Regioselective 1-Hexene Oligomerization Using Cationic Bis(phenolato) Group 4 Metal Catalysts: Switch from 1,2- to 2,1-Insertion**

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In memory of Ernst Otto Fischer

Catalytic oligomerization of α-olefins is an important process in the petrochemical industry.[1] Current focus is on the selective ethylene oligomerization to produce linear α-olefins.[1a,2,3] Oligomerization of α-olefins would lead to useful processes,[1b,c] provided that activity and selectivity can be controlled by the rational choice of metal and ligand sphere: even dimerization of an α-olefin by a metal hydride catalyst would give rise to ten constitutional isomers, if 1,2-insertion, 2,1-insertion, and β-H elimination are combined. Regioselectivity can be controlled, for example, cobalt catalysts were recently reported to selectively form linear dodecenes by a sequence of 1,2- and 2,1-insertion followed by β-H elimination of 1-hexene ("head-to-head" dimerization).[4] Early-transition-metal metallocene catalysts commonly incorporate (enchain) α-olefins into the growing chain with 1,2-regioselectivity,[5] whereas propagation with 2,1-regioselectivity[6] is mostly limited to non-metallocene systems.[7] Herein we report that cationic Group 4 metal catalysts containing a bis(phenolato) ligand[8] efficiently catalyze 1-hexene oligomerization and that the regioselectivity of insertion is switched upon changing the metal center from titanium to zirconium or hafnium (Scheme 1).

Catalyst precursors **2–4** were synthesized according to reported procedures.[8a,c] The synthesis of the dimethyl complex **1a** by methylation of [Ti(edtbp)Cl₂] (edtbpH₂ = (HOC₆H₂-*t*Bu-4,6)₂(SCH₂CH₂S)) failed, but reaction of [TiMe₂Cl₂][9] with Li₂(edtbp) cleanly gave **1a** as thermally robust, brown crystals in 73% yield. Its molecular structure was determined both in the solid state and in solution.[8a,c,11]

Upon treatment of complex **1a** with B(C₆F₅)₃ in toluene, CD₂Cl₂ or C₆D₅Br, a thermally labile cationic methyl complex formed. However, in the presence of a Lewis base L, such as THF or DMPE (DMPE = Me₂PCH₂CH₂PMe₂), the cation [Ti(edtbp)Me(L)]⁺ was formed as part of the ion pair [Ti(edtbp)Me(L)]⁺[MeB(C₆F₅)₃]⁻ (**5**-L) and found to be
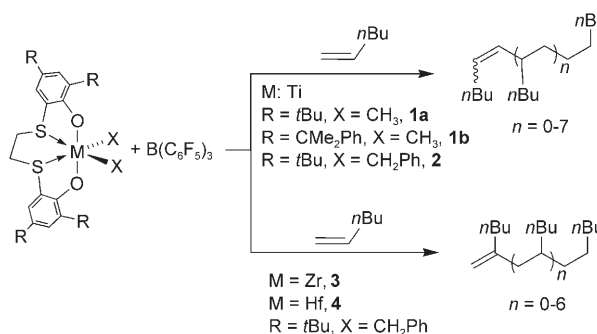
Scheme 1. 1-Hexene oligomerization using complexes **1–4** activated by B(C₆F₅)₃.

thermally stable up to 60°C for at least 2 days. Complex **5**-L was fully characterized by ¹H, ¹³C, ¹¹B, and ¹⁹F NMR spectroscopy. Results of a single-crystal X-ray crystallography (Figure 1) of the dmpe complex features ion pairs of the
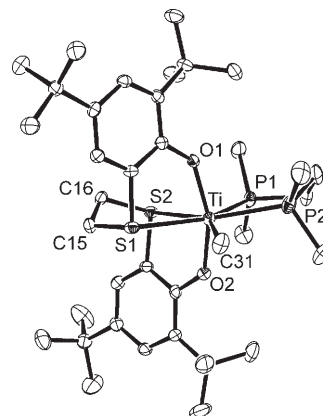

Figure 1. Cation of **5**-DMPE. (Hydrogen atoms and the anion omitted for clarity.)[11]

titanium cation and the borate anion [MeB(C₆F₅)₃]⁻.[11] The sterically rather open titanium center is coordinated by two *trans*-oxygen and two *cis*-sulfur donors of the helical edtbp framework,[8a,c] the two phosphorus atoms of the dmpe, and the methyl group, resulting in a pentagonal bipyramidal geometry.

Representative results of catalytic 1-hexene oligomerization by complexes **1–4** activated by one equivalent of B(C₆F₅)₃ are given in Table 1. Oligomerization of neat 1-hexene using

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Table 1: Oligomerization of 1-hexene using complexes **1–4** activated by B(C₆F₅)₃.[a]

Entry	Precat.	Yield [%]	TOF[b]	M_n[c]	M_w/M_n[c]	[vinylene]/[vinylidene][d]
1	**1a**	97	20700	352	1.30	92:8
2	**1b**	97	20700	256	1.22	99:1
3	**2**	94	19960	352	1.33	93:7
4	**3**	22	196	224	1.23	5:95
5[e]	**3**	<1	–	–	–	–
6	**4**	3.4	3.8	338	1.38	7:93

[a] Conditions: [precat.] = [B(C₆F₅)₃] = 0.02 mmol; 1-hexene (3.0 g, 36 mmol); reaction temperature 20°C; reaction time: 5 min for entries 1–3, 120 min for entries 4 and 5, and 960 min for entry 6; method: a solution of complex in 1-hexene (1.5 g) was added to a solution of B(C₆F₅)₃ in 1-hexene (1.5 g) followed by quenching with HCl/MeOH. [b] (mol of 1-hexene converted)(mol of M)$^{-1}$h^{-1}. [c] Determined by GPC in THF versus polystyrene standards. [d] Ratio of the signals intensity (R¹)CH=CH(R²):(R³)(R⁴)C=CH₂ in oligomer, determined by ¹H NMR spectroscopy in CDCl₃. [e] Reaction temperature −40°C.

1a/B(C₆F₅)₃ at room temperature was complete in less than 5 min to yield oligo(1-hexene)s ($M_n = 352$, $M_w/M_n = 1.30$) with turnover frequency TOF > 20700 h^{-1} (Table 1, entry 1). The zirconium and hafnium complexes **3** and **4** were found to be less active by two and four orders of magnitude, respectively, than the titanium homologue **1a** (Table 1, entries 4 and 6). Preliminary kinetic analysis for the oligomerization catalyzed by complex **1a**/B(C₆F₅)₃ in toluene at −60°C indicated zero-order dependence on the monomer concentration. The oligomer distributions deviate from the Schulz–Flory statistic. The product maximum is for trimer ($n = 1$ in Scheme 1) followed by dimer and tetramer (see Supporting Information for further details).

Remarkably, the nature of the end groups in the resulting oligomers is highly dependent on the central metal. In the oligomers produced by the B(C₆F₅)₃-activated titanium complexes **1** and **2**, vinylene resonances are observed at $\delta = 5.38$ ppm[5d,10] in the ¹H NMR spectrum, indicating the presence of internal olefins *E*- and *Z*-R¹CH=CHR² (Figure 2a). This result suggests that the oligo(1-hexene)s were formed by β-H-elimination from a 2,1-enchained titanium alkyl complex (92–99%). Complex **1b** with the cumyl-substituted ligand gave oligomers with up to 99% vinylene end groups. In contrast, zirconium and hafnium catalysts based on **3** and **4** selectively produce oligo(1-hexene)s with vinylidene end groups R³R⁴C=CH₂, as indicated by the resonances at $\delta = 4.68$ ppm in the ¹H NMR spectra of sample produced by **3**/B(C₆F₅)₃ (Figure 2b).

At lower temperatures, the titanium catalyst gave product mixtures that showed both vinylene and vinylidene end groups (ca. 50:50 at −80°C, Table 2). The zirconium catalysts did not exhibit any temperature dependence for the regio-isomer distribution in the range of −80 to +50°C. Under the same conditions, the tendency for 2,1-insertion increased with the steric bulk of the ligand sphere (**1b** versus **1a**) as well as with that of the growing chain.

The use of [1-¹³C] labeled 1-hexene allowed some insight into the structure of the oligomers.[5d] Olefins produced by B(C₆F₅)₃-activated titanium complex **1a** are mainly linear (in
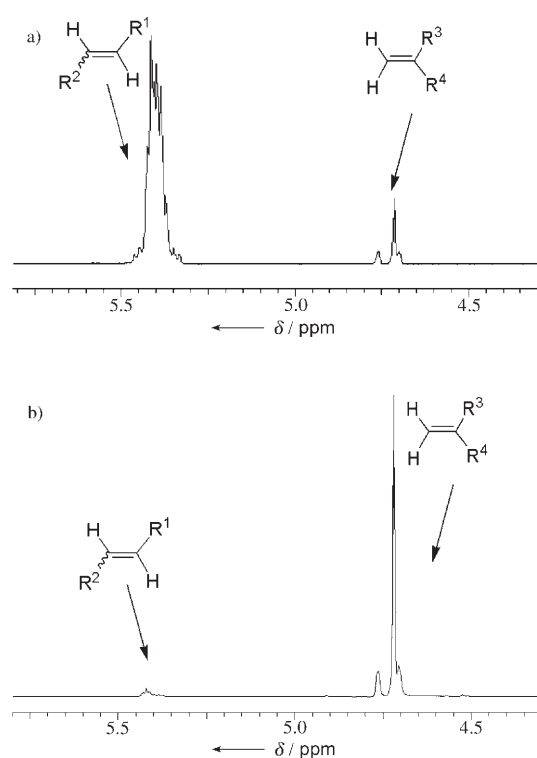

Figure 2. ¹H NMR spectra of the end groups for oligo(1-hexene)s produced by a) the titanium catalyst **1a**/B(C₆F₅)₃ and b) the zirconium catalyst **3**/B(C₆F₅)₃, both at 20°C.

Table 2: Oligomerization of 1-hexene at different temperatures using complex **1a** activated by B(C₆F₅)₃.[a]

| Entry	T [°C]	Yield [%]	M_n[b]	M_w/M_n[b]	[vinylene]/[vinylidene][c]
1	+50	50	360	1.33	90:10
2	+20	>99	354	1.34	90:10
3	±0	>99	358	1.33	88:12
4	−20	>99	376	1.40	82:18
5	−40	>99	370	1.43	79:21
6	−60	>99	348	1.41	70:30
7	−80	>99	317	1.46	52:48

[a] Conditions: [1a] = [B(C₆F₅)₃] = 0.02 mmol; 1-hexene (1.01 g, 12 mmol); toluene (10 mL); reaction time: 5 min; method: a solution of complex **1a** in toluene (8 mL) and 1-hexene (1.01 g) was added to a solution of B(C₆F₅)₃ in toluene (2 mL) followed by quenching with HCl/MeOH. [b] Determined by GPC in THF versus polystyrene standards. [c] Ratio of the signals intensity (R¹)CH=CH(R²):(R³)(R⁴)C=CH₂ in oligomer, determined by ¹H NMR spectroscopy in CDCl₃.

the case of dimers) with the label mostly detected in the positions α and β to the vinylene group, and to lesser extent in the double bond and in terminal methyl groups (Scheme 2). On the other hand, the product mixture obtained using the zirconium catalyst showed the label mostly in the 1-(terminal) and 3-position of the head-to-tail product.

Although we cannot conclusively exclude a metallacycle[1f,2] as the active species for the oligomerization, we assume that a cationic titanium alkyl cation accounts for the switch in regioselectivity (Scheme 3). Following initial 1,2-
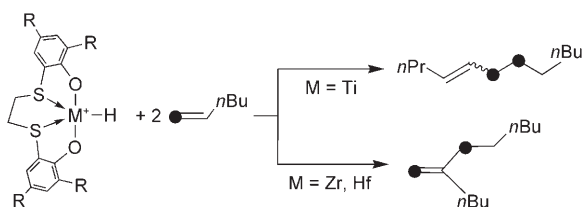
Scheme 2. Major components of 1-hexene dimerization products using labeled (●) [1-^{13}C]-1-hexene.
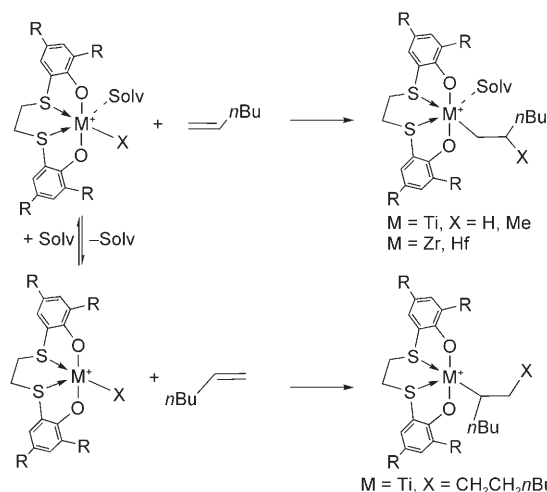
Scheme 3. Plausible explanation for the origin of the regioselectivity switch based on solvent dissociation.

insertion into the metal–hydride bond, 1-hexene is enchained with 2,1-regioselectivity for titanium at higher temperatures. This process is proposed to be the result of a steric effect: with a larger growing chain X and bulkier substituents R, dissociation of the solvent becomes important for titanium, particularly at higher temperature. At low temperature and for zirconium and hafnium which have stronger metal–solvent dissociation energies, thermodynamically preferred 1,2-insertion predominates. β-Hydride elimination in each case leads to the release of oligo(1-hexene)s. Given the virtually identical coordination sphere (**2**[8a] and **4**[8c] are isotypical) the difference is assumed to stem from the position/rate of the solvent-dissociation equilibrium.

In an NMR-tube experiment, 1-hexene was found to insert into the Ti–^{13}CH$_3$ bond of B(C$_6$F$_5$)$_3$-activated [Ti-(edtbp)(^{13}CH$_3$)$_2$] in 1,2-mode (intense signal at $\delta = 22.17$ ppm in the ^{13}C NMR spectrum in C$_6$D$_6$). In addition, for the oligomer fractions produced by **1a**/B(C$_6$F$_5$)$_3$, the amount of vinylene versus vinylidene products increased with the degree of oligomerization (82% for dimer, 95% for trimer, and 97% for tetramer). Finally, decreasing the steric strain within the ligand sphere by introducing a C$_1$- rather than a C$_2$-linker results in deterioration of the secondary regioselectivity for the titanium catalyst.[12] These data indicate a steric effect of the propagating chain on the degree of 2,1-selectivity during the oligomerization process. Furthermore, **1a**/B(C$_6$F$_5$)$_3$ does not react with 2-pentene, indicating the absence of isomerization/chain walking.

In conclusion, we have shown that the regioselectivity during 1-hexene oligomerization by a Group 4 metal catalyst with a bis(phenolato) [OSSO]-type ligand switches when the metal center is changed from titanium to its heavier homologues. Studies on the detailed mechanism on the oligomerization by kinetic analysis as well as the extension of this system to other monomers are underway.

[1] a) D. Vogt in *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1 (Eds.: B. Cornils, W. Herrmann), VCH, New York, **1996**, pp. 245–257; b) Y. Chauvin, H. Olivier in *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1 (Eds.: B. Cornils, W. Herrmann), VCH, New York, **1996**, pp. 258–268; c) G. W. Parshall, S. D. Ittel, *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, Wiley, New York, **1992**; d) J. Skupińska, *Chem. Rev.* **1991**, *91*, 613–648; e) K. Weissermel, H.-J. Arpe in *Industrial Organic Chemistry*, 4th ed., Wiley-VCH, New York, **2003**; f) S. J. McLain, J. Sancho, R. R. Schrock, *J. Am. Chem. Soc.* **1979**, *101*, 5451–5453.

[2] For papers on ethylene trimerization, see: a) J. T. Dixon, M. J. Green, F. M. Hess, D. H. Morgan, *J. Organomet. Chem.* **2004**, *689*, 3641–3668; b) P. J. W. Deckers, B. Hessen, J. H. Teuben, *Angew. Chem.* **2001**, *113*, 2584–2587; *Angew. Chem. Int. Ed.* **2001**, *40*, 2516–2519; c) P. J. W. Deckers, B. Hessen, J. H. Teuben, *Organometallics* **2002**, *21*, 5122–5135; d) J. Huang, T. Wu, Y. Qian, *Chem. Commun.* **2003**, 2816–2817; e) D. F. Wass, *Dalton Trans.* **2007**, 816–819.

[3] A. Bollmann, K. Blann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. S. McGuinness, D. H. Morgan, A. Neveling, S. Otto, M. Overett, A. M. Z. Slawin, P. Wasserscheid, S. Kuhlmann, *J. Am. Chem. Soc.* **2004**, *126*, 14712–14713.

[4] a) B. L. Small, *Organometallics* **2003**, *22*, 3178–3183; b) B. L. Small, R. Schmidt, *Chem. Eur. J.* **2004**, *10*, 1014–1020; c) K. P. Tellmann, V. C. Gibson, A. J. P. White, D. J. Williams, *Organometallics* **2005**, *24*, 280–286; d) R. D. Broene, M. Brookhart, W. M. Lamanna, A. F. Volpe, Jr., *J. Am. Chem. Soc.* **2005**, *127*, 17194–17195.

[5] a) J. J. W. Eshuis, Y. Y. Tan, A. Meetsma, J. H. Teuben, J. Renkema, G. G. Evens, *Organometallics* **1992**, *11*, 362–369; b) W. P. Kretschmer, S. I. Troyanov, A. Meetsma, B. Hessen, J. H. Teuben, *Organometallics* **1998**, *17*, 284–286; c) Y. Suzuki, T. Yasumoto, K. Mashima, J. Okuda, *J. Am. Chem. Soc.* **2006**,

Communications

128, 13017–13025; d) Z. Liu, E. Somsook, C. B. White, K. A. Rosaaen, C. R. Landis, *J. Am. Chem. Soc.* **2001**, *123*, 11193–11207.

[6] a) M. Lamberti, D. Pappalardo, A. Zambelli, C. Pellecchia, *Macromolecules* **2002**, *35*, 658–663; b) P. D. Hustad, J. Tian, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 3614–3621; c) M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, T. Nakano, T. Fujita, *J. Am. Chem. Soc.* **2003**, *125*, 4293–4305.

[7] a) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; b) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315.

[8] This catalyst polymerizes styrene isospecifically: a) C. Capacchione, A. Proto, H. Ebeling, R. Mülhaupt, K. Möller, T. P. Spaniol, J. Okuda, *J. Am. Chem. Soc.* **2003**, *125*, 4964–4965; b) C. Capacchione, F. De Carlo, C. Zannoni, J. Okuda, A. Proto, *Macromolecules* **2004**, *37*, 8918–8922; c) K. Beckerle, R. Manivannan, T. P. Spaniol, J. Okuda, *Organometallics* **2006**, *25*, 3019–3026; d) K. Beckerle, R. Manivannan, B. Lian, G.-J. Meppelder, G. Raabe, T. P. Spaniol, H. Ebeling, F. Pelascini, R. Mülhaupt, J. Okuda, *Angew. Chem.* **2007**, *119*, 4874–4877; *Angew. Chem. Int. Ed.* **2007**, *46*, 4790–4793.

[9] H. Makio, T. Oshiki, K. Takai, T. Fujita, *Chem. Lett.* **2005**, *34*, 1382–1383.

[10] R. Baumann, R. Stumpf, W. M. Davis, L.-C. Liang, R. R. Schrock, *J. Am. Chem. Soc.* **1999**, *121*, 7822–7836.

[11] X-ray crystal structural data for complexes **1a** and **5** (see Supporting Information): CCDC-654167 (**1a**) and CCDC-654168 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

[12] [Ti(mdtbp)Me$_2$] (mdtbpH$_2$ = (HOC$_6$H$_2$-tBu$_2$-4,6)$_2$(SCH$_2$S)) was synthesized in a fashion analogous to that for the preparation of **1a**. Upon activation with B(C$_6$F$_5$)$_3$ at 20°C, 1-hexene is oligomerized into a mixture with a [vinylene]/[vinylidene] ratio of 56:44.