Chromium(III) Complexes of Sterically Crowded Bidentante {ON^R} and Tridentate {ONN^R} Naphthoxy-Imine Ligands: Syntheses, Structures, and Use in Ethylene Oligomerization‡

Evgueni Kirillov,*,† Thierry Roisnel,† Abbas Razavi,# and Jean-François Carpentier*,†

Catalysis and Organometallics, UMR 6226 Sciences Chimiques de Rennes, CNRS-University of Rennes 1, 35042 Rennes Cedex, France, and Total Petrochemicals Research, Zone Industrielle C, 7181 Feluy, Belgium

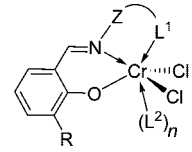
Received December 18, 2008

New bidentate {ON^R}H (R = C_6F_5, **2c**) and tridentate {ONN^R}H (R = quinolyl, **2a**; 2-pyridylmethyl, **2b**} naphthol-imine and phenol-imine (R = quinolyl, **2d**) pro-ligands sterically encumbered by an *ortho*-triphenylsilyl moiety have been prepared and converted to the corresponding naphthoxy-imino (**3a**−**c**) and phenoxy-imino (**3d**) $CrBr_2${ON(N)^R}(CH_3CN) complexes, respectively, via reaction with (*p*-tolyl)$CrBr_2(THF)_3$ and subsequent recrystallization from acetonitrile. The molecular structures of **2a**, **2d**, **3a**, and **3b** have been established by single-crystal X-ray diffraction studies. Upon activation with MAO, complexes **3a**, **3b**, and **3d**, despite the presence of coordinated acetonitrile in those precursors, lead to highly active catalysts for the oligomerization of ethylene (activities up to 23 730 kg mol^{-1} h^{-1} at 25−100 °C, 6 bar), yielding selectively linear α-olefins (89−96% vinyl-end; M_n = 600−1450 g mol^{-1}, M_w/M_n = 1.9−2.3).

Introduction

Discrete group 3−6 metal complexes bearing various chelating aryloxide-based ligands have demonstrated astonishing performances in the oligomerization/polymerization of ethylene and α-olefins.[1] In particular, phenoxy-imine type ligands have attracted considerable attention due to the flexibility these ligand platforms afford for tuning the stereoelectronic properties of the precatalysts and, in turn, control the catalytic performances.[2,3] Although these Schiff base ligands have been used mostly with group 4 metals, they have led also to very valuable catalyst systems when associated with chromium. Chromium holds a quite interesting position among transition metals, since effective catalysts for both ethylene polymerization and oligomerization,[4] including selective tri-[5] and tetramerization,[6] have been reported for this element. Recently, Gibson et al. identified via high-throughput screening of a 205-member Schiff base salicylaldimine ligand library, reacted *in situ* with (*p*-tolyl)$CrCl_2(THF)_3$, two new classes of highly active chromium-based systems for the oligomerization and polymerization of ethylene, respectively (Chart 1).[7] The polymerization system comprised bidentate *ortho*-substituted anthracenyl Schiff bases bearing small primary or secondary alkyl-imine substituents, while the oligomerization catalysts were based on tridentate *ortho*-triptycenyl-substituted Schiff bases with pyridylmethyl or quinolyl substituents.

Chart 1. Typical Cr(III) Phenoxy-Imine Compounds Disclosed in the Literature[7] That Are Suitable for the Oligomerization or Polymerization of Ethylene



n = 1, 2
R = *t*Bu, adamantyl, anthracenyl, triptycenyl
Z = linker or non-coordinating alkyl/aryl group
L^1 = pendant donor group (amino, pyridyl, quinolyl)
L^2 = donor molecule (THF, pyridine)

‡ Dedicated to Prof. M. N. Bochkarev on the occasion of his 70th birthday.

* Corresponding authors. Fax: (+33)(0)223-236-939. E-mail: evgueni.kirillov@univ-rennes1.fr; jean-francois.carpentier@univ-rennes1.fr.

† CNRS-University of Rennes 1.

Total Petrochemicals Research.

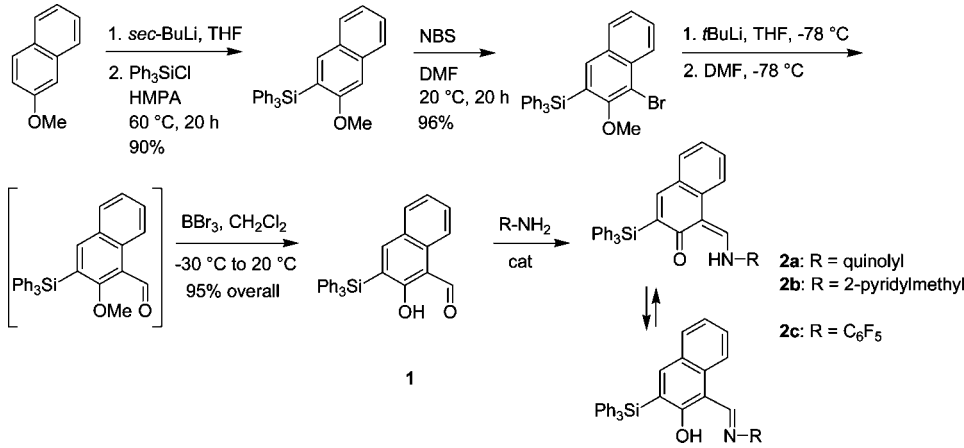
(1) For leading reviews on "post-metallocene" complexes of groups 3−6 and the lanthanides related to olefin oligo/polymerization, see: (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428. (b) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236. (c) Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H. *Chem. Rev.* **2002**, *102*, 1851. (d) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (e) Gromada, J.; Mortreux, A.; Carpentier, J.-F. *Coord. Chem. Rev.* **2004**, *248*, 397. (f) Corradini, P.; Guerra, G.; Cavallo, L. *Acc. Chem. Res.* **2004**, *37*, 231. (g) Kol, M.; Segal, S.; Groysman, S. In *Stereoselective Polymerization with Single-Site Catalysts*; CRC Press LLC: Boca Raton, FL, 2008; pp 345−361. (h) Okuda, J. *Stud. Surf. Sci. Catal.* **2007**, *172*, 11. (i) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30.

(2) (a) Matsugi, T.; Fujita, F. *Chem. Soc. Rev.* **2008**, *37*, 1264. (b) Makio, H.; Fujita, T. *Macromol. Rapid Commun.* **2007**, *28*, 698. (c) Terao, H.; Ishii, S.; Saito, J.; Matsuura, S.; Mitani, M.; Nagai, N.; Tanaka, H.; Fujita, T. *Macromolecules* **2006**, *39*, 8584. (d) Nakayama, Y.; Saito, J.; Bando, H.; Fujita, T. *Chem.−Eur. J.* **2006**, *12*, 7546. (e) Saito, J.; Suzuki, Y.; Makio, H.; Tanaka, H.; Onda, M.; Fujita, T. *Macromolecules* **2006**, *39*, 4023. (f) Mitani, M.; Nakano, T.; Fujita, T. *Chem.−Eur. J.* **2003**, *9*, 2396. (g) Mitani, M.; Furuyama, R.; Mohri, J.; Saito, J.; Ishii, S.; Terao, H.; Nakano, T.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc.* **2003**, *125*, 4293. (h) Makio, H.; Kashiwa, N.; Fujita, T. *Adv. Synth. Catal.* **2002**, *344*, 477. (i) Mitani, M.; Furuyama, R.; Mohri, J.; Saito, J.; Ishii, S.; Terao, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 7888. (j) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 3327. (k) Saito, J.; Mitani, M.; Mohri, J.; Yoshida, Y.; Matsui, S.; Ishii, S.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2918. (l) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847.

(3) (a) Mason, A. F.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 10798. (b) DeRosa, C.; Circelli, T.; Auriemma, F.; Mathers, R. T.; Coates, G. W. *Macromolecules* **2004**, *37*, 9034. (c) Mason, A. F.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 16326. (d) Reinartz, S.; Mason, A. F.; Lobkovsky, E. B.; Coates, G. W. *Organometallics* **2003**, *22*, 2542. (e) Hustad, P. D.; Tian, J.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 3614. (f) Tian, J.; Coates, G. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3626.

10.1021/om801196d CCC: $40.75
Publication on Web 03/30/2009

Scheme 1. Synthetic Route Used for the Preparation of Naphthol-Imine {ONN^R}H and {ON^R}H Pro-ligands



In this contribution, we report derivatives of these known ligands, but with a naphthol platform sterically encumbered by a bulky *ortho*-triphenylsilyl substituent. Cr(III) complexes derived from these new bi- and tridentate naphthol-imine pro-ligands have been prepared and structurally characterized. For comparative studies, a related *ortho*-$SiPh_3$-substituted *phenol*-imine pro-ligand and its chromium complex were also synthesized. The valuable performances of some of these complexes in ethylene oligomerization, yielding eventually vinyl-end-capped $C_{\sim 50}$ oligoethylenes in high selectivity, upon activation with alkylaluminum reagents, are discussed as well.

Results and Discussion

Synthesis of Pro-Ligands. The synthesis of bidentate ({ON^R}H; R = C_6F_5, **2a**) and tridentate ({ONN^R}H; R = 2-pyridylmethyl, **2b**, or quinolyl, **2c**) naphthol-imine pro-ligands was achieved starting from commercially available and inexpensive 2-methoxynaphthalene (Scheme 1). The initial four-step procedure ended up with the formation of 3-triphenylsilyl-substituted 2-hydroxy-1-naphthaldehyde (**1**) in high overall yield (82%). The latter compound can be straightforwardly condensed with aromatic or aliphatic primary amines to the corresponding naphthol-imines **2a**−**c** under standard conditions, using either HCOOH (cat.) in MeOH or PTSA (*p*-toluenesulfonic acid) (cat.) in toluene (see the Experimental Section for details). The phenol-based tridentate ligand ({ONN^R}H, R = quinolyl, **2d**) was prepared by an analogous condensation reaction (HCOOH (cat.) in MeOH) from 2-hydroxy-5-methyl-3-(triphenylsilyl)benzaldehyde[8] and 8-aminoquinoline.

The obtained products were authenticated by elemental analysis, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and an X-ray diffraction study for **2a** and **2d**. It is noteworthy that, in striking contrast with the quinolyl-based imino-phenol {ONN}H pro-ligand molecule disclosed by Gibson et al.,[7a] the most stable tautomeric form found for molecules of **2a** and **2b** is the keto-enamine one. This keto-enamine structure persists not only in the solid state, as evidenced for **2a** (*vide infra*), but also in CD_2Cl_2 solution. In fact, the room-temperature ^{13}C{^{1}H} NMR spectra of both **2a** and **2b** display a single set of signals that include resonances at δ 185.2 and 180.6 ppm, respectively, which are unambiguously assigned to C=O groups. The ^{13}C{^{1}H} NNR spectra of **2c** and **2d** at 25 °C (in CD_2Cl_2 and/or $CDCl_3$) feature a different pattern indicative of an imino-phenol structure on the NMR time scale, that is, no signal in the carbonyl region but two resonances at δ 166.7 (*ipso*-C phenol) and 164.7 ppm

(4) (a) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **2005**, *127*, 1082. (b) Theopold, K. H. *Eur. J. Inorg. Chem.* **1998**, 15. (c) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738. (d) Döhring, A.; Göhre, J.; Jolly, P. W.; Kryger, B.; Rust, J.; Verhovnik, G. P. J. *Organometallics* **2000**, *19*, 388. (e) Rogers, J. S.; Bu, X. H.; Bazan, G. C. *Organometallics* **2000**, *19*, 3948. (f) Enders, M.; Fernandez, P.; Ludwig, G.; Pritzkow, H. *Organometallics* **2001**, *20*, 5005. (g) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 1651. (h) MacAdams, L. A.; Kim, W. K.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952. (i) Gibson, V. C.; Mastroianni, S.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2000**, 1969. (j) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Duchateau, R. *Organometallics* **2007**, *26*, 3201. (k) Albahily, K.; Koç, E.; Al-Baldawi, D.; Savard, D.; Gambarotta, S.; Burchell, T. J.; Duchateau, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 1. (l) Albahily, K.; Al-Baldawi, D.; Gambarotta, S.; Koç, E.; Duchateau, R. *Organometallics* **2008**, *27*, 5943. (m) Junges, F.; Kuhn, M. C. A.; dos Santos, A. H. D. P.; Rabello, C. R. K.; Thomas, C. M.; Carpentier, J.-F.; Casagrande, O. L. *Organometallics* **2007**, *26*, 4010.

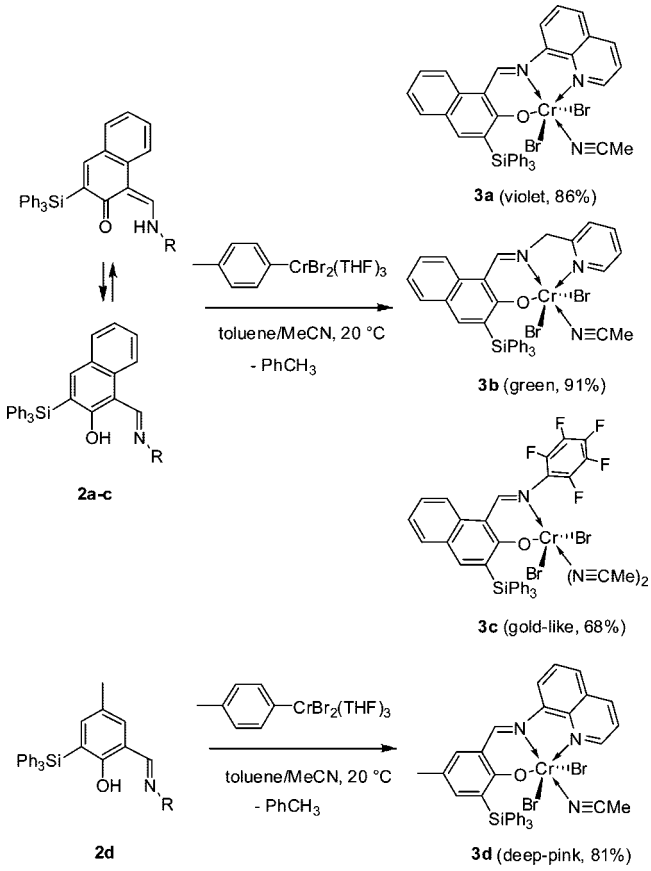
(5) (a) Reagan, W. K. (Phillips Petroleum Co.) *Eur. Pat. 0417477*, 1991. (b) Mimura, H.; Aoyama, T.; Yamamoto, T.; Oguri, M.; Koie, Y. (Tosoh Corp.) *Jap. Patent 09268133*, 1997. (c) Emrich, R.; Heinemann, O.; Jolly, P. W.; Krueger, C.; Verhovnik, G. P. J. *Organometallics* **1997**, *16*, 1511. (d) Kohn, R. D.; Haufe, M.; Kociok-Kohn, G.; Grimm, S.; Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4337. (e) Wass, D. F. (BP Chemicals Ltd) WO Patent 004119, 2002. (f) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858. (g) Yoshida, T.; Yamamoto, T.; Okada, H.; Murakita, H. (Tosoh Corp.) *U.S. Patent 0035029*, 2002. (h) Mohamed, H. A.; Bollmann, A.; Dixon, J.; Gokul, V.; Griesel, L.; Grove, J. J. C.; Hess, F.; Maumela, H.; Pepler, L. *Appl. Catal., A* **2003**, *255*, 355. (i) Grove, J. J. C.; Mohamed, H. A.; Griesel, L. (Sasol Technology Ltd) *WO Patent 03/004158*, 2002. (j) Dixon, J. T.; Wasserscheid, P.; McGuinness, D. S.; Hess, F. M.; Maumela, H.; Morgan, D. H.; Bollmann, A. (Sasol Technology Ltd) *WO Patent 03053890*, 2001. (k) McGuinness, D.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. *J. Am. Chem. Soc.* **2003**, *125*, 5272. (l) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Hu, C.; Englert, U.; Dixon, J. T.; Grove, C. *Chem Commun.* **2003**, 334. (m) Agapie, T.; Day, M. W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2006**, *25*, 2733. (n) Schofer, S. J.; Day, M. W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2006**, *25*, 2743. (o) Jabri, A.; Temple, C.; Crewdson, P.; Gambarotta, S.; Korobkov, I. V.; Duchateau, R. *J. Am. Chem. Soc.* **2006**, *128*, 9238. (p) Temple, C.; Gambarotta, S.; Korobkov, I. V.; Duchateau, R. *Organometallics* **2007**, *26*, 4598. (q) Albahily, K.; Al-Baldawi, D.; Gambarotta, S.; Duchateau, R.; Koç, E.; Burchell, T. J. *Organometallics* **2008**, *27*, 5708.

(6) (a) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712. (b) Jabri, A.; Crewdson, P.; Gambarotta, S.; Korobkov, I. V.; Duchateau, R. *Organometallics* **2006**, *25*, 715.

(7) (a) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 11037. (b) van Meurs, M.; Britovsek, G. J. P.; Gibson, V. C.; Cohen, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 9913. (c) Gibson, V. C.; O'Reilly, R. K. *U.S. Pat. Appl. 0258867*, 2006. (d) Gibson, V. C.; Mastroianni, S.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2000**, 1969.

(8) Thadani, A. N.; Huang, Y.; Rawal, V. H. *Org. Lett.* **2007**, *9*, 3873.

Scheme 2. Synthesis of Cr(III) Dibromide Naphthoxy- and Phenoxy-Imino Complexes 3a−d



(C═N), and δ 168.5 (*ipso*-C phenol) and 165.9 ppm (C═N), respectively. This observation is further corroborated by the solid-state structure of **2d** (*vide infra*). Apparently, stabilization of either keto-enamine or imino-phenol tautomer results from a delicate balance between electronic effects induced by the substituent at the imino nitrogen atom, the additional ring of the naphthoxy (vs phenoxy) platform, and possibly the β-effect of silicon[9] induced by the $SiPh_3$ substituent as well.

One-Step Synthesis of Cr(III) Complexes by σ-Bond Metathesis. A direct approach toward the targeted chromium complexes was used, which involves the protonolysis reaction of the (*p*-tolyl)$CrBr_2(THF)_3$[10] precursor with the corresponding naphthol-imine pro-ligand **2a−c** in toluene.[7a] Complex **3d**, bearing the phenoxy-imino ligand, was similarly obtained. After evaporation and recrystallization of the resultant materials from acetonitrile, Cr(III) dibromide complexes were isolated in high yields (Scheme 2). Elemental analyses indicated that complex **3c**, which is based on the bidentate ligand, contains two coordinated acetonitrile molecules, while complexes **3a**, **3b**, and **3d**, which are based on tridentate ligands, contain a single coordinated acetonitrile molecule. The latter feature was further confirmed by single-crystal X-ray diffraction studies for **3a** and **3b**. In addition, complexes **3a−d** were authenticated by UV−vis spectroscopy, FAB-MS, and SQUID methods (see Experimental Section and Supporting Information for details).

(9) Lambert, J. B.; Yan, Z.; Emblidge, R. W.; Salvador, L. A.; Xiaoyang, L.; So, J.-H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183, and references therein.

(10) (*p*-tolyl)$CrBr_2(THF)_3$ was obtained from the transmetalation/transhalogenation reaction of $CrCl_3$ and (*p*-tolyl)MgBr, carried out in THF. This compound was isolated in 18% yield after two consecutive recrystallizations; see ref 19.

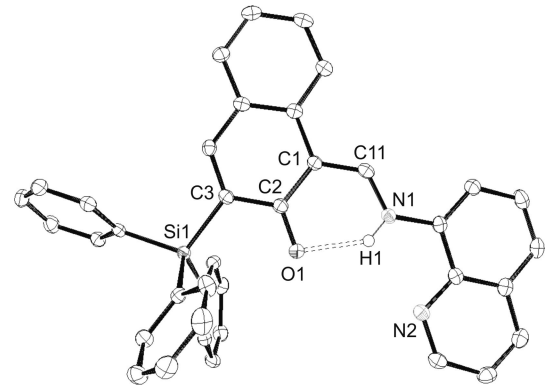


Figure 1. Molecular structure of pro-ligand **2a** (ellipsoids drawn at the 50% probability level; all hydrogen atoms, except H(1)−N(1), removed for the sake of clarity).

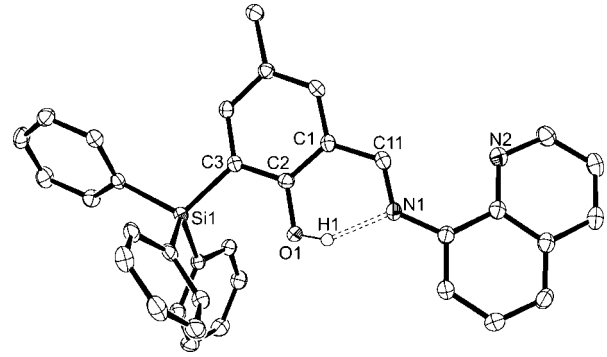


Figure 2. Molecular structure of pro-ligand **2d** (ellipsoids drawn at the 50% probability level; all hydrogen atoms, except H(1)−O(1), removed for the sake of clarity).

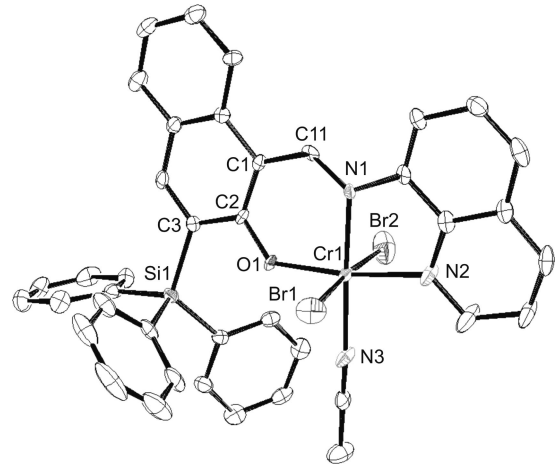


Figure 3. Molecular structure of complex **3a** (ellipsoids drawn at the 50% probability level (all hydrogen atoms removed for the sake of clarity).

Solid-State Molecular Structures. Single-crystal X-ray diffraction studies were performed for pro-ligands **2a** and **2d** and chromium dibromide complexes **3a** and **3b** (Figures 1−4). Crystallographic data and structural determination details are summarized in Table 1, and important bond distances and angles are given in Table 2.

The distribution of formally single and double bonds in pro-ligand **2a** in the solid state (Figure 1) is in agreement with the aforementioned keto-enamine solution structure of this molecule. Thus, the O(1)−C(1) bond distance in **2a** (1.265(2) Å) is significantly shorter than the corresponding bond distances

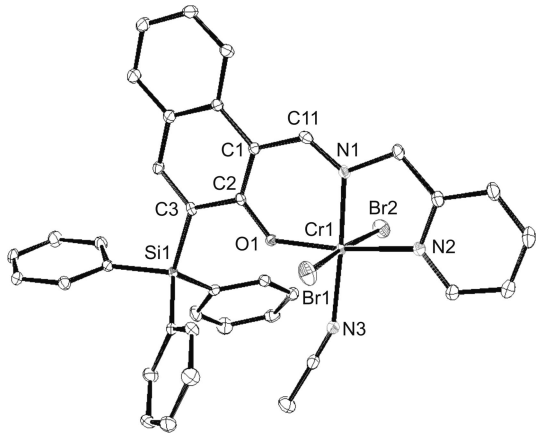


Figure 4. Molecular structure of complex **3b** (ellipsoids drawn at the 50% probability level; all hydrogen atoms removed for the sake of clarity).

observed in imino- and keto-phenols described by Gibson et al. (1.323−1.354(2) Å).[7a] Also, the C(1)−C(11) bond distance is shorter than the endocyclic C(1)−C(2) (1.384(2) vs 1.460(2) Å), and the C(11)−N(1) bond distance (1.336(2) Å) is elongated as compared to the value (1.288(2) Å) observed for a typical C═N bond in an imino-phenol molecule, such as in **2d**. In fact, the imino-phenol structure of **2d**, determined by NMR in solution (*vide supra*), was confirmed in the solid state by X-ray analysis (Figure 2).

Both complexes **3a** and **3b** feature a mononuclear structure in the solid state, with the chromium center in a slightly distorted octahedral environment (Figures 3 and 4). The tridentate ligand adopts a meridional coordination, with the two bromide ligands occupying mutually *trans* positions and the acetonitrile molecule coordinated *trans* to the imino nitrogen donor. In fact, these molecular structures reveal that coordination of **2a** and **2b** onto Cr(III) eventually results in the formation of naphthoxy-imino complexes. The Cr(1)−O(1) bond distances in **3a** and **3b** (1.912(4), 1.905(2) Å, respectively) are in the range (1.890(3)−1.923(3) Å) of those determined for related phenoxy-based {ONN^R}$CrCl_2$(solvent) (solvent = MeCN, THF, pyridine) complexes.[7a] Also, the C(11)−N(1) bond distance in **3a** is shortened, while the C(1)−C(11) bond distance is elongated, as compared to those in pro-ligand **2a**. The O(naphthoxy)−Cr−N(acetonitrile) bond angles (**3a**, 91.8(2)°; **3b**, 85.81(10)°) are similar to the corresponding O(phenoxy)−Cr−N(solvent) bond angles (R = quinolyl, solvent = pyridine, 87.51(2)°; R = 2-pyridylmethyl, solvent = acetonitrile, 90.49(2)−92.55(2)°) observed in the *ortho*-triptycenyl-phenoxy $CrCl_2$(ONN^R)-(solvent) complexes reported by Gibson et al.[7a] This observation may indicate that the *ortho*-triptycenyl and -triphenylsilyl substituents bring similar steric crowding around the salicylaldiminato oxygen and Cr(III) center.

Studies on the Reactivity toward Ethylene. Selective Preparation of Vinyl End-Capped Higher Oligoethylenes. The catalytic activity of combinations based on Cr(III) dibromo complexes **3a**−**d** and a coactivator was evaluated in the oligo/polymerization of ethylene. Three different possible coactivators, namely, MAO, $AlEt_2Cl$, and Al(*i*Bu)$_3$, were used. The reaction conditions and representative examples of catalytic activity and polymer analyses data are summarized in Table 3.

Activation of complexes **3a**,**b** with $AlEt_2Cl$ or Al(*i*Bu)$_3$ as cocatalyst (500 equiv vs Cr) was found to be inefficient (entries 1 and 2). Also, systems based on precursor **3c**, which incorporates a bidentate ligand, proved to be very poorly active or almost inactive, using either MAO or $AlEt_2Cl$ as the activator, respectively (entries 8 and 9). These observations are in line with those made by Gibson et al.[7a,11] On the other hand, activation of Cr(III) precursors **3a** and **3b** with MAO (500−800 equiv) afforded stable and very productive catalytic systems (entries 3−7). Activities up to 14 160 and 12 600 kg mol^{-1} h^{-1} were observed for complexes **3a** and **3b**, respectively, under 6 bar of ethylene at a temperature of 50 °C. Performing the reaction with **3a** from room temperature for a shorter reaction time gave a very high activity of 23 730 kg mol^{-1} h^{-1} (entry 6). Complex **3d**, which is based on a triphenylsilyl-substituted *phenoxy*-imine ligand, was ca. 2 times less active than its *naphthoxy* analogues **3a**,**b** under the same conditions (entry 10). Those reactions are quite exothermic due to the very high activity even with low catalyst loadings, and the temperature of the reaction mixture is hard to control, often reaching up to 80−100 °C after a few minutes (see Table 3). Monitoring of the ethylene uptake indicated that the activity is quite steady under such conditions and thus that the catalysts are thermally stable in this temperature range. Not surprisingly, the activity (and productivity) observed at 100 °C is, however, somewhat lower than under the previous conditions (entry 5).

The catalytic performance of complexes **3a**,**b**, and even those of the somehow less active complex **3d**, contrasts sharply with those of the acetonitrile complexes based on tridentate phenoxy-imine reported by Gibson et al., which all proved to be inactive.[7a] In this case, it was suggested that the acetonitrile ligand may interfere with the activation process or may even be retained by the metal center. Obviously, our results evidence that the apparently innocent replacement of the triptycenyl for a triphenylsilyl *ortho*-substituent (despite the aforementioned similar steric protection they seem to confer) in those Schiff base chromium acetonitrile complexes drastically affects their catalytic performance. In this respect, it is noteworthy that no significant change in activities of complexes **3a** and **3d** was observed when an excess of donor (acetonitrile, THF, or pyridine; 4 equiv vs Cr) was deliberately introduced in the polymerization medium (entries 12, 16−18).

Products obtained with catalyst systems based on **3a**, **3b**, and **3d** are all solid oligomers with T_m = 114−122 °C.[12] The M_n values are typically in the range 600−1600 g mol^{-1} as determined by ^{1}H NMR and HT GPC, with monomodal distributions (M_w/M_n = 1.9−2.3) as shown by HT GPC (Figure 5). ^{1}H and ^{13}C{^{1}H} NMR analyses revealed linear oligomers with remarkably high contents of vinyl ends (ca. 90 mol %) (Figures 6 and 7), that is, essentially linear α-olefins.[13,14] The catalyst system derived from preformed **3d** (entry 10), or generated *in situ* from **2d** with (*p*-tolyl)$CrBr_2(THF)_3$ (entry 15), showed a slightly higher propensity to produce terminal olefins (92−96 mol %). As aforementioned in terms of activity,

(11) Gibson et al. have shown on related Cr-{phenoxy-imine} systems that (i) substitution of the salicylaldehyde in the *para*-position with the electron-withdrawing CF_3 substituent and (ii) replacement of a phenyl for a 3-F-4-BrC_6H_3 group at the imino N atom generally results in slightly decreased catalytic activity (see ref 7a). We thus assume that the inactivity of complex **3c** is likely a consequence of the general poor ability of systems based on aryloxy-imine bidentate ligands derived from arylamines, combined with the electron-withdrawing effect of the C_6F_5 substituent.

(12) Only minor amounts (<5% of consumed ethylene) of low oligomers (1-hexene, 1-octene) were also detected by GLC and GLC-MS.

(13) Small amounts (ca. 2−6 mol %) of internal olefins were also detected; see Figure 6. A small percentage of alkanes, which likely arise by chain transfer to aluminum, accounts for the balance.

(14) (a) Vinyl end-capped (≥90%) low molecular weight polyethylenes (M_w = 1000−10 000 g mol^{-1}) were obtained with FI catalysts bearing phenoxy-cycloalkylimine ligands: (b) Ishii, S.; Mitani, M.; Saito, J.; Matsuura, S.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2002**, 740.

Table 1. Summary of Crystal and Refinement Data for Compounds 2a, 2d, 3a, and 3b

	2a·CH_2Cl_2	**2d**	**3a**·toluene	**3b**·0.5toluene
empirical formula	$C_{38}H_{28}N_2OSi \cdot CH_2Cl_2$	$C_{35}H_{28}N_2OSi$	$C_{40}H_{30}Br_2CrN_3OSi \cdot C_7H_8$	$C_{37}H_{30}Br_2CrN_3OSi \cdot 0.5C_7H_8$
fw	641.64	520.68	808.58	825.63
temp, K	100(2)	100(2)	100(2)	100(2)
wavelength, Å	0.71073	0.71073	0.71073	0.71073
cryst system	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1a$	$P2_1a$	$P\bar{1}$
a, Å	9.2733(16)	10.9845(5)	19.245(2)	11.5073(8)
b, Å	9.9482(15)	12.1870(6)	10.3843(11)	11.5843(8)
c, Å	17.772(3)	20.0955(10)	20.931(2)	13.8235(11)
β, deg	90	94.952(2)	116.442(3)	90
volume, Å^3	1591.6(5)	2680.1(2)	3745.4(7)	1789.5(2)
Z	2	4	4	2
density (calc), Mg/m^3	1.339	1.29	1.434	1.532
absorp coeff, mm^{-1}	0.277	0.120	2.505	2.624
cryst size, mm^3	0.34 × 0.21 × 0.19	0.45 × 0.28 × 0.23	0.22 × 0.18 × 0.04	0.27 × 0.20 × 0.08
reflns collected	22 065	19 151	38 517	36 633
indep reflns	7218 [*R*(int) = 0.0390]	6071 [*R*(int) = 0.0445]	8586 [*R*(int) 0.1003]	8119 [*R*(int) 0.0396]
max. and min. transmn	0.949 and 0.905	0.973 and 0.857	0.905 and 0.567	0.811 and 0.485
data/restraints/params	7218/0/409	6071/0/354	8586/0/434	8119/0/444
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0416, wR2 = 0.0999	R1 = 0.0438, wR2 = 0.0996	R1 = 0.0808, wR2 = 0.2367	R1 = 0.0427, wR2 = 0.1220
R indices (all data)	R1 = 0.0526, wR2 = 0.1062	R1 = 0.0514, wR2 = 0.1054	R1 = 0.1434, wR2 = 0.2666	R1 = 0.0529, wR2 = 0.1286
goodness-of-fit on F^2	1.034	1.036	1.059	1.025 and −1.102
largest diff peak, e Å^{-3}	0.419 and −0.474	0.321 and −0.329	1.217 and −1.481	

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 2a, 2d, 3a, and 3b

	2a	**2d**	**3a**	**3b**
O(1)−C(1)	1.265(2)	1.350(2)	1.316(7)	1.316(4)
C(1)−C(2)	1.460(2)	1.414(2)	1.409(9)	1.413(4)
C(1)−C(11)	1.384(2)	1.449(2)	1.416(9)	1.439(4)
C(11)−N(1)	1.336(2)	1.288(2)	1.304(8)	1.299(4)
Cr(1)−O(1)			1.912(4)	1.905(2)
Cr(1)−Br(1)			2.4360(14)	2.4675(6)
			2.4498(15)	2.4819(6)
Cr(1)−Br(2)			2.4498(15)	2.4819(6)
Cr(1)−N(1)			1.999(5)	1.974(3)
Cr(1)−N(2)			2.053(3)	2.062(3)
Cr(1)−N(3)			2.076(6)	2.096(3)
O(1)−Cr(1)−N(1)			90.0(2)	90.77(10)
O(1)−Cr(1)−N(2)			171.5(2)	172.95(10)
O(1)−Cr(1)−N(3)			91.8(2)	85.81(10)
N(1)−Cr(1)−N(2)			81.5(2)	82.18(10)
N(1)−Cr(1)−N(3)			177.5(2)	176.49(10).
N(2)−Cr(1)−N(3)			96.7(2)	101.24(10)
N(1)−Cr(1)−Br(1)			93.75(16)	90.61(8)
N(2)−Cr(1)−Br(1)			87.72(17)	87.94(7)
N(3)−Cr(1)−Br(1)			87.92(17)	90.30(7)
O(1)−Cr(1)−Br(2)			91.97(14)	94.32(7)
Br(1)−Cr(1)−Br(2)			174.68(6)	173.41(2)

changing the nature of the donor (acetonitrile, THF, or pyridine; 4 equiv vs Cr) had no significant effect on properties of the isolated oligoethylenes (entries 12, 16−18). The observation that different donor molecules have the same effect as acetonitrile suggests that the donor is not implicitly involved in the active catalytic species. Rather, we assume that, by ensuring only monomeric Cr is present, it has a role in affecting the activation pathway followed with MAO.[15]

Conclusions

New bulky bidentate and tridentate naphthol-imine proligands have been straightforwardly prepared and easily installed onto Cr(III) as dibromide acetonitrile adducts. The chromium complexes bearing tridentate ligands, upon activating with MAO, showed very high activities in the oligomerization of ethylene to afford selectively vinyl end-capped oligoethylenes. Those triphenylsilyl *ortho*-substituted naphthoxy-imino and phenoxy-imino Cr systems feature some peculiarities as compared to the related triptycenyl-substituted phenoxy-imino complexes reported by Gibson, namely, the tolerance of coordinated acetonitrile in the precursor and even of excess added donors such as acetonitrile, THF, or pyridine. Those catalyst systems afford selectively linear α-olefins. The latter products can serve as valuable macromers in copolymerization reactions with ethylene or α-olefins for the production of long-chain branched polymers.[16,17]

Experimental Section

All experiments were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled under nitrogen from Na/benzophenone (THF and Et_2O), CaH_2 (acetonitrile), or Na/K alloy (toluene, pentane), degassed thoroughly, and stored under nitrogen prior to use.

(15) We thank a reviewer for suggesting this hypothesis.

(16) (a) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 1830. (b) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 12379. (c) Diamond, G. M.; Leclerc, M. K.; Murphy, V.; Okazaki, M.; Bazan, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 15280.

(17) Dong, J.-Y.; Hu, Y. *Coord. Chem. Rev.* **2006**, *250*, 47.

Table 3. Ethylene Oligomerization Catalyzed by $CrBr_2\{ON(N)^R\}(CH_3CN)$ (3a−d)/Alkylaluminum Combinations[a]

entry	cat. (μmol)	co-cat. ([Al]/[Cr])	temp[b] (°C)	$P(C_2H_4)$ (bar)	time (min)	product (g)	activity (kg mol^{-1} h^{-1})	$M_{n,NMR}$[c] (g mol^{-1})	$M_{n,GPC}$[d] (g mol^{-1})	M_w/M_n[d]	vinyl[c] (mol %)	T_m[e] (°C)
1	**3a** (5.0)	$AlEt_2Cl$ (500)	50	6	60	0.11	22					
2	**3a** (5.0)	$Al(iBu)_3$ (500)	50	6	60	0	0					
3	**3a** (5.0)	MAO (500)	50	1	20	4.29	2 570	1 450	nd	nd	90	119
4	**3a** (5.0)	MAO (500)	50 (90)	6	10	11.80	14 160	1 140	800	2.23	90	118
5	**3a** (5.0)	MAO (500)	100	6	10	2.24	2 690	1 300	nd	nd	89	118
6	**3a** (5.0)	MAO (500)	25 (107)	6	5	9.89	23 730	1 100	nd	nd	87	119
7	**3b** (5.0)	MAO (500)	50 (83)	6	10	10.50	12 600	1 340	850	2.22	91	122
8	**3c** (5.0)	MAO (500)	50	6	60	0.20	40					
9	**3c** (5.0)	$AlEt_2Cl$ (500)	50	6	60	traces						
10	**3d** (5.0)	MAO (500)	50 (83)	6	10	5.57	6 680	1 140	nd	nd	93	116
11[f]	**2a**/Cr (23.0)[f]	MAO (800)	50	1	60	3.50	150	nd[j]	630	1.99	<40[j]	114
12[f,g]	**2a**/Cr (21.0)[f,g]	MAO (800)	50	1	60	1.15	55	1 130	nd	nd	90	119
13[f]	**2a**/Cr (5.0)	MAO (500)	50 (93)	6	10	9.22	11 060	1 070	nd	nd	85	118
14[f]	**2b**/Cr (23.0)[f]	MAO (800)	50	1	60	0.62	27	1 430	800	2.10	67	119
15[f]	**2d**/Cr (5.0)	MAO (500)	50	6	10	0.20	240	1 290	nd	nd	96	121
16[h]	**3a** (5.0)[h]	MAO (500)	50 (94)	6	10	8.75	10 500	1 320	nd	nd	88	118
17[i]	**3a** (5.0)[i]	MAO (500)	50 (93)	6	10	12.43	14 900	1 210	nd	nd	88	118
18[g]	**3d** (5.0)[g]	MAO (500)	50 (74)	6	10	5.68	6 820	1 200	nd	nd	92	117

[a] Unless otherwise stated, reactions were performed in a 300 mL double-mantled glass reactor using toluene (80 mL) as solvent. [b] Temperature of circulating water in the double mantle of the reactor; data in brackets are the maximal temperature reached in the reactor, due to the exothermicity of the reaction. [c] Determined from the ^1H NMR spectrum in $C_2D_2Cl_4$ at 100 °C. [d] Determined by GPC at 150 °C in trichlorobenzene vs polystyrene standards. [e] Determined by DSC; the T_m values refer to peak maxima. [f] Reactions conducted in a Schlenk flask (1 atm) or in an autoclave (6 atm), by mixing pro-ligand **2a**,**b**,**d** with (*p*-tolyl)$CrBr_2(THF)_3$ (1:1). [g] MeCN (4 equiv vs Cr) was added. [h] THF (4 equiv vs Cr) was added. [i] Pyridine (4 equiv vs Cr) was added. [j] Internal olefin products ($CH_3-CH=CH-$) amounted to ca. 50%, and the presence of alkanes was also observed but could not be quantified, hampering exact determination of $M_{n,NMR}$.

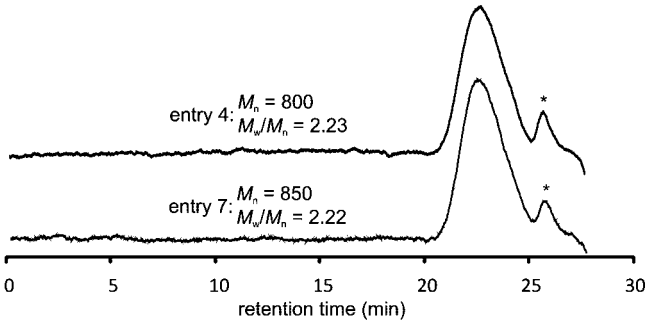


Figure 5. Typical HT-GPC (SEC) traces for oligoethylenes prepared with **3a**/MAO (top) and **3b**/MAO (bottom) systems. The * marker stands for the solvent signal.

Deuterated solvents (benzene-d_6, toluene-d_8, Eurisotop) were vacuum-transferred from Na/K alloy into storage tubes. Starting materials were purchased from Acros, Strem, and Aldrich and used as received. NMR spectra of diamagnetic compounds were recorded on Bruker AC-300 and AM-500 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm vs $SiMe_4$ and were determined by reference to the residual solvent peaks. Assignment of resonances for pro-ligands was made from $^1H-^{13}C$ HMQC and HMBC NMR experiments. Coupling constants are given in Hertz. Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations. Magnetic moment data were obtained on a Quantum Design SQUID MPMS magnetometer, operating with a constant magnetic field of 1000 Oe. UV spectra were recorded on a Varian Cary 5000 UV−vis−NIR spectrophotometer. FAB-HRMS spectra were recorded on a high-resolution MS/MS Micromass ZAB-SpecTOF spectrometer.

(3-Methoxy-2-naphthyl)(triphenyl)silane. *sec*-BuLi (15.3 mL of a 1.3 M solution in hexane/cyclohexane, 19.91 mmol) was added dropwise, over a period of time of 15 min, to a stirred solution of 2-methoxynaphthalene (3.00 g, 18.96 mmol) in THF (70 mL) at −30 °C. The reaction mixture was stirred overnight at room temperature, and a solution of Ph_3SiCl (5.87 g, 19.91 mmol) and hexamethylphosphoramide (HMPA, 3.46 mL, 19.88 mmol) in THF (50 mL) was added. The reaction mixture was refluxed for 20 h, then cooled to room temperature and diluted with water (ca. 500 mL). The organic part was extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried over $MgSO_4$ and evaporated to dryness. The crude residue was recrystallized from heptane and dried under vacuum to give (3-methoxy-2-naphthyl)(triphenyl)silane (7.11 g, 90%). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ 7.80 (m, 2H), 7.67 (m, 7H), 7.55−7.23 (m, 12 H), 3.69 (s, 3H, OCH_3). Anal. Calcd for $C_{29}H_{24}OSi$: C, 83.61; H, 5.81. Found: C, 82.15; H, 5.23.[18]

(4-Bromo-3-methoxy-2-naphthyl)(triphenyl)silane. A 150 mL Schlenk flask was charged with (3-methoxy-2-naphthyl)(triphenyl)-silane (4.68 g, 11.23 mmol) and *N*-bromosuccinimide (NBS, 2.20 g, 12.36 mmol) under argon, followed by addition of DMF (10 mL). The resultant mixture was stirred overnight at room temperature, then diluted with water (ca. 500 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with water (ca. 200 mL) and brine and dried over Na_2SO_4. The product was purified by passing through a short silica column using heptane/EtOAc (15:1) as the eluent to afford the product as an off-white solid (5.28 g, 96%). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ 8.29 (d, J = 8.4 Hz, 1H), 7.80 (s, 1H), 7.66 (m, 8H), 7.52−7.27 (m, 10 H), 3.18 (s, 3H, OCH_3). Anal. Calcd for $C_{29}H_{23}BrOSi$: C, 70.30; H, 4.68. Found: C, 68.99; H, 4.56.[18]

2-Hydroxy-3-(triphenylsilyl)-1-naphthaldehyde (1). *tert*-BuLi (16.1 mL of a 1.5 M solution in pentane, 24.10 mmol) was added dropwise to a stirred solution of (4-bromo-3-methoxy-2-naphthyl)-(triphenyl)silane (6.02 g, 12.1 mmol) in Et_2O (50 mL) at −78 °C. The reaction mixture was stirred for 1.5 h at −78 °C and then 30 min at 0 °C, followed by addition of DMF (0.94 mL, 12.1 mmol). The resultant mixture was stirred overnight at room temperature and diluted with water (ca. 200 mL). The organic part was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic extracts were dried over $MgSO_4$. The resultant solution was transferred into a Schlenk flask under argon, and a solution of BBr_3 (24.1 mL of 1 M solution in CH_2Cl_2, 24.1 mmol) was added dropwise at −78

(18) Low carbon values were repetitively obtained. We ascribe this problem to the presence of silicon, which is known to form noncombustible SiC. Similar difficulty in obtaining satisfactory elemental analyses for silicon-containing complexes of group 3 metals has been encountered by other workers; see e.g.: (a) Arredondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633. (b) Mitchell, P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045. (c) Kirillov, E.; Toupet, L.; Lehmann, C. W.; Razavi, A.; Carpentier, J.-F. *Organometallics* **2003**, *22*, 4467.

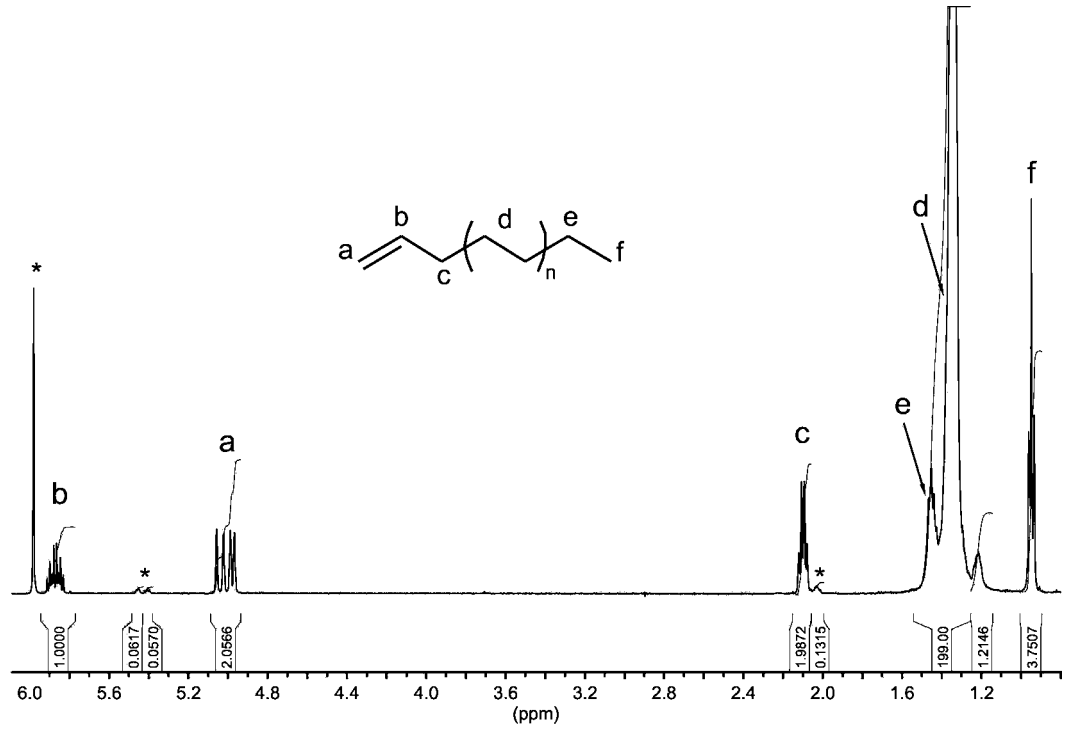


Figure 6. Typical ^{1}H (500 MHz) NMR spectrum ($C_2D_2Cl_4$, 373 K) of vinyl end-capped oligoethylenes produced with **3a**/MAO (Table 3, entry 4); $M_{n,NMR} = 1140$ g mol^{-1}, $n \approx 38$. The * markers in the ^{1}H NMR spectrum stand for resonances of internal olefin ($CH_3-CH{=}CH-$) products.

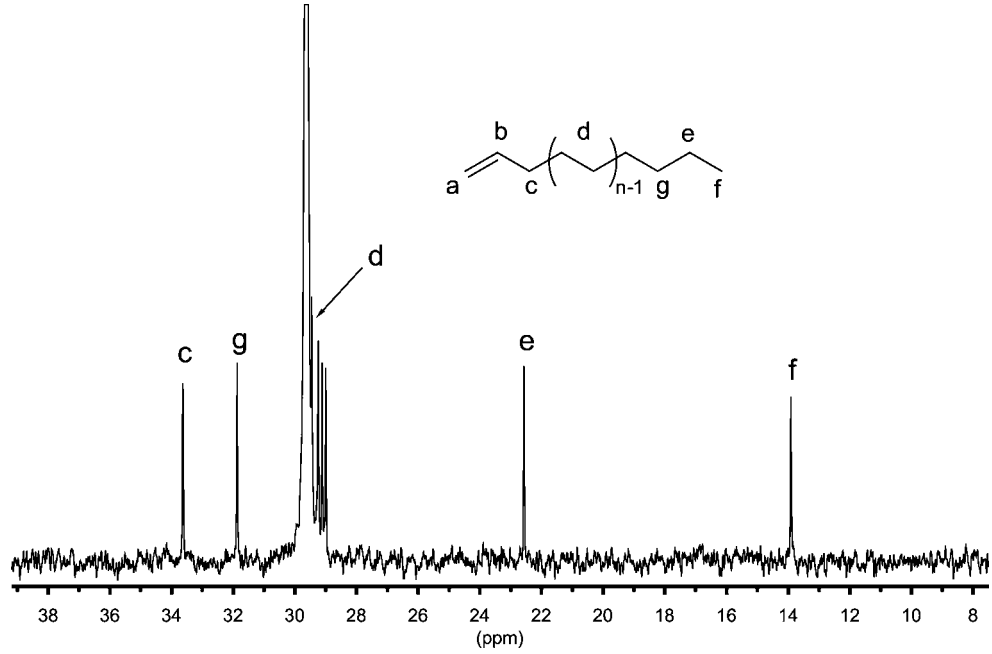


Figure 7. Typical $^{13}C\{^1H\}$ (125 MHz) NMR (high-field region) spectrum ($C_2D_2Cl_4$, 373 K) of vinyl end-capped oligoethylenes produced with **3a**/MAO (Table 3, entry 4); $n \approx 38$.

°C. The reaction mixture was stirred overnight at room temperature and carefully hydrolyzed with water (ca. 500 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic extracts were dried over $MgSO_4$ and evaporated to dryness. The crude residue was recrystallized from methanol at room temperature and dried under vacuum to give **1** as an off-white solid (5.44 g, 95%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 13.58 (s, 1H, O*H*), 10.88 (s, 1H, ═C*H*O), 8.40 (d, $J = 8.4$ Hz, 1H), 8.03 (s, 1H), 7.67 (m, 6H), 7.43 (m, 12H). Anal. Calcd for $C_{29}H_{22}O_2Si$: C, 80.90; H, 5.15. Found: C, 80.17; H, 4.67.[18]

1-[(Quinolin-8-ylamino)methylene]-3-(triphenylsilyl)naphthalen-2-one (2a). To a stirred mixture of **1**(1.09 g, 2.53 mmol) and 8-aminoquinoline (0.37 g, 2.53 mmol) in methanol (40 mL) was added a catalytic amount of formic acid (ca. 10 mg) at room temperature. The mixture was refluxed for 25 h, over which time period the product precipitated as a microcrystalline powder. The reaction mixture was transferred onto a Schott filter and filtered. The orange solid obtained was washed with a minimal amount of cold methanol and dried under vacuum to give **2a** as an orange solid (0.77 g, 55%). Crystals of **2a** suitable for X-ray diffraction

studies were obtained by recrystallization from CH_2Cl_2 at room temperature. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 15.31 (d, J = 11.1 Hz, 1H, N*H*), 9.31 (d, J = 11.1 Hz, 1H, =C*H*N), 9.02 (dd, J = 1.8 Hz, J = 4.4 Hz, 1H), 8.26 (dd, J = 1.8 Hz, J = 8.2 Hz, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.81 (m, 2H), 7.73 (m, 7H), 7.66 (m, 1H), 7.57−7.40 (m, 12H), 7.27 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 25 °C): δ 185.2 (C=O), 151.7, 150.1, 146.4, 139.8, 137.4, 136.4, 136.1, 135.8, 135.0, 133.2, 130.0, 129.3, 129.2, 129.0, 127.7, 126.6, 126.5, 124.4, 123.5, 122.3, 118.3, 113.9, 108.2. Anal. Calcd for $C_{38}H_{28}N_2OSi$: C, 81.98; H, 5.07; N, 5.03. Found: C, 81.04; H, 4.98; N, 5.1.[18]

1-{[(Pyridin-2-ylmethyl)amino]methylene}-3-(triphenylsilyl)-naphthalen-2-one (2b). Using the same protocol as the one described above for **2a**, pro-ligand **2b** was prepared as a yellow solid in 60% yield (0.78 g), starting from **1** (1.08 g, 2.51 mmol) and 2-aminomethylpyridine (0.29 g, 2.50 mmol). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 14.44 (br m, 1H, N*H*), 8.96 (d, J = 8.8 Hz, 1H), 8.63 (d, J = 4.1 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.79 (s, 1H), 7.70 (m, 1H), 7.67 (m, 6H), 7.60−7.35 (m, 11H), 7.32 (d, J = 8.0 Hz, 1H), 7.25 (m, 1H), 7.23 (m, 1H), 4.88 (m, 2H, CH_2Py). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 25 °C): δ 180.6 (C=O), 158.6, 156.4, 149.8, 149.3, 136.9, 136.3, 135.6, 135.1, 131.5, 129.8, 129.2, 128.9, 127.7, 126.1, 122.8, 122.6, 121.9, 117.8, 106.1, 57.7. Anal. Calcd for $C_{35}H_{28}N_2OSi$: C, 80.73; H, 5.42; N, 5.38. Found: C, 79.94; H, 5.00; N, 5.3.[18]

Synthesis of 1-[(Pentafluorophenyl)imino]methyl}-3-(triphenylsilyl)-2-naphthol (2c). Pro-ligand **2c** was synthesized by condensation of **1** (1.04 g, 2.42 mmol) and pentafluorophenylaniline (0.44 g, 2.42 mmol) in toluene at reflux for 40 h in the presence of PTSA (ca. 5 wt %), using a Dean−Stark apparatus. The final reaction mixture was evaporated to dryness, and the solid residue was recrystallized from methanol to give **2c** as a yellow solid (0.93 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 14.49 (s, 1H, O*H*), 9.76 (s, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.96 (s, 1H), 7.71 (d, J = 6.7 Hz, 6H), 7.69 (d, J = 10.2 Hz, 1H), 7.62 (t, J = 10.2 Hz, 1H), 7.52−7.30 (m, 10H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C): δ 168.5, 165.9 (ipso-C phenol and C=N), 148.1, 136.4, 134.2, 134.0, 130.2, 129.6, 129.4, 127.9, 127.7, 126.3, 123.9, 118.9, 108.8 (signals from the C_6F_5 group were not observed). ^{19}F{^{1}H} NMR (188 MHz, $CDCl_3$, 25 °C): δ −152.4 (m, 2F), −159.1 (t, 1F), −162.8 (m, 2F). Anal. Calcd for $C_{35}H_{22}F_5NOSi$: C, 70.58; H, 3.72; N, 2.35. Found: C, 69.89; H, 3.52; N, 2.45.[18]

Synthesis of 4-Methyl-2-[(quinolin-8-ylimino)methyl]-6-(triphenylsilyl)phenol (2d). Using the same protocol as the one described above for **2a**, pro-ligand **2d** was prepared as a pink solid in 66% yield (7.34 g), starting from 2-hydroxy-5-methyl-3-(triphenylsilyl)-benzaldehyde[8] (8.47 g, 21.46 mmol) and 8-aminoquinoline (3.10 g, 21.46 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 13.62 (s, 1H, N*H*), 9.04 (s, 1H, =C*H*N), 8.93 (dd, J = 2.0 Hz, J = 4.0 Hz, 1H), 8.19 (dd, J = 2.0 Hz, J = 8.5 Hz, 1H), 7.69 (m, 7H), 7.57 (m, 2H), 7.45−7.38 (m, 13H), 7.17 (d, J = 2.0 Hz,), 2.26 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C): δ 166.7, 164.7 (ipso-C phenol and C=N), 150.4, 145.7, 143.2, 141.9, 136.5, 136.1, 135.5, 135.3, 135.2, 134.8, 129.8, 129.3, 127.7, 126.6, 125.8, 121.6, 121.0, 118.7, 20.5. Anal. Calcd for $C_{35}H_{28}N_2OSi$: C, 80.73; H, 5.42; N, 5.38. Found: C, 80.00; H, 5.28; N, 5.30.[18]

(4-$CH_3C_6H_4$)$CrBr_2(THF)_3$. The synthesis of (*p*-tolyl)-$CrBr_2(THF)_3$ was performed using a modified literature procedure,[19] starting from $CrCl_3$ and (*p*-tolyl)MgBr in THF (18% yield after two recrystallizations from THF at 0 °C). Anal. Calcd for $C_{19}H_{31}Br_2CrO_3$: C, 43.95; H, 6.02. Found: C, 43.81; H, 5.78.

(ONN^{Quin})$CrBr_2$(MeCN) (3a). A Schlenk flask was charged with **2a** (0.150 g, 0.269 mmol) and (*p*-tolyl)$CrBr_2(THF)_3$ (0.140 g, 0.269 mmol), and toluene (5 mL) was vacuum transferred in. The reaction mixture was stirred overnight at room temperature and evaporated to dryness under vacuum. The deep pink residue was recrystallized from dry acetonitrile (ca. 20 mL) to give **3a** as a violet crystalline solid (0.187 g, 86%). Crystals suitable for X-ray diffraction analysis were obtained from this batch. UV−vis (CH_2Cl_2, 298 K, mol^{-1} dm^3 cm^{-1}): ε_{527} 5660, ε_{500} 5296, ε_{371} 6455. FAB-HRMS ($CHCl_3$, *m/z*): calcd for $C_{76}H_{54}N_4O_2Si_2{}^{52}Cr$ ($[CrL_2]^{+\bullet}$)[20] 1162.3190; found 1162.3201. μ(BM) = 3.87. Anal. Calcd for $C_{40}H_{30}Br_2CrN_3OSi$: C, 59.42; H, 3.74; N, 5.20. Found: C, 58.65; H, 3.52; N, 5.12.[18]

(ONN^{Py})$CrBr_2$(MeCN) (3b). Complex **3b** was prepared in a similar manner to that described above for **3a**, starting from **2b** (0.100 g, 0.192 mmol) and (*p*-tolyl)$CrBr_2(THF)_3$ (0.100 g, 0.192 mmol). **3b** was recovered as a green crystalline solid (0.135 g, 91%). Crystals suitable for X-ray diffraction analysis were obtained from this batch. UV−vis (CH_2Cl_2, 298 K, mol^{-1} dm^3 cm^{-1}): ε_{456} 2865, ε_{319} 7384. FAB-HRMS ($CHCl_3$, *m/z*): calcd for $C_{70}H_{54}N_4O_2Si_2{}^{52}Cr$ ($[CrL_2]^{+\bullet}$)[20] 1090.3190; found: 1090.3181. Anal. Calcd for $C_{37}H_{30}Br_2CrN_3OSi$: C, 57.52; H, 3.91; N, 5.44. Found: C, 57.1; H, 3.75; N, 5.35.[18]

(ON^{C6F5})$CrBr_2(MeCN)_2$ (3c). Complex **3c** was prepared in a similar manner to that described above for **3a**, starting from **2c** (0.100 g, 0.168 mmol) and (*p*-tolyl)$CrBr_2(THF)_3$ (0.087 g, 0.168 mmol). **3c** was recovered as a golden crystalline solid (0.101 g, 68%). UV−vis (CH_2Cl_2, 298 K, mol^{-1} dm^3 cm^{-1}): ε_{438} 6500, ε_{337} 10035, ε_{303} 9626. FAB-HRMS ($C_2H_4Cl_2$, *m/z*): calcd for $C_{70}H_{42}N_2O_2F_{10}Si_2{}^{52}Cr$ ($[CrL_2]^{+\bullet}$)[20] 1240.2030; found 1240.2039. μ(BM) = 3.87. Anal. Calcd for $C_{39}H_{27}Br_2CrF_5N_3OSi$: C, 52.72; H, 3.06; N, 4.73. Found: C, 51.89; H, 2.78; N, 4.80.[18]

($O^{Phen}NN^{Quin}$)$CrBr_2$(MeCN) (3d). Complex **3d** was prepared in a similar manner to that described above for **3a**, starting from **2d** (0.186 g, 0.357 mmol) and (*p*-tolyl)$CrBr_2(THF)_3$ (0.185 g, 0.357 mmol). **3d** was isolated as a deep pink crystalline solid (0.223 g, 81%). UV−vis (CH_2Cl_2, 298 K, mol^{-1} dm^3 cm^{-1}): ε_{505} 3636, ε_{358} 7684. FAB-HRMS ($CHCl_3$, *m/z*): calcd for $C_{70}H_{54}N_4O_2Si_2{}^{52}Cr$ ($[CrL_2]^{+\bullet}$)[20] 1090.3197; found 1090.3190. Anal. Calcd for $C_{37}H_{30}Br_2CrN_3OSi$: C, 57.52; H, 3.91; N, 5.44. Found: C, 56.93; H, 3.88; N, 5.36.[18]

Crystal Structure Determination of 2a, 2d, 3a, and 3b. Crystals of **2a**, **2d**, **3a**, and **3b** suitable for X-ray diffraction analysis were obtained by recrystallization of purified products (see Experimental Section). Diffraction data were collected at 100 K using a Bruker APEX CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). A combination of ω and ϕ scans was carried out to obtain at least a unique data set. The crystal structures were solved by means of the Patterson method; remaining atoms were located from difference Fourier synthesis followed by full matrix least-squares refinement based on F^2 (programs SHELXS-97 and SHELXL-97).[21] Many hydrogen atoms could be found from the Fourier difference analysis. Carbon- and nitrogen-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystals of **3a** were found to contain lattice disordered solvent molecules, which could not be sufficiently modeled in the refinement cycles. These molecules were removed using the SQUEEZE procedure[22] implemented in the PLATON package.[23] The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of

(19) Daly, J. J.; Sneeden, R. P. A.; Zeiss, H. H. *J. Am. Chem. Soc.* **1966**, *88*, 4287.

(20) The bis(ligand) complex fragment has been also observed as the most intense peak in MS spectra of some related phenoxy-imino Cr(III) dichloride complexes; see ref 7a.

(21) (a) Sheldrick, G. M. *SHELXS-97, Program for the Determination of Crystal Structures*; University of Goettingen: Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Goettingen: Germany, 1997.

(22) van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

(23) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C-34.

no chemical significance. Crystal data and details of data collection and structure refinement for the different compounds are given in Table 1. Main crystallographic data (excluding structure factors) are available as Supporting Information, as cif files.

Oligomerization of Ethylene. In a typical procedure, a 300 mL glass high-pressure reactor (Top Industrie) was charged with 80 mL of freshly distilled toluene under argon flash. Mechanical stirring (Pelton turbine, 1000 rpm) was started. The reactor was then purged with ethylene, loaded with a solution of cocatalyst/scavenger selected from MAO, $AlEt_2Cl$, or $Al(iBu)_3$, at atmospheric pressure, and then kept at the desired temperature by circulating thermostatted water in the reactor double wall. A solution of precatalyst **3a**−**d** in 5 mL of toluene was injected in by syringe. The gas pressure in the reactor was immediately set up at the desired pressure and kept constant with a back regulator throughout the experiment. The ethylene consumption was monitored via an Aalborg flowmeter. After a given time period, the reactor was depressurized and the reaction was quenched by adding about 5 mL of a 10% solution of HCl in methanol. The oligomeric materials were further precipitated by adding 500 mL of methanol, washed, and dried under vacuum overnight at room temperature. The reaction conditions are summarized in Table 3.

The percentage of vinyl termination was determined by ^{1}H NMR, according to the following formula: vinyl content $= 1 - [(I_f - 1.5I_a)/2I_f]$, where I_f and I_a are the relative intensities for CH_2CH_3 and $CH{=}CH_2$, respectively (see Figure 6). The average number molecular weight determined by NMR was calculated from the following formula: $M_{n,NMR}$ = vinyl content(%) $\times$ $[(I_d + I_e - I_a)/2(I_a)] \times M_{(C2H4)} + M_{(C5H10)}$, where I_d, I_e, and I_a are the relative intensities for $(CH_2CH_2)_n$, CH_2CH_3, and $CH{=}CH_2$, respectively (see Figure 6), and $M_{(C2H4)} = 28$ g mol^{-1} and $M_{(C5H10)} = 70$ g mol^{-1}.

Acknowledgment. This work was financially supported by Total Petrochemicals (grant to E.K.). We gratefully thank Prof. Richard F. Jordan (The University of Chicago) for the HT-GPC analyses. We are also grateful to Thierry Guizouarn for SQUID measurements and Philippe Jehan for FAB-MS analysis. J.F.C. thanks the Institut Universitaire de France for a Junior IUF fellowship (2005−2009).

Supporting Information Available: Crystallographic data for **2a**, **2d**, **3a**, and **3b** as CIF files; NMR spectra for pro-ligands **2a**,**d**, UV−vis and FAB-MS spectra for complexes **3a**−**d**, magnetic data for complexes **3a**,**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM801196D