New Insight into the Role of the Metal Oxidation State in Controlling the Selectivity of the Cr-(SNS) Ethylene Trimerization Catalyst

Claire N. Temple,[†] Sandro Gambarotta,*[,†] Ilia Korobkov,[†] and Robbert Duchateau*[,‡]

Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa ON K1N 6N5, Canada, and Department of Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB, The Netherlands

Received May 7, 2007

The tri- and divalent complexes of the 2,6-bis($RSCH_2$)pyridine [R = Ph, Cy] ligands have been prepared. Upon activation with MAO, both species are catalysts for ethylene oligomerization of moderate activity. However, while the trivalent catalysts produced only 1-hexene, the divalent species gave a statistical distribution of oligomers. This clear difference in catalytic behavior indicates that the two oxidation states are not interconnected during the catalytic cycle as it happens instead with other oligomerization catalytic systems. The trivalent precursor is not reduced and the divalent is not oxidized. Treatment of the trivalent catalyst precursors with either MAO or other R_3Al species afforded intractable materials. Instead, similar reactions with the divalent complexes gave new cationic species, which have been characterized by X-ray analysis. These complexes have preserved the divalent state of chromium during the reaction and still produce, upon further activation, a statistical distribution of oligomers. This reiterates the non-interconvertibility of the di- and trivalent oxidation states and the different degree of selectivity for which they are responsible.

Introduction

Research in the area of ethylene oligomerization is currently aimed at the discovery of trimerization[1] and tetramerization[2] catalysts capable of combining high activity with selectivity. In fact, catalytic activity has been found with a large series of diversified metals and ligands, but selective oligomerization catalysts remain rare.[3−5] The recently reported Sasol trimerization catalyst [$CrCl_3$(SNS)] [(SNS) = $RSCH_2CH_2N(H)CH_2CH_2$-SR, R = Me, Et, *n*-Bu, or *n*-Dec] has been shown to be not only extremely active but also 98% selective for 1-hexene.[6] Given its simplicity, this remarkable catalyst obviously provides an excellent substrate for studying the factors responsible for the unique selectivity that may in turn assist with the design of new catalysts. In fact, there are only three features in these complexes that may be responsible for the exceptional selectivity: the metal oxidation state of the catalytically active species, the N−H function, and the particular nature of the sulfur donor atoms.

Clarifying the chromium oxidation state in the catalytically active species is central to the design of new and more potent catalysts. Recent studies[9] on the unique Sasol PNP tetramerization catalyst[2] and on other catalytic systems[7,8,10] have clearly

* Corresponding author. Fax: (+1) (613-562-5170). E-mail: sgambaro@uottawa.ca.

[†] University of Ottawa.

[‡] Eindhoven University of Technology.

(1) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, *689*, 3641.

(2) (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* (45), 14712. (b) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S. *Chem. Commun*. **2005**, *622*. (c) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Haasbroek, D.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H. *J. Am. Chem. Soc.* **2005**, *127*, 10723.

(3) (a) Deckers, P. J. W.; Hessen, B. J.; Teuben, H. *Organometallics* **2002**, *21*, 5122. (b) Deckers, P. J. W.; Hessen, B. J.; Teuben, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2516−2519. (c) Deckers, P. J. W.; Hessen, B. J.; Teuben, H.; (Stichting Dutch Polymer Institute) WO 02/066404, August 29, 2002. (d) Deckers, P. J. W.; Hessen, B. J.; Teuben, H. (Stichting Dutch Polymer Institute) WO 02/066405, August 29, 2002.

(4) (a) Wass, D. F. (BP Chemicals Ltd) WO 02/04119, January 17, 2002. (b) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun*. **2002**, 858.

(5) (a) Reagan, W. K. (Phillips Petroleum Co.) EP 0417477, 1991. (b) Conroy, B. K.; Pettijohn, T. M.; Benham, E. A. (Phillips Petroleum Co.) EP 0608447, 1994. (c) Freeman, J. W.; Buster, J. L.; Knudsen, R. D. (Phillips Petroleum Co.) US 5,856,257, 1999.

(6) (a) McGuinness, D. S.; Wasserscheid, P.; Morgan, D. H.; Dixon, J. T. *Organometallics* **2005**, *24*, 552. (b) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. *J. Am. Chem. Soc*. **2003**, *125*, 5272. (c) Dixon, J. T.; Wasserscheid, P.; McGuinness, D. S.; Hess, F.; Maumela, H.; Morgan, D. H.; Bollmann, A. (Sasol Technology (Pty) Ltd) WO 03053890, 2001.

(7) Jabri, A.; Temple, C.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *J. Am. Chem. Soc*. **2006**, *128*, 9238.

(8) (a) McGuinness, D. S.; Brown, D. B.; Tooze, R. P.; Hess, F. M.; Dixon, J. T.; Slawin, A. M. Z. *Organometallics* **2006**, *25*, 3605. (b) Blom, B.; Klatt, G.; Fletcher, J. C. Q.; Moss, J. R. *Inorg. Chim. Acta* **2007**, *360*, 2890. (c) Bowen, L. E.; Haddow, M. F.; Orpen, A. G.; Wass, D. F. *Dalton Trans.* **2007**, 1160. (d) Nenu, C. N.; Lingen, J. N. J.; van de Groot, F. M. F.; Koningsberger, D. C.; Weckhuysen, B. M. *Chem.−Eur. J.* **2006**, *12*, 4756. (e) van Rensburg, W. J.; van den Berg, J. A.; Steynberg, P. J. *Organometallics* **2007**, *26*, 1000. (f) McGuinness, D. S.; Overett, M.; Tooze, R. P.; Blann, K.; Dixon, J. T.; Slawin, A. M. Z. *Organometallics* **2007**, *26*, 1108. (g) McGuinness, D. S.; Rucklidge, A. J.; Tooze, R. P.; Slawin, A. M. Z. *Organometallics* **2007**, *26*, 2561. (h) Wass, D. F. *Dalton Trans.* **2007**, 816. (i) Rucklidge, A. J.; McGuinness, D. S.; Tooze, R. P.; Slawin, A. M.; Pelletier, J. D. A.; Hanton, M. J.; Webb, P. B. *Organometallics* **2007**, *26*, 2782. (j) McGuinness, D. S.; Brown, D. B.; Tooze, R. P.; Hess, F. M.; Dixon, J. T.; Slawin, A. M. *Organometallics* **2006**, *25*, 3605. (k) Janse van Rensburg, W.; Grove, C.; Steynberg, J. P.; Stark, K. B.; Huyser, J. J.; Steynberg, P. J. *Organometallics* **2004**, *23*, 1207. (l) Agapie, T.; Schofer, S. J.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc*. **2004**, *126*, 1304. (m) Small, B. L.; Carney, M. J.; Holman, D. M.; O'Rourke, C. E.; Halfen, J. A. *Macromolecules* **2004**, *37*, 4375. (n) Morgan, D. H.; Schwikkard, S. L.; Dixon, J. T.; Nair, J. J.; Hunter, R. *Adv. Synth. Catal.* **2003**, *345*, 1. (o) Köhn, R. D.; Smith, D.; Mahon, M. F.; Prinz, M.; Mihan, S.; Kociok-Köhn, G. *J. Organomet. Chem.* **2003**, *683*, 200.

(9) Jabri, A.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Organometallics* **2006**, *25*, 715.

10.1021/om700452u CCC: $37.00
Publication on Web 07/13/2007

shown that the formation of divalent chromium is, at least in some cases, the first step toward the formation of the catalytically active species. This, together with the general poor stability of the trivalent organochromium function,[11] suggests that perhaps reduction to the divalent state might be a trend for chromium catalysts. In fact, work by Bercaw has clearly shown that oligomerization may be carried out by an even lower valence state.[12] On the other hand, in the case of the SNS system it was observed that divalent precursors are more inclined to lose selectivity, and even further, the divalent species can be *oxidized* via disproportionation by an alkyl aluminum to the original catalytically active trivalent complex.[10] The working hypothesis emerging from these observations was that although both the divalent and trivalent states can be catalytically active, *only the trivalent state is capable of selective trimerization*.[10]

Recent work in our group[7] has established that the SNS ligand is not as readily deprotonated as previously thought.[6a,8] On the other hand, several cationic, organochromium species containing a non-deprotonated SNS ligand were prepared by the reaction of $[CrCl_3(SNS)]$ [(SNS) = $CySCH_2CH_2N(H)CH_2CH_2SCy$] with a range of alkyl aluminum reagents. Catalytic tests confirmed that cationization and alkylation of the neutral catalyst precursor is directly linked to catalyst performance.[7] Among all the species related to this catalytic system that have been isolated and tested, the N−H moiety always remained intact in the presence of a variety of activators (i.e., MAO, $AlMe_3$, $AlEt_3$, *i*-BAO).

Herein, we report the results of a further investigation with both Cr^{III} and Cr^{II} complexes containing an "SNS" ligand motif that does not contain an N−H function and the implications of these findings with regard to catalyst selectivity.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. Samples for magnetic susceptibility were preweighed inside a drybox equipped with an analytical balance and measured on a Johnson Matthey magnetic susceptibility balance. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination were obtained with a Bruker diffractometer equipped with a 1K Smart CCD area detector. NMR spectra were collected on a Varian Inova 500 MHz instrument. $CrCl_3(THF)_3$ and $CrCl_2(THF)_2$ were prepared according to standard procedures. The 2,6-bis(phenylthiomethyl)pyridine **1** ligand was prepared with a slightly modified literature procedure.[13] The reagents $AlMeCl_2$ (Aldrich) and MAO (Chemtura and Aldrich) were used as received.

Preparation of 2,6-Bis(cyclohexylthiomethyl)pyridine (2). A mixture of NaOH (1.87 g, 0.047 mol) and cyclohexyl mercaptan (5.7 mL, 0.047 mol) in ethanol (30 mL, 99%) was stirred at room temperature for 1 h. The resulting solution was added dropwise over 10 min to a solution of 2,6-bis(chloromethyl)pyridine (3.91 g, 0.022 mol) in ethanol (25 mL, 99%) and stirred at room temperature for 18 h. The solvent was removed *in vacuo*, then water (100 mL) and chloroform (100 mL) were added to the white residue. The organic layer was separated and the aqueous layer extracted with chloroform (3 × 50 mL). The organic extracts were combined and dried over $MgSO_4$, and the solvent was removed *in vacuo* to yield **2** as an analytically pure pale oil (5.8 g, 0.017 mol, 79%). Anal. Calcd (found) for $C_{19}H_{29}NS_2$: C 68.01 (67.99); H 8.71 (8.68); N 4.17 (4.15). ^1H NMR (300.13 MHz, $CDCl_3$, 300 K) δ: 1.25 (m, 10H, C$\underline{H}_2$-Cy), 1.60 (m, 2H, C$\underline{H}_2$-Cy), 1.75 (m, 4H, C$\underline{H}_2$-Cy), 1.97 (m, 4H, C$\underline{H}_2$-Cy), 2.65 (m, 2H, C$\underline{H}$-Cy), 3.80 (s, 4H, C$\underline{H}_2$), 7.20 (d, 2H, C$\underline{H}$-Py), 7.55 (t, 1H, C$\underline{H}$-Py). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 300 K) δ: 26.02, 26.22, 33.61 (3 × s, $\underline{C}H_2$-Cy), 36.75 (s, $\underline{C}H_2$), 43.50 (s, $\underline{C}H$-Cy), 121.08, (s, $\underline{C}$-Py), 137.38, 158.91 (2 × s, $\underline{C}H$-Py). MS: ES^+ 337 ($M^+ + H^+$).

Preparation of $[(2,6\text{-}(PhSCH_2)_2\text{-}py)CrCl_3]\cdot CH_3CN$ (3). To a suspension of $CrCl_3(THF)_3$ (0.127 g, 0.33 mmol) in toluene (10 mL) was added 2,6-bis(phenylthiomethyl)pyridine **1** (0.110 g, 0.34 mmol), and the resulting green suspension was stirred at room temperature for 30 min. The suspension was centrifuged, and the green solid was washed with hexanes (3 × 10 mL) and dried *in vacuo* to yield complex **3** as a green microcrystalline solid (0.150 g, 0.29 mmol, 88%). Single crystals suitable for X-ray crystallography were grown from a concentrated acetonitrile solution stored at −35 °C. Anal. Calcd (found) for $C_{21}H_{20}N_2S_2Cl_3Cr$: C 48.24 (47.94); H 3.86 (3.72); N 5.36 (5.27). μ_{eff} = 3.96 μ_B. Acetonitrile-free samples for catalytic runs were obtained by exposing samples of crystalline **3** to vacuum overnight and at 60 °C.

Preparation of $[(2,6\text{-}(CySCH_2)_2\text{-}py)CrCl_3]\cdot(CH_3CN)_{0.25}$ (4). The same procedure as for complex **3** was followed by replacing ligand **1** with **2**. Complex **4** was isolated as a green microcrystalline solid (0.73 g, 1.48 mmol, 99%). Single crystals suitable for X-ray crystallography were grown from a concentrated acetonitrile solution stored at −35 °C. Satisfactory analytical data were obtained only for samples dried *in vacuo*. Anal. Calcd (found) for $C_{19}H_{29}NS_2CrCl_3$: C 46.20 (46.17); H 5.92 (5.86); N 2.84 (2.77). μ_{eff} = 3.88 μ_B. Acetonitrile-free samples for catalytic runs were obtained by exposing samples of crystalline **4** to vacuum overnight and at 60 °C.

Preparation of $[2,6\text{-}(PhSCH_2)_2\text{-}py]CrCl_2$. A mixture of $CrCl_2(THF)_2$ (0.054 g, 0.202 mmol) in toluene (5 mL) with 2,6-bis(phenylthiomethyl)pyridine **1** (0.065 g, 0.202 mmol) was stirred at room temperature for 1 h, affording a pale orange solid (0.075 g). Anal. Calcd (found) for $C_{19}H_{17}NS_2CrCl_2$: C 51.13 (51.04); H 3.84 (3.72); N 3.14 (3.11).

Preparation of $[2,6\text{-}(CySCH_2)_2\text{-}py]CrCl_2$. A mixture of $CrCl_2(THF)_2$ (0.054 g, 0.202 mmol) in toluene (5 mL) with 2,6-bis(cyclohexylthiomethyl)pyridine (**2**) (0.068 g, 0.202 mmol) was stirred at room temperature for 1 h, affording a pale orange solid (0.069 g). Anal. Calcd (found) for $C_{19}H_{29}NS_2CrCl_2$: C 49.78 (49.64); H 6.38 (6.32); N 3.06 (3.07).

Preparation of $\{2,6\text{-}(CySCH_2)_2\text{-}py]Cr\text{-}\mu\text{-}Cl\}_2\cdot 2[AlMeCl_3]\cdot$ toluene (5). The addition of a solution of $AlMeCl_2$ (0.2 mL, 0.202 mmol) in hexanes (1.0 M) to a suspension of 2,6-$(CySCH_2)_2$-py)-$CrCl_2$ (0.091 g, 0.200 mmol) turned the color of the suspension to green with formation of an oily green-blue residue. The supernatant was decanted into a vial and stored at room temperature, yielding complex **5** as blue single crystals suitable for X-ray crystallography. The substantial contamination of oily material prevented analytical characterization in this case.

Preparation of $\{2,6\text{-}(CySCH_2)_2\text{-}py]CrCl\}[AlMe_2Cl_2]\cdot$toluene (6). A suspension of $CrCl_2(THF)_2$ (0.393 g, 2.95 mmol) in toluene (5 mL) was treated with **2** (0.494 g, 2.94 mmol) and stirred at room temperature for 1 h. The addition of a solution of MAO (4.25 mL, 14.75 mmol) in toluene (10 wt %) to the resulting pale orange suspension produced a green solution with formation of a green precipitate. The suspension was centrifuged, and the green solid was washed with hexanes (3 × 10 mL) and dried *in vacuo* to yield complex **6** as a green microcrystalline solid (0.548 g, 0.85 mmol,

(10) Temple, C.; Jabri, A.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Angew. Chem., Int. Ed.* **2006**, *45*, *7050*.

(11) See for example: (a) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738. (b) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Golen, J. A.; Rheingold, A. L.; Theopold K. H. *Chem. Commun.* **2003**, 1164.

(12) (a) Elowe, P. R.; McCann, C.; Pringle, P. G.; Spitzmesser, S. K.; Bercaw, J. E. *Organometallics* **2006**, *25*, 5255. (b) Schofer, S. J., Day, M. W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2006**, *25*, 2743.

(13) Canovese, L.; Chessa, G.; Marangoni, G.; Pitteri, B.; Uguagliati, P.; Visentin. F. *Inorg. Chim. Acta* **1991**, *186*, 79.

Table 1. Crystal, Structure Solution, and Refinement Data

	3	4	5	6
formula	$C_{21}H_{20}Cl_3CrN_2S_2$	$C_{39}H_{59.50}Cl_6Cr_2N_{2.50}S_4$	$C_{27}H_{40}AlCl_4CrNS_2$	$C_{28}H_{43}NS_2CrCl_3Al$
M_w	522.86	1008.33	663.50	643.08
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic
space group	*P*2(1)2(1)2(1)	*P*2/*n*	*P*2(1)/*c*	$P\bar{1}$
a (Å)	7.783(3)	22.081(7)	13.871(5)	10.91(2)
b (Å)	14.181(5)	9.809(3)	16.849(6)	11.81(2)
c (Å)	20.516(7)	22.623(7)	14.368(5)	14.52(3)
α (deg)				86.87(3)
β (deg)		90.276(4)	95.566(5)	74.34(3
γ (deg)				75.86(3)
V (Å^3)	2264.4(12)	4900(3)	3342(2)	1747(6)
Z	4	4	4	2
radiation (Kα, Å)	0.71073	0.71073	0.71073	0.71073
T (K)	203(2)	203(2)	203(2)	200(2)
D_{calcd} (g cm^{-3})	1.534	1.367	1.319	1.222
μ_{calcd} (mm^{-1})	1.055	0.971	0.831	0.718
F_{000}	1068	2100	1384	676
R, R_w[2] [a]	0.0421 0.0995	0.0764, 0.1921	0.0643, 0.1410	0.0664, 0.1517
GoF	1.034	1.063	1.007	1.053

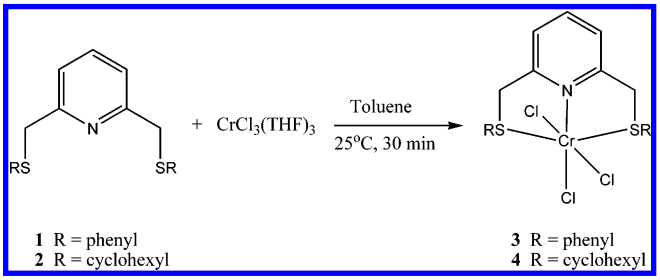
[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F|$. $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

58%). The supernatant was decanted into a vial and stored at room temperature. Green single crystals of complex **6** suitable for X-ray crystallography were isolated from the decanted mother liquor stored in a vial at room temperature. Anal. Calcd (found) for $C_{28}H_{43}NS_2CrCl_3Al$: C 52.29 (52.19); H 6.74 (6.65); N 2.18 (2.05). μ_{eff} = 4.40 μ_B.

General Oligomerization Procedure. A 250 mL steel Büchi reactor was dried in an oven at 120 °C for 3 h prior to each run and then placed under vacuum for 30 min. The reactor was then preheated, charged with toluene and the desired amount of MAO, pressurized with 35 bar of ethylene, and stirred at 50 °C. After 15 min the pressure was momentarily released to allow injecting the catalyst solution into the reactor under a stream of nitrogen, and then the reactor was immediately repressurized. The reaction was allowed to run for 30 min, after which the temperature was rapidly reduced to 5 °C, the reactor was depressurized, and a mixture of EtOH/HCl was injected to quench the reaction. The organic and aqueous phases were then separated from the polymer. Precautions were taken to maintain the temperature as low as possible during the workup to minimize loss of volatiles. Polymeric materials were sonicated with an aqueous solution of HCl and dried at 60 °C for 18 h under reduced pressure before the final mass was weighed. Yields of oligomers were obtained by GC by using calibrated standard solutions. The overall catalytic activity was determined by both GC and by integrating the intensity of the olefinic NMR resonances versus the protons of the toluene solvent, always obtaining consistent results. Samples of **3** and **4** for catalytic runs were dried *in vacuo*, and the complete loss of lattice CH_3CN was monitored by IR.

X-ray Crystallography. Suitable crystals were selected, mounted on a thin, glass fiber with paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1 k CCD diffractometer. For all the compounds data collection was performed with three batch runs at $\phi = 0.00°$ (650 frames), at $\phi = 120.00°$ (650 frames), and at $\phi = 240.00°$ (650 frames). Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. The systematic absences and unit-cell parameters were consistent for the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. All the non-hydrogen atoms in all the structures were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.12 program library. One fully occupied molecule of acetonitrile was found per Cr atom in the lattice of **3** and per four Cr atoms in the lattice of **4**. Crystal data are reported in Table 1, and relevant bond distances and angles in Table 2.

Scheme 1



Results and Discussion

Ligands 2,6-$(RSCH_2)_2$pyridine [R = Ph (**1**), Cy (**2**)] were prepared according to a modified literature method.[13] Although 2,6-bis(phenylthiomethyl)pyridine **1** is already known in the literature for its complexes with Pd,[14] Ni,[15] Cu,[16] and Ru,[17] its chemistry with Cr remains unknown to date. The cyclohexyl derivative **2** was prepared to prevent anticipated solubility problems and would provide a system directly comparable to the previous studies on the cyclohexyl-containing SNS ligand.[7,10]

Complexes [2,6-$(RSCH_2)_2$pyridine]$CrCl_3$ [R = Ph (**3**), Cy (**4**)] were prepared via a simple reaction in toluene of the ligand with $CrCl_3(THF)_3$ (Scheme 1). In both **3** and **4** the tridentate ligands (Figures 1 and 2) are coordinated to the Cr^{III} centers through both sulfur atoms and the nitrogen of the pyridine, in the expected *meridional* manner.

The results of the catalytic testing for ethylene trimerization (30 μmol of catalyst at 50 °C, 150 mL of toluene, 35 bar of ethylene, 30 min reaction time) are summarized in Table 3. Complexes **3** and **4** are exceptionally selective for the production of 1-hexene (>99%) in the presence of MAO activator, with no significant difference in activity or selectivity between the

(14) Canovese, L.; Visentin, F.; Chessa, G.; Uguagliati, P.; Levi, C.; Dolmella, A.; Bandoli, G. *Organometallics* **2006**, *25*, 5355.
(15) Ball, R. J.; Genge, A. R. J.; Radford, A. L.; Skelton, B. W.; Tolhurst V.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2807.
(16) Teixidor, F.; Sanchez-Castello, G.; Lucena, N.; Escriche, L.; Kivekas, R.; Sundberg; M.; Casabo, J. *Inorg. Chem.* **1991**, *30*, 4931.
(17) Viñas, C.; Anglès, P.; Sánchez, G.; Lucena, N.; Teixidor, F.; Escriche, L.; Casabó, J.; Piniella, J. F.; Alvarez-Larena, A.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **1998**, *37*, 701.

Table 2. Selected Bond Distances (Å) and Angles (deg)

3	4	5	6
Cr(1)−Cl(1) = 2.2934(18)	Cr(1)−Cl(1) = 2.325(3)	Cr(1)−Cl(1) = 2.676(3)	Cr(1)−Cl(1) = 2.389(5)
Cr(1)−Cl(2) = 2.2900(19)	Cr(1)−Cl(2) = 2.283(3)	Cr(1)−S(2) = 2.446(3)	Cr(1)−S(2) = 2.541(4)
Cr(1)−Cl(3) = 2.3226(18)	Cr(1)−Cl(3) = 2.320(3)	Cr(1)−S(1) = 2.453(3)	Cr(1)−S(1) = 2.527(4)
Cr(1)−N(1) = 2.096(5)	Cr(1)−N(1) = 2.069(7)	Cr(1)−N(1) = 2.070(8)	Cr(1)−N(1) = 2.140(7)
Cr(1)−S(1) = 2.4458(18)	Cr(1)−S(1) = 2.424(3)	Cr(1)−Cl(1a) = 2.356(3)	Cr(1)···Cl(1a) = 2.813(8)
Cr(1)−S(2) = 2.4205(19)	Cr(1)−S(2) = 2.453(3)	Cr(1)···Cl(2) = 3.287(8)	Cr(1)···Cl(2) = 2.840(9)
Cl(1)−Cr(1)−Cl(2) = 91.80(7)	Cl(1)−Cr(1)−Cl(2) = 92.59(10)	Cl(1)−Cr(1)−N(1) = 97.3(2)	Cl(1)−Cr(1)−N(1) = 177.81(16)
Cl(1)−Cr(1)−Cl(3) = 176.10(7	Cl(1)−Cr(1)−Cl(3) = 174.91(11)	l(1)−Cr(1)−S(1) = 103.29(11)	Cl(1)−Cr(1)−S(1) = 102.35(10)
Cl(1)−Cr(1)−N(1) = 87.64(13)	Cl(1)−Cr(1)−N(1) = 88.1(2)	CCl(1)−Cr(1)−S(2) = 84.54(10)	Cl(1)−Cr(1)−S(2) = 96.89(8)
Cl(1)−Cr(1)−S(1) = 96.16(7)	Cl(1)−Cr(1)−S(1) = 83.92(10)	N(1)−Cr(1)−S(1) = 82.5(2)	N(1)−Cr(1)−S(1) = 79.19(17)
Cl(1)−Cr(1)−S(2) = 82.83(7)	Cl(1)−Cr(1)−S(2) = 95.03(10)	N(1)−Cr(1)−S(2) = 82.7(2)	N(1)−Cr(1)−S(2) = 81.47(16)
Cl(2)−Cr(1)−Cl(3) = 91.90(7)	Cl(2)−Cr(1)−Cl(3) = 92.32(11)	S(1)−Cr(1)−S(2) = 164.04(11)	S(1)−Cr(1)−S(2) = 160.41(9)
Cl(2)−Cr(1)−N(1) = 179.44(14)	Cl(2)−Cr(1)−N(1) = 177.5(2)		
Cl(2)−Cr(1)−S(1) = 97.69(7)	Cl(2)−Cr(1)−S(1) = 93.95(10)		
Cl(2)−Cr(1)−S(2) = 96.41(7)	Cl(2)−Cr(1)−S(2) = 98.87(10)		
Cl(3)−Cr(1)−N(1) = 88.65(13)	Cl(3)−Cr(1)−N(1) = 87.0(2)		
Cl(3)−Cr(1)−S(1) = 84.53(6)	Cl(3)−Cr(1)−S(1) = 97.08(10)		
Cl(3)−Cr(1)−S(2) = 95.56(7)	Cl(3)−Cr(1)−S(2) = 82.88(10)		
N(1)−Cr(1)−S(1) = 82.42(13)	N(1)−Cr(1)−S(1) = 83.8(2)		
N(1)−Cr(1)−S(2) = 83.47(13)	N(1)−Cr(1)−S(2) = 83.4(2)		
S(1)−Cr(1)−S(2) = 165.89(7)	S(1)−Cr(1)−S(2) = 167.17(10)		

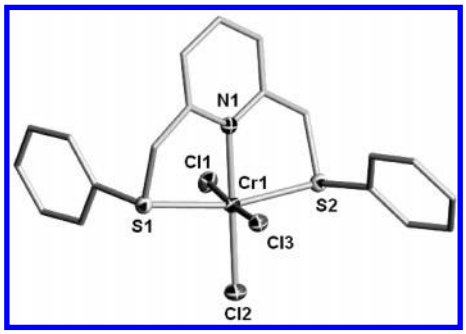


Figure 1. Complex **3** with 30% thermal ellipsoids (solvent molecule omitted for clarity).

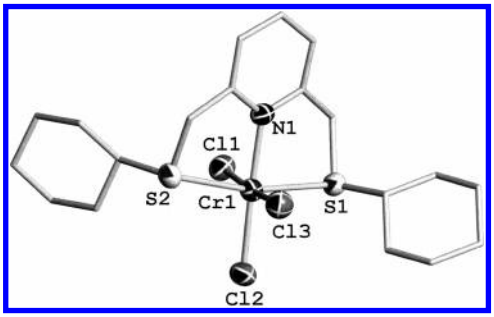


Figure 2. Complex **4** with 30% thermal ellipsoids (solvent molecule omitted for clarity).

Table 3. Cr^{III} Oligomerization Results[a]

				product [mol %]	
catalyst	Al:Cr ratio	PE (g)	activity (g/gCr/h)	C_4	C_6
3	1000	1.8	5263	0.7	99.0
4	1000	1.3	3883	0.0	99.8
4	500	1.3	5177	0.4	99.6
4	100	0.3	3451	1.0	99.0
4	50	trace	863	0	99.5
4	500[b]	0.6	781	0	99.3
4	500[c]	trace	0	0	0.0
4	500[d]	3.4	301	0	99.2

[a] Standard conditions: 30 μmol of catalyst, T = 50 °C, 150 mL of toluene, 35 bar of ethylene, 30 min reaction time. [b] P = 10 bar. [c] T = 22 °C. [d] T = 22 °C, time = 900 min.

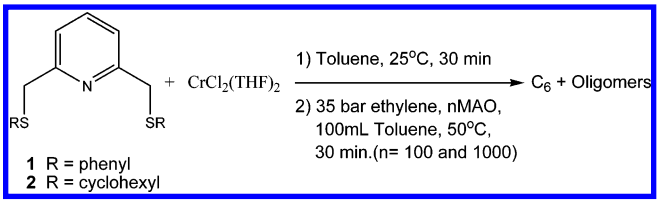
two. When complex **4** was treated with increased loadings of MAO, the general trend (up to 500 equiv) was an increase in activity along with slightly increased polyethylene formation, but there was no concomitant change in the selectivity. At 1000 equiv of MAO the catalyst activity drops, but again there is no change in the selectivity for 1-hexene. At 10 bar of ethylene pressure, the activity was again reduced, but the catalyst was still >99% selective for 1-hexene. Finally, two runs were conducted at room temperature. After 30 min, no activity could be detected, but after 15 h a small amount of 1-hexene was formed.

Table 4. Cr^{II} Oligomerization Results

			product (mol %)						
catalyst	PE (g)	activity (g/gCr/h)	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}
Ph[a]	3.0	5233	5.4[c]	57.8	18.8	8.9	4.9	2.4	1.7
Ph[b]	0.37	6625	6.4[c]	51.2	21.6	10.7	5.7	2.9	1.5
Cy[a]	1.6	5200	3.2[c]	57.2	20.1	10.0	5.3	2.8	1.5
Cy[b]	0.5	660	16.6	83.4	0	0	0	0	0
6[a]	0.4	780	9.9	49.5	20.4	10.3	5.6	2.7	1.6

[a] Al:Cr ratio = 1000. [b] Al:Cr ratio = 100. [c] Venting of the autoclave was performed between 0 and 5 °C to minimize loss.

Scheme 2



To ascertain whether the selectivity of this system is exclusive to the Cr^{III} oxidation state, attempts to prepare Cr^{II} derivatives were carried out. When $CrCl_2(THF)_2$ was treated in the same manner with ligands **1** and **2**, pale orange solids were isolated. Attempts to recrystallize and structurally characterize these solids were hindered by a lack of solubility in all common organic solvents. Therefore, their formulation relies exclusively on analytical data. Interestingly, when dissolved in dichloromethane, an immediate oxidation reaction was observed resulting in a color change and the formation of the Cr^{III} complexes **3** and **4**. This phenomenon has been observed before with the original SNS system.[6a] When the orange solids were treated with THF, the pale blue $CrCl_2(THF)_2$ starting material precipitated, leading to the conclusion that the ligand system is quite labile within these two Cr^{II} complexes. This lability has been observed previously with the Sasol-type SNS Cr^{II} complex [η^1-(SNS)$CrCl_2$(THF)], in which the ligand is coordinated through the nitrogen only and the ligand is easily displaced in THF solutions.[7] When the Cr^{II} species were tested for oligomerization activity under identical conditions (Scheme 2), a complete loss of selectivity was observed in comparison to their Cr^{III} analogues, resulting in a distribution of oligomers centered at 1-hexene (~57%, Table 4). The activity in these runs was

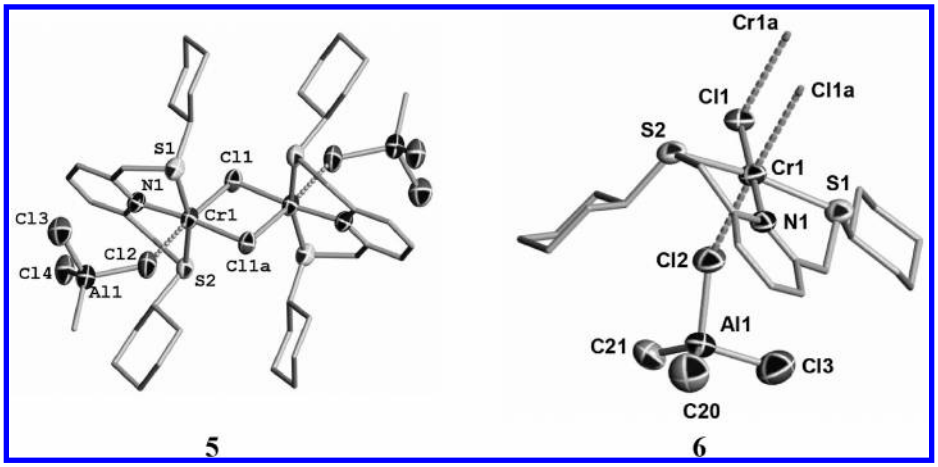
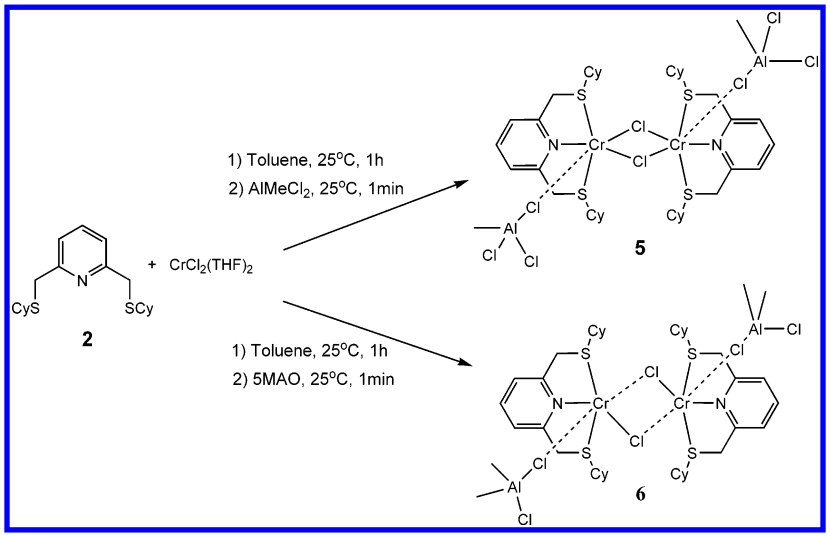


Figure 3. Complexes **5** and **6** with 30% thermal ellipsoids (solvent molecule omitted for clarity).

Scheme 3



comparable to those obtained with the trivalent complexes **3** and **4**. Only in the case of the cyclohexyl derivative with low MAO loading, the higher oligomers disappear in favor of 1-hexene and 1-butene. On the other hand, even the activity shows a 10-fold decrease, possibly suggesting that some other mechanism may become operational under these circumstances.

The distinct difference in catalytic behavior between the divalent and trivalent complexes clearly indicates that the two oxidation states are not readily interchanged during the catalytic cycle. In contrast to the behavior of the $CySCH_2CH_2N(H)CH_2CH_2SCy$ catalytic system, *the trivalent species are not reduced to the divalent state.* Therefore, each oxidation state maintains its integrity during the interaction with the aluminum activator and the oligomerization reaction.

Although we found no conclusive evidence for the reoxidation of Cr^{II} to the trivalent state (as observed with the regular $CySCH_2CH_2N(H)CH_2CH_2SCy$ system), there is a perplexing observation that can be made from the product distribution obtained from the divalent complex. When looking at the α values of the distributions, it is obvious that an enhanced fit can be obtained for the C_8-C_{16} (especially C_8-C_{14}) fractions compared to the C_6-C_{16} fraction. It is tempting to suggest that a small amount of Cr^{III} might indeed be slowly generated from Cr^{II} during the catalytic cycle, possibly via the usual disproportionation mechanism.[10] The trivalent species may be responsible for the amount of 1-hexene exceeding the S−F distribution.

In an attempt to better assess the stability of the metal centers and the difference in behavior of the different oxidation states, complexes **3** and **4** were treated with various alkyl aluminum reagents in order to isolate organochromium species. Regrettably, all reactions yielded oily materials that could not be properly characterized. However, crystalline materials were obtained upon reaction of the corresponding Cr^{II} species with $AlMeCl_2$ and, even more surprisingly, with MAO (the actual activator of the oligomerization cycle) (Scheme 3).

The molecular structures of the corresponding {[2,6-(Cy-$SCH_2)_2$-py]Cr-μ-Cl}$_2$·2[$AlMeCl_3$]·toluene (**5**) and {[2,6-(Cy-$SCH_2)_2$-py]CrCl}[$AlMe_2Cl_2$]·toluene (**6**) were elucidated by X-ray crystallography and are displayed in Figure 3. In both complexes, the metal center is cationized and *the divalent oxidation state was preserved during the reaction,* thus lending further support to the proposal that in the case of the trivalent precursor no reduction occurs in the presence of R_3Al. Complexes **5** and **6** are similar in terms of the coordination environment around the pseudo-octahedral chromium atom and resemble the {SN(H)SCr(μ-Cl)}$_2${(i-Bu)$_2$$AlCl_2$}$_2$ earlier reported.[7] In both complexes, the SNS ligand occupies three coordination sites and the fourth is occupied by one chloride. In the case of **5**, the fifth coordination site is occupied by the bridging chlorine of one identical unit, which builds the dinuclear frame. The last site is defined by the loose coordination of one chloride of the [$MeAlCl_3$]$^-$ counteranion [Cr(1)·Cl(2) = 3.287(8) Å].

The structure of **6** is perhaps better described as monomeric, containing a square-planar chromium atom, given that the bond

with the bridging chlorine of the identical unit is noticeably stretched [Cr(1)··Cl(2) = 2.813(9) Å]. The remaining difference resides in the aluminate counteranion, which appears to be $[Me_2AlCl_2]^-$, with the chloride atom oriented toward the sixth chromium coordination site [Cr(1)··Cl(2) = 2.840(9)Å], but substantially closer to Cr than in **5**. Thus, the coordination geometry around the metal center in **6** may also be regarded as axially very distorted octahedral.

The formation of the divalent **5** and **6** sharply contrasts with the behavior of the Sasol SNS system,[10] which clearly showed the possibility of reoxidation of the metal center upon treatment with the aluminum activators. Unfortunately, since complex **5** could not be isolated in an analytically pure form, it could not be tested in a meaningful manner for catalytic activity. Instead, complex **6** gave, upon further activation with MAO, the same product distribution as observed for the ligand/$CrCl_2$ catalytic system.

In conclusion, we have successfully prepared, characterized, and tested a pyridine-based SNS ligand system and isolated two trivalent complexes **3** and **4**. These species are selective (>99%) catalyst precursors for the trimerization of ethylene to 1-hexene. Unfortunately, the observed activities for these catalysts are only moderate. Structural characterization of the divalent counterpart has been possible only after treatment with alkyl aluminum activators. Of particular interest is the result of the reaction with MAO, which is the actual activator for the catalytic cycle, resulting in the formation of complex **6**. The structure of complex **6** highlights the cationic nature of the metal center, while the true nature of the catalytically active species at this stage can only be speculated upon. Nonetheless, all the divalent derivatives of this ligand system are clearly active but with a complete lack of selectivity. These results concur with the working hypothesis that the stabilization of a trivalent alkyl-Cr is crucial to obtain selective trimerization. Different from the SNS Sasol system, where the trivalent catalyst precursor can be reduced and the trivalent reoxidized in what seems to be steps of the same complex reactivity pattern, the presence of the pyridine ring in the present system stabilizes the individual oxidation states. The fact that the ligand system does not contain an N−H function in the backbone proves that the N−H moiety is *not* responsible for the exceptional selectivity of the SNS class of ligand system and unequivocally demonstrates that the N−H function is not required.

Acknowledgment. This work was supported by the Natural Science and Engineering Council of Canada (NSERC).

Supporting Information Available: Complete crystallographic data (CIF) for the complexes reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700452U