = 6.4$ Hz, $TiCH_2Ph$ *o*-H, 1H, other *o*-H obscured around δ 6.9 ppm). ^{13}C NMR (126 MHz, C_6D_5Br, −35 °C): δ 76.14 (t, $J = 151.1$ Hz, $TiCH_2$). An upfield-shifted MCH_2Ph *ipso*-C resonance is also indicative of an η^2-benzyl group, but for **6** this resonance was not unambiguously assigned.

[10] For representative examples of coordinated and noncoordinated $PhCH_2B(C_6F_5)_3$ anion, see: Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473 and ref 13b.

[11] (a) Cheng, H. N.; Ewen, J. A. *Makromol. Chem.* **1989**, *190*, 1931. (b) McKnight, A. L.; Masood, Md. A.; Waymouth, R. M.; Straus, D. A. *Organometallics* **1997**, *16*, 2879.

[12] **7**. ^{1}H NMR (500 MHz, C_6D_5Br, −20 °C): δ 3.69, 3.35 (m, OCH_2), 2.84, 2.20 (d, $J = 11.2$ Hz, $TiCH_2SiMe_3$), 2.05, 1.76 (d, $J = 14.2$ Hz, $TiCH_2SiMe_2O$), 2.11, 1.74, 1.69, 1.60 (s, CpMe), 1.96, 1.7 (m, $CpCH_2$), 1.56, 0.81 (m, bridge CH_2), 1.14 (br, BMe), 0.35, 0.14 (s, $OSiMe_2$), −0.08 (s, $SiMe_3$). ^{13}C NMR (126 MHz, C_6D_5Br, −20 °C): δ 137.22, 135.71, 132.76, 130.35, 123.93 (s, CpC), 110.22 (dd, $J = 106.3$, 111.9 Hz, $TiCH_2SiMe_3$), 80.58 (dd, $J = 124.9$, 136.2 Hz, $TiCH_2SiMe_2O$), 70.06 (t, $J = 148.3$ Hz, OCH_2), 30.01 (t, $J = 128.7$ Hz, bridge CH_2), 21.85 (t, $J = 130.6$ Hz, $CpCH_2$), 13.26, 12.95 (2×), 12.89 (q, $J = 128{-}129$ Hz, CpMe), 11.08 (br, BMe), 1.79 (q, $J = 118.5$ Hz, $SiMe_3$), −0.06 (q, $J = 121.2$ Hz, Si*Me*Me), −4.03 (q, $J = 125.0$ Hz, SiMe*Me*) (C_6F_5 resonances omitted). ^{19}F NMR (282 MHz, C_6D_5Br, 25 °C): δ −133.56 (*o*-F), −165.75 (*p*-F), −168.28 (*m*-F), $\Delta\delta(m-p) = 2.53$ ppm. For ^{29}Si NMR see ref 14.

[13] (a) Horton, A. D.; de With, J. *J. Chem. Soc., Chem. Commun.* **1996**, 1375. (b) Bennett, C. R.; Bradley, D. C. *J. Chem. Soc., Chem. Commun.* **1974**, 29. (c) Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, *2*, 16.

of the remaining (trimethylsilyl)methyl methylene group (δ 110.22 ppm, dd, $^1J_{CH} = 106.3$, 111.9 Hz). ^{29}Si NMR[14] shows a considerable downfield shift of one of the two Si atoms to δ 9.96 ppm. The NMR data of the anion are consistent with those of a noncoordinating MeB(C_6F_5)$_3$ anion.[15]

The Si atom in the Ti−O−Si−C moiety of **7** is prone to nucleophilic attack, in which the O atom, which in **7** is shared between Ti and Si, is restored to the Ti center. For example, when a solution of **7** is reacted with gaseous anhydrous HCl, Me_3SiCl and Me_4Si are formed in equimolar amounts and **1** is regenerated (Scheme 2).[16] In this case, nucleophilic attack by the chloride anion on the Si atom in the cationic complex **7** occurs. In contrast, reaction of **7** with the Lewis base THF takes place on the most Lewis-acidic center (Ti), which induces an intramolecular nucleophilic attack of the Me_3SiCH_2 group on the Si atom to yield {[η^5:η^1:η^1-$C_5Me_4(CH_2)_3O$]-$Ti(CH_2SiMe_2CH_2SiMe_3)$(THF)}[MeB(C_6F_5)$_3$] (**8**, Scheme 2). This compound was identified by ^{1}H, ^{13}C, and ^{29}Si NMR[17] and by its reaction with DCl, which yields **1** and $Me_3SiCH_2SiMe_2(CH_2D)$ (NMR, GC/MS).

A possible route of formation for **7** could involve nucleophilic attack of the alkoxide functionality on the Si atom, with the borane acting as an acceptor for the methyl anion. This would be similar to the alkoxide-induced cleavage of Si−C bonds observed for alkylsilanes (e.g., with *t*-BuOK/DMSO[18] or NaOH/MeOH[19]). An alternative pathway involving β-Me elimination and formation of a silaethene intermediate, as suggested for the thermolysis of *cis*-$(R_3P)_2Pt(CH_2SiMe_3)_2$ yielding $(R_3P)_2Pt(Me)(CH_2SiMe_2CH_2SiMe_3)$,[20] would probably have too high an activation barrier, even if the borane would initially interact with the alkoxide moiety (certainly considering that the neopentyl derivative **5** is unreactive under the same conditions). Experiments on NMR-tube scale show that **7** is still able to effect the catalytic polymerization of olefins, and the reactivity of this species is currently the subject of further study.

In conclusion, we have shown that a stable cationic $[(Cp{-}alkoxide)Ti(CH_2Ph)]^+$ species can be prepared and that this species is active in catalytic olefin polymerization. However, it is clear that the Cp−alkoxide ancillary ligand is not always innocent and that the alkoxide moiety can engage in nucleophilic reactivity. Presently, we are investigating the extent in which this functionality can be involved in reactivity with other Lewis-acidic reagents.

Supporting Information Available: Experimental procedures and characterization data for the reported compounds (8 pages). Ordering information is given on any current masthead page.

OM970867E

---

(14) ^{29}Si-DEPT NMR data (99.3 MHz, C_6D_5Br, −20 °C): **4** δ 0.18; **7** δ 9.96 ($OSiMe_2$) and 2.50 ($TiCH_2SiMe_3$); **8** δ 3.24 ($TiCH_2SiMe_2C$) and 0.25 (CH_2SiMe_3). For comparison, $SiMe_4$ δ 0.00; $Me_3SiOSiMe_3$ δ 6.7.

(15) For data on coordinating and noncoordinating MeB(C_6F_5)$_3$ anions, see, e.g.: (a) Horton, A. D. *Organometallics* **1996**, *15*, 2675. (b) Beck, S.; Prosenc, M.-H.; Brintzinger, H.-H.; Goretzki, R.; Herfert, N.; Fink, G. *J. Mol. Catal. A* **1996**, *111*, 67. (c) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(16) Use of DCl instead of HCl yields $SiMe_4$-d_1 and $SiMe_3Cl$-d_1, consistent with bonding of both fragments to Ti.

(17) **8**. Selected NMR data. ^{1}H NMR (500 MHz, C_6D_5Br, −20 °C): δ 1.96, −0.10 (d, $J = 13.2$ Hz, $TiCH_2Si$), 0.08 (s, $SiMe_3$), 0.01, −0.09 (s, $SiMe_2$), −0.36, −0.44 (d, $J = 13.2$ Hz, $SiCH_2Si$). ^{13}C NMR (126 MHz, C_6D_5Br, −20 °C): δ 87.60 (dd, $J = 105.8$, 113.3 Hz, $TiCH_2$), 5.73 (t, $J = 110.1$ Hz, $SiCH_2Si$), 2.32 (q, $J = 118.8$ Hz, $SiMe_2$), 2.05 (q, $J = 118.8$ Hz, $SiMe_3$), 1.34 (q, $J = 118.1$ Hz, $SiMe_2$). For ^{29}Si NMR data, see ref 14.

(18) Price, C. C.; Sowa, J. R. *J. Org. Chem.* **1967**, *32*, 4126.

(19) Bott, R. W.; Eaborn, C.; Swaddle, T. W. *J. Chem. Soc.* **1963**, 2342.

(20) Ankianiec, B. C.; Christou, V.; Hardy, D. T.; Thomson, S. K.; Young, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9963.