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Role of the Metal Oxidation State in the SNS−Cr Catalyst for Ethylene Trimerization: Isolation of Di- and Trivalent Cationic Intermediates

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Abstract: The reaction of the highly selective $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_3$ catalyst precursor with alkyl aluminum activators was examined with the aim of isolating reactive intermediates. Reaction with Me_3Al afforded a cationic trivalent chromium alkyl species $\{[CySCH_2CH_2N(H)CH_2CH_2SCy]CrMe(\mu\text{-}Cl)\}_2\text{-}\{(AlMe_3)_2(m\text{-}Cl)\}_2\cdot(C_7H_8)_2$ (**1a**). Although it was not possible to obtain crystalline samples of sufficient quality from the reaction with MAO (the most preferred activator), the near-to-identical EPR spectra indicated a very close structural similarity with **1a**. Ethylene oligomerization tests clearly revealed that **1** and other cationic trivalent dimeric complexes $\{[CySCH_2CH_2N(H)CH_2CH_2SCy]\ CrCl(\mu\text{-}Cl)\}_2\{AlCl_4\}_2\cdot(C_7H_8)_{1.5}$ (**2**), monomeric $[(CySCH_2CH_2N(H)CH_2CH_2SCy)CrCl_2\ (THF)][AlCl_4]$ (**3**), and $\{[CySCH_2CH_2N(H)CH_2CH_2SCy]\text{-}Cr(\eta^2\text{-}AlCl_4)\}\{Al_2Cl_7\}$ (**4**) adducts display the same catalyst selectivity as the $[CySCH_2CH_2N(H)CH_2CH_2\text{-}SCy]CrCl_3$ complex and, therefore, are probably all precursors to the same catalytically active species. **2**, **3**, and **4** were obtained upon treatment of $[CySCH_2CH_2N(H)CH_2CH_2SCy]\ CrCl_3$ with different stoichiometric ratios of $AlCl_3$.. When *i*-BAO activator was used, reduction of the metal center occurred readily, affording $\{([CySCH_2CH_2N(H)CH_2CH_2S\ Cy]Cr)(\mu\text{-}Cl)]_2\}\{(i\text{-}Bu)_2AlCl_2\}_2$ (**5**). **5** is also a selective catalyst, thus indicating that trivalent species are most probably precursors to a divalent catalytically active complex. Reaction of $CrCl_2(THF)_2$ with the ligand afforded the labile divalent adduct $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_2(THF)$ (**6**), also catalytically active and selective. Instead, deprotonation of the ligand with *n*-BuLi followed by reaction with $CrCl_2(THF)_2$ gave the dinuclear complex $[(\mu\text{-}CySCH_2CH_2NCH_2CH_2SCy)CrCl]_2$ (**7**), which did not produce oligomers.

Introduction

The interest for ethylene oligomerization is increasingly focusing on the preparation of selective catalysts for the formation of 1-hexene and 1-octene (the most industrially relevant oligomers) and improving catalytic activity.[1] The starting point for the rational design of new catalysts is obviously based on the understanding of the mechanism of the catalytic cycle. It is, therefore, not surprising that considerable debate is focused on the initiation step of the catalytic cycle, the metal oxidation state, the type of chain growth and termination, and, most importantly, about how these factors may affect the selectivity of the reaction.[2] Although chromium appears to be the most preferred metal,[1a] it is not uncommon to find transition-metal complexes across the periodic table that, under Ziegler−Natta conditions, provide promising catalytic oligomerization activity.[3] However, in the vast majority of cases, these reactions afford a statistical distribution of oligomers (Schulz−Flory).[4] Catalysts capable of producing 1-hexene with high selectivity have been found in only two cases,[2l,m,5] and a sole case of a catalyst that predominantly forms 1-octene has only recently been reported.[6]

Trivalent chromium is by far the most commonly encountered species in these catalytic systems,[4−6] and only a few cases

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describing interesting activity from divalent chromium compounds have been documented.[1c,4h,7] However, given the well-established ability of trivalent organo-chromium to give spontaneous reduction to the divalent state upon alkylation,[8] it is conceivable that reduction of the metal center may occur in the early stage of the activation. On the other hand, cationization of a trivalent chromium alkyl via treatment with strong Lewis acids has also been shown to afford oligomerization.[2n] On the contrary, the possibility that the chromium center might be reduced to an even lower monovalent state has also been demonstrated to be, at least in two cases, a viable possibility.[4f,h]

To address the important point of the chromium oxidation state in the catalytically active species and of how this may affect the selectivity of the oligomerization process, we have embarked on a project aimed at isolating and characterizing complexes arising from the reaction of trivalent or divalent chromium complexes with alkyl aluminum derivatives. To this end, we have analyzed the remarkable $[PNP]CrCl_3$ $[PNP = Ph_2PN(R)PPh_2$; R = Cy, Ph] catalytic tetramerization system,[6] finding that the primary interaction of the catalyst precursor with the MAO activator is reduction to the divalent state and cationization.[9] Because one of the most efficient and selective systems for oligomerization involves the use of pyrrole as a ligand system,[1b] we have also examined a highly active catalyst of a s/p-bonded tripyrrole ligand, finding that, again, the trivalent complex acts as a precursor to a divalent species.[10]

Having observed in two cases that reduction of the metal center readily occurs without modification of the catalyst performance, we have herein examined one of the most remarkable catalytic system, $[RSCH_2CH_2N(H)CH_2CH_2SR]CrCl_3$, which provides a rare case of an extremely selective and highly active catalyst for 1-hexene formation.[5d,e] In particular, the questions posed and so far unanswered by this exceptional system are: (1) the metal oxidation state in the catalytically active species or catalyst precursor; and (2) the nature of the complex generated upon the reaction of the trivalent complex with the activator; and (3) the role, if any, of the fairly acidic N−H bond. In addition, will cationization of the metal center occur similarly to the case of the [PNP] tetramerization catalyst[6] and would a divalent $[RSCH_2CH_2N(H)CH_2CH_2SR]Cr$ complex provide the same outstanding selectivity as the starting Cr(III) precursor? In an attempt to address these points and hopefully to assist future catalyst design, we have now reacted the trivalent $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_3$ catalyst precursor and divalent analogues with three different alkyl aluminum activators. The resulting complexes were isolated and tested to assess both activity and selectivity. In addition, we have also examined the effect of the deprotonation of the ligand system.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. The reaction mixtures were analyzed using a CP 9000 gas chromatograph (GC) fitted with a 30 m × 0.32 mm i.d. capillary CP volamine column and with an FID detector. Infrared spectra were recorded on an ABB Bomem FTIR instrument from Nujol mulls prepared in a drybox. 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 1 K Smart CCD area detector. $CrCl_3(THF)_3$ and $CrCl_2(THF)_2$ were prepared according to standard procedures. The $CySCH_2CH_2N(H)CH_2CH_2SCy$ ligand was prepared using a slightly modified literature procedure.[5d] Complex $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_3$ was prepared by adapting the procedure reported in the literature for the phenyl derivative.[5d] Aluminum activators, i-BAO (Aldrich), TMA (Strem), MAO (Chemtura) were used as received.

Preparation of $\{[CySCH_2CH_2N(H)CH_2CH_2SCy]CrMe(\mu\text{-}Cl)\}_2\{(AlMe_3)_2(m\text{-}Cl)\}_2\cdot(C_7H_8)_2$ (1a). A mixture of $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_3$ (0.503 g, 1.1 mmol) and TMA (2.2 mL in hexane 2.0 M, 4.4 mmol) in toluene (10 mL) was stirred at 22 °C resulting in a dark-green suspension. After centrifugation and decantation, the resulting green solution was concentrated in vacuo and stored at −35 °C for 1 day. Green crystals of analytically pure **1a** (0.279 g, 0.20 mmol, 36% based on Cr) were isolated from the solution. IR (Nujol, cm^{-1}) ν_{N-H}: 3181. Anal. Calcd (found) for $C_{30}H_{60}NS_2CrCl_2Al_2$: C 53.32 (53.21); H 8.95 (8.83); N 2.07 (2.01). $\mu_{eff} = 3.94\mu_B$.

Reaction of $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_3$ with MAO Formation of 1b. A mixture of $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_3$

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Table 1. Crystal Data and Structure Analysis Results

	1a	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_{29.85}H_{59.55}-Al_2Cl_{2.15}CrNS_2$	$C_{26.50}H_{43}N-S_2CrCl_6Al$	$C_{20}H_{39}Al-Cl_6CrNOS_2$	$C_{16}H_{30}Al_3-Cl_{12}CrNS_2$	$C_{24}H_{49}Al-Cl_3CrNS_2$	$C_{20}H_{39}Cl_2-CrNOS_2$	$C_{16}H_{30}Cl-CrNS_2$
Mw	678.83	731.42	665.32	858.87	601.09	495.53	387.9(7)
space group	$P2(1)/c$	$P2(1)/n$	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$
a (Å)	13.782(12)	10.8236(18)	7.4228(16)	9.467(5)	10.987(4)	11.198(7)	8.019(3)
b (Å)	12.776(11)	29.167(5)	25.919(6)	11.999(7)	12.816(5)	20.051(15)	8.794(4)
c (Å)	21.606(19)	11.750(2)	16.281(3)	17.895(10	13.475(5)	12.262(9)	14.224(6)
α				83.573(10)	67.230(6)		79.18(3)
β	96.037(16)	104.261(3)	92.681(4)	81.026(10)	83.158(6)	115.98(3)	78.75(6)
γ				67.885(9)	66.385(6)		85.58(4)
V (Å^3)	3783(6)	3595.1(10)	3128.9(12)	1857.1(18)	1601.7(10)	2475(3)	965.5(7)
Z	4	4	4	2	2	4	2
radiation	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	208(2)	198(2)	198(2)	207(2)	208(2)	208(2)	209(2)
D_{calcd} (g cm^{-3})	1.192	1.351	1.412	1.536	1.246	1.330	1.335
μ_{calcd} (mm^{-1})	0.630	0.923	1.054	1.367	0.778	0.857	0.941
F_{000}	1457	1520	1380	864	640	1052	412
R, Rw^{2a}	0.0734, 0.1659	0.0684, 0.1643	0.0676, 0.1262	0.0969, 0.2271	0.0734, 0.1328	0.0642, 0.1173	0.0397, 0.0671
GoF	1.042	1.027	1.040	1.069	1.033	1.012	1.012

[a] $R = \sum jFoj - jFcj/\sum jFj$. $Rw = [\sum(jFoj - jFcj)2/\sum wFo2]^{1/2}$.

(0.475 g, 1.03 mmol) and a 10% MAO solution (3.4 mL toluene, 5.15 mmol) in toluene (15 mL) was stirred at 22 °C, affording a green precipitate (0.599 g). IR (Nujol, cm^{-1}) ν_{N-H}: 3191. Anal. Calcd (found): C (50.91); H (7.63); N (2.31)

Degradation of 1b and Formation of CrCl$_3$(pyridine)$_3$. A suspension of **1b** (0.250 g) in THF (10 mL) was treated with neat pyridine (2 mL). The insoluble solid partly dissolved, and after centrifugation, the resulting solution was allowed to stand at room temperature for 3 days. Dark-green X-ray quality crystals of CrCl$_3$(pyridine)$_3$ separated (0.098 g). Anal. Calcd (found) for $C_{15}H_{15}N_3CrCl_3$: C 45.54(45.41); H 3.82 (3.79); N 10.62 (10.61). $\mu_{eff} = 3.87\ \mu_B$. Crystallographic cell parameters were identical to those reported in the literature.[11]

Preparation of {[CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy]CrCl(μ-Cl)}$_2$-{AlCl$_4$}$_2$·(C$_7$H$_8$)$_3$ (2). A mixture of CrCl$_3$(THF)$_3$ (0.498 g, 1.3 mmol), CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy (0.402 g, 1.3 mmol), and AlCl$_3$(1.729 g, 13.0 mmol) in toluene (15 mL) was refluxed for 5 min, forming a dark-green solution, which was filtered. Dark-green crystals of analytically pure **2** (0.639 mg, 0.43 mmol, 66% based on chromium) were grown during storage at 22 °C for 1 day, followed by storage at −35 °C for 1 day. IR (Nujol, cm^{-1}) ν: 3188. Anal. Calcd (found) for $C_{26.50}H_{43}NS_2CrCl_6Al$: C 43.51 (43.49); H 5.93 (5.88); N, 1.91 (1.86). [$\mu_{eff} = 3.94\mu_B$.]

Preparation of {[CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy]CrCl$_2$(THF)}-{AlCl$_4$} (3). A mixture of CrCl$_3$(THF)$_3$ (0.510 g, 1.3 mmol), CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy (0.402 g, 1.3 mmol), and anhydrous AlCl$_3$ (0.355 g, 2.7 mmol) in toluene (15 mL) was refluxed for 5 min, forming a blue solution, which was filtered. Blue-green crystals of analytically pure **3** (0.752 g, 1.13 mmol, 87%) were grown during storage at −35 °C for a few days. IR (Nujol, cm^{-1}) ν: 3178. Anal. Calcd (found) for $C_{20}H_{39}Cl_6CrNOS_2Al$: C 36.10 (36.09); H 5.91 (5.88); N 2.11 (2.06). $\mu_{eff} = 3.78\mu_B$.

Preparation of {[CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy]Cr(η^2-AlCl$_4$)}-{Al$_2$Cl$_7$} (4). A mixture of CrCl$_3$(THF)$_3$ (0.503 g, 1.3 mmol), CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy (0.402 g, 1.3 mmol), and AlCl$_3$ (3.46 g, 26 mmol) in toluene (15 mL) was refluxed for 5 min, forming a red solution, which was filtered. Red crystals of **4** mixed together with unknown blue-colored materials (0.726 mg,) were separated during storage at −35 °C for a few days. Regrettably, the purification of **4** proved impossible and prevented meaningful analytical determination and catalytic activity testing.

Preparation of {[([CySCH^{2}CH$_2$N(H)CH$_2$CH$_2$SCy]Cr)(μ-Cl)]$_2$}-{(i-Bu)$_2$AlCl$_2$}$_2$ (5). A mixture of [CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy]CrCl$_3$ (0.693 g, 1.5 mmol) and a 10% IBAO solution (7 mL toluene, 2.0 mmol) in toluene (15 mL) was stirred at 22 °C, forming a blue-green suspension. Pale green-blue crystals of **5** (0.333 g, 0.28 mmol, 37% based on chromium) were grown from a centrifuged solution during storage at −35 °C for 1 day. IR (Nujol, cm^{-1}) ν_{N-H}: 3169. Anal. Calcd (found) for $C_{24}H_{49}AlCl_3CrNS_2$: C 47.95 (47.91); H 8.22 (8.19); N 2.33 (2.28). $\mu_{eff} = 4.60\ \mu_B$.

Preparation of [CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy]CrCl$_2$(THF) (6). A mixture of CrCl$_2$(THF)$_2$ (0.507 g, 1.9 mmol) and CySCH$_2$CH$_2$N(H)CH$_2$ CH$_2$SCy (0.570 g, 1.9 mmol) in toluene (30 mL) was stirred at 22 °C, forming a blue solution. Crystals of **6** (0.870 g, 1.8 mmol, 95%) formed over the course of 1 h at −35 °C. IR (Nujol, cm^{-1}) ν: 3173. Anal. Calcd (found) for $C_{20}H_{39}Cl_2CrNOS_2$: C 48.38 (48.31); H 7.92 (7.88); N 2.82 (2.79). $\mu_{eff} = 4.86\ \mu_B$.

Preparation of [(μ-CySCH$_2$CH$_2$NCH$_2$CH$_2$SCy)CrCl]$_2$ (7). To a stirring solution of CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy (0.500 g, 1.6 mmol) in THF (15 mL) *n*-BuLi (0.67 mL of a 2.5 M solution, 1.7 mmol) was added at −35 °C, and the resulting mixture was allowed to warm to room temperature. The addition of CrCl$_2$(THF)$_2$ (0.427 g, 1.6 mmol) to this solution afforded a light-blue solution, which was evaporated to dryness under vacuum. The solid residue was recrystallized from hot toluene to yield blue crystals of **7** (0.560 g, 0.58 mmol, 87% based on chromium) at room temperature. Anal. Calcd (found) for $C_{16}H_{30}ClCrNS_2$: C 49.53 (49.49); H 7.79 (7.73); N 3.61 (3.57). $\mu_{eff} = 3.95\mu_B$.

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 **1a** and **6**, data collection was performed with three batch runs at phi = 0.00 deg (600 frames), at phi = 120.00 deg (600 frames), and at phi = 240.00 deg (600 frames). For **5** and **7**, data collection is performed with four batch runs at phi = 0.00 deg (600 frames), at phi = 90.00 deg (600 frames), at phi = 180.00 deg (600 frames), and at phi = 270.00 deg (600 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 non-hydrogen atoms 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.

Complex **1** has one molecule of toluene per chromium atom in the lattice whose methyl group was disordered over two positions with

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(11) Howard, S. A.; Hardcastle, K. I. *J. Cryst. Spectrosc. Res.* **1985**, *15*, 643.

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

1a	2	3	4
Cr(1)−C(17) = 2.049(5)	Cr(1)−Cl(1) = 2.233(3)	Cr(1)−Cl(1) = 2.295(2)	Cr(1)−Cl(1) = 2.498(4)
Cr(1)−N(1) = 2.088(4)	Cr(1)−N(1) = 2.057(7)	Cr(1)−Cl(2) = 2.292(2)	Cr(1)−Cl(2) = 2.409(3)
Cr(1)−Cl(1) = 2.339(2)	Cr(1)−Cl(2) = 2.364(3)	Cr(1)−N(1) = 2.068(6)	Cr(1)−Cl(3) = 2.229(3)
Cr(1)−S(1) = 2.445(2)	Cr(1)−S(1) = 2.436(3)	Cr(1)−S(1) = 2.440(2)	Cr(1)−N(1) = 2.058(10)
Cr(1)−S(2) = 2.446(2)	Cr(1)−S(2) = 2.447(3)	Cr(1)−S(2) = 2.443(2)	Cr(1)−S(1) = 2.447(4)
Cr(1)−Cl(1a) = 2.519(2)	Cl(1)−Cr(1)−S(1) = 93.41(11)	Cr(1)−O(1) = 2.034(5)	Cr(1)−S(2) = 2.464(4)
Al(1)−Cl(2) = 2.412(3)	Cl(1)−Cr(1)−Cl(2) = 94.34(10)	O(1)−Cr(1)−Cl(1) = 91.92(15)	Al(1)−Cl(1) = 2.218(5)
C(17)−Cr(1)−N(1) = 91.8(2)	Cl(1)−Cr(1)−N(1) = 91.7(2)	O(1)−Cr(1)−Cl(2) = 90.64(15)	Al(1)−Cl(2) = 2.247(5)
C(17)−Cr(1)−Cl(1) = 94.03(16)	Cl(1)−Cr(1)−S(2) = 93.45(10)	O(1)−Cr(1)−S(1) = 95.50(15)	N(1)−Cr(1)−Cl(2) = 170.6(4)
N(1)−Cr(1)−Cl(1) = 174.09(12)	Cl(1)−Cr(1)−Cl(2a) = 179.10(11)	O(1)−Cr(1)−S(2) = 95.38(15)	Cl(1)−Cr(1)−Cl(3) = 178.20(13)
C(17)−Cr(1)−S(1) = 94.67(15)	S(1)−Cr(1)−S(2) = 166.94(11)	O(1)−Cr(1)−N(1) = 179.0(2)	S(1)−Cr(1)−S(2) = 166.16(12)
N(1)−Cr(1)−S(1) = 83.63(13)	S(2)−Cr(1)−Cl(2) = 95.35(9)	N(1)−Cr(1)−Cl(1) = 89.08(18)	Cr(1)−Cl(1)−Al(1) = 90.91(14)
Cl(1)−Cr(1)−S(1) = 95.09(7)	S(1)−Cr(1)−Cl(2) = 95.20(10)	N(1)−Cr(1)−S(1) = 84.31(17)	Cl(1)−Cr(1)−Cl(2) = 82.89(11)
S(1)−Cr−S(2) = 164.87(6)	N(1)−Cr(1)−S(1) = 84.4(2)	Cl(1)−Cr(1)−Cl(2) = 177.12(9)	Cl(1)−Al(1)−Cl(2) = 93.36(16)
Al(1)−Cl(2)−Al(2) = 114.28(9)	N(1)−Cr(1)−S(2) = 84.3(2)	S(1)−Cr(1)−S(2) = 169.12(8)	

5	6	7
Cr(1)−N(1) = 2.134(5)	Cr(1)−O(1) = 2.098(6)	Cr(1)−N(1) = 2.071(3)
Cr(1)−Cl(1) = 2.3486(19)	Cr(1)−N(4) = 2.142(7)	Cr(1)−N(1a) = 2.093(3)
Cr(1)−S(2) = 2.511(2)	Cr(1)−Cl(2) = 2.372(3)	Cr(1)−Cl(1) = 2.3581(16)
Cr(1)−Cl(1a) = 2.714(2)	Cr(1)−Cl(1) = 2.405(3)	Cr(1)−S(2) = 2.5359(17)
N(1)−C(2) = 1.454(8)	Cr (1)−S (1) = 2.846(6)	Cr(1)−S(1) = 2.6948(17)
N(1)−Cr(1)−Cl(1) = 178.79(16)	Cr (1)−S (2) = 2.840(6)	Cr(1)−Cr(1)#1 = 2.9796(18)
N(1)−Cr(1)−S(2) = 82.45(17)	O(1)−Cr(1)−N(4) = 175.4(3)	N(1)−Cr(1)−N(1a) = 88.61(11)
Cl(1)−Cr(1)−S(2) = 97.07(7)	O(1)−Cr(1)−Cl(2) = 90.49(18)	N(1)−Cr(1)−Cl(1) = 176.29(8)
N(1)−Cr(1)−Cl(1a) = 187.57(16)	N(4)−Cr(1)−Cl(2) = 92.0(2)	N(1a)−Cr(1)−Cl(1) = 94.68(8)
	O(1)−Cr(1)−Cl(1) = 90.00(18)	N(1)−Cr(1)−S(2) = 80.26(8)
	N(4)−Cr(1)−Cl(1) = 87.6(2)	N(1a)−Cr(1)−S(2) = 154.52(8)

Table 3[a]

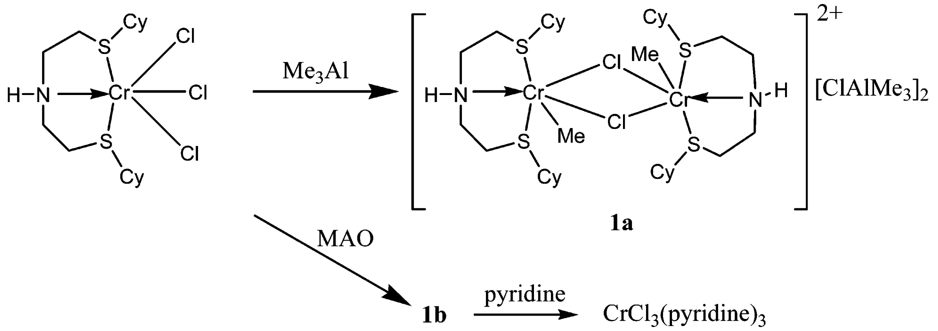
catalyst	MAO (equiv)	alkenes[b] (mL)	PE (g)	activity (g/mol/h)	activity (g/gCr/h)	C_6[c] (mol %)	C_8 (mol %)	C_{10} (mol %)	C_{12} (mol %)	C_{14} (mol %)	C_{16} (mol %)
(SNS)CrCl$_3$	1000	13.5	0.08	302 850	5824	>98	traces	traces	traces	traces	traces
1a	2000	3.5	4.36	78.516	1510	31.98	28.19	18.37	10.98	6.20	4.28
	1000	16.0	0.8	358 933	6903	>98	traces	traces	traces	traces	traces
	500	18.5	0.4	415 016	8024	>98	traces	traces	traces	traces	traces
1b	2000	4.5	3.2	100 950	1941	96.69	0.74	0.74	0.74	0.64	0.44
	1000	5.1	2.3	114 410	2200	>98	traces	traces	traces	traces	traces
2	1000	10.5	0.18	235 550	4530	>98	traces	traces	traces	traces	traces
3	1000	32.2	1.01	723 475	13913	>98	traces	traces	traces	traces	traces
5	2000	3.8	1.47	85 247	1639	53.37	17.90	12.26	8.37	5.04	3.06
	1000	6.0	0.86	134 600	2588	70.79	9.23	8.61	5.66	3.47	2.24
	500	8.2	0.78	185 075	3559	96.53	0.99	0.87	0.72	0.49	0.41
	300	10.5	0.70	235 550	4530	>98	0.36	0.39	0.29	0.19	0.20
6	1000	6.7	2.6	151 425	2912	>98	traces	traces	traces	traces	traces
7	1000	0	0.12	0	0	0	0	0	0	0	0
blank	1000	0	0.08	0	0	0	0	0	0	0	0
CrCl$_2$(THF)$_2$	1000	0	0.42	n/a	n/a	traces	traces	0	0	0	0

[a] $T = 50$ °C, $V = 150$ mL, $P = 35$ bar, catalyst = 30m mole, time = 60 min. [b] By integration of the NMR olefinic resonances with respect to the Me of the toluene solvent. [c] By G.C.; values of C_4 are not given due to volatility.

equal occupancy. The $(Me_3Al)_2(m\text{-}Cl)$ counteranion had one of the six methyl groups carbon atom not properly behaving during the refinement. By arbitrarily attributing 15% chlorine character and the remaining as carbon character, it was possible to obtain a satisfactory refinement. Complex **2** has one and a half molecule of toluene per chromium containing unit. Relevant crystal data and bond distances and angles are given in Tables 1 and 2, respectively.

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 and purged with three cycles of Ar/vacuum. 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 ethylene, and then the reactor was immediately repressurized. The reaction was allowed to run for 45 min, after which the temperature was rapidly reduced, 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. Ratios (or selectivity) of oligomers were obtained by GC by using calibrated standard solutions. The overall catalytic activity was determined by integrating the intensity of the olefinic NMR resonances versus the Me group of the toluene solvent. Results are summarized in Table 3.

Scheme 1



Results and Discussion

The reaction of the catalyst precursor $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_3$ with excess Me_3Al (10 equiv) afforded a good yield of $\{[CySCH_2CH_2N(H)CH_2CH_2SCy]Cr(Me)(m\text{-}Cl\}_2\{(Me_3Al)_2(\mu\text{-}Cl)\}_2$ (**1a**) (Scheme 1), which was isolated as an X-ray quality dark-green crystalline sample.

The structure of **1a** consists of a symmetry generated dicationic dimer with an overall edge-sharing bi-octahedral structure (Figure 1) counterbalanced by two aluminate $[(Me_3Al)_2(m\text{-}Cl)]^-$ anions. The two slightly distorted octahedral chromium atoms in the cationic unit are connected by two bridging chlorine atoms [Cr(1)−Cl(1) = 2.339(2) Å; Cr(1)−Cl(1a) = 2.519(2) Å] forming a Cr_2Cl_2 planar core [Cl(1)−Cr(1)−Cl(1a) = 85.54(6)°; Cr(1)−Cl(1)−Cr(1a) = 94.46(6)°]. The equatorial plane [Cl(1)−Cr(1)−N(1) = 174.09(12)°; Cl(1)−Cr(1)−C(17) = 94.03(16)°; N(1)−Cr(1)−C(17) = 91.8(2)°] around each chromium atom is defined by the two bridging chlorines, the terminally bonded Me group [Cr(1)−C(17) = 2.049(5) Å], and the protonated nitrogen atom of the ligand [Cr(1)−N(1) = 2.088(4) Å]. The sulfur atoms of each ligand are placed on the two axial positions [Cr(1)−S(1) = 2.445(2) Å; Cr(1)−S(2) = 2.446(2) Å], showing substantial deviation from linearity [S(1)−Cr(1)−S(2) = 164.87(6)°]. The presence of the hydrogen on the ligand nitrogen atom is clearly indicated by the deviation of the nitrogen coordination geometry from planarity [C(2)−N(1)−Cr(1) = 113.0(3)°; C(3)−N(1)−Cr(1) = 112.4(3)°; C(2)−N(1)−C(3) = 111.7(4)°]. Two $[(Me_3Al)_2(m\text{-}Cl)]$ anions unconnected to the dicationic chromium unit and two molecules of interstitial toluene complete the structure.

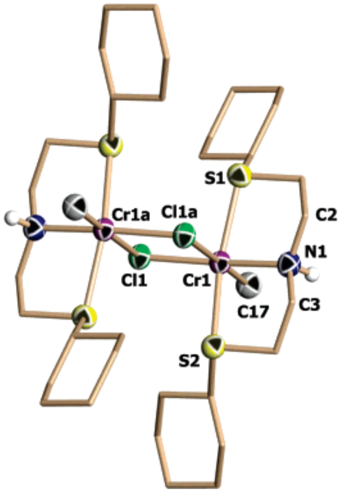
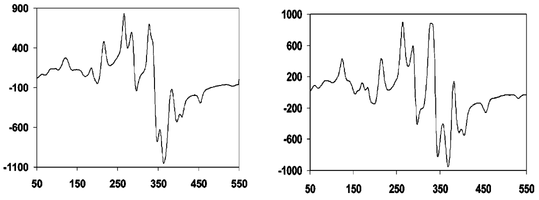


Figure 1. Drawing of the dicationic part of **1a**. The two $[(Me_3Al)_2(m\text{-}Cl)]$ counteranions and two interstitial toluene molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.



1a **1b**

Figure 2. Powder EPR spectrum of Cr(III) of **1a** and **1b** at −160 °C. Frequency = 9118.995 and 9119.687 MHz, respectively. *X* axis in mT.

The fact that the two cationic chromium atoms have retained the original trivalent state is in striking contrast with the $Ph_2PN(R)PPh_2$ [PNP][9] and tripyrrolide chromium[10] catalytic systems where reduction to the divalent state occurred rapidly at room temperature upon mixing the trivalent precursor with an alkyl aluminum. Furthermore, **1a** is thermally robust and showed signs of partial decomposition only after *1 h of reflux in toluene*. However, the rate of the decomposition was greatly accelerated by the presence of excess MAO or Me_3Al. Complete decomposition occurred at room temperature within 1 h upon treatment with 100 equiv of alkyl aluminum reagent. The cationization of the metal center is in line with the behavior of the [PNP] system[9] and provides another case of cationic organochromium species.[2i,n,9,12] The second surprising feature, as indicated by both the structural parameters and the IR spectrum [$\nu_{N-H} = 3181\ cm^{-1}$], is that the N−H function of the ligand remained apparently unmodified in the presence of the alkylating agent.

The same reaction of $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_3$ carried out with MAO (the most preferred activator) afforded also a dark-green homogeneous crystalline substance (**1b**), which regrettably was of insufficient quality for X-ray structural determination. Furthermore, its very low solubility in hydrocarbon solvents prevented recrystallization. However, the very close similarity of the colors of **1a** and **1b** suggested the possibility that the two species might both possess trivalent chromium with similar coordination environments. To substantiate these points, we have recorded EPR spectra of both complexes (Figure 2), because the d^3 and d^4 electronic configurations of Cr(III) and Cr(II) provide distinctively different

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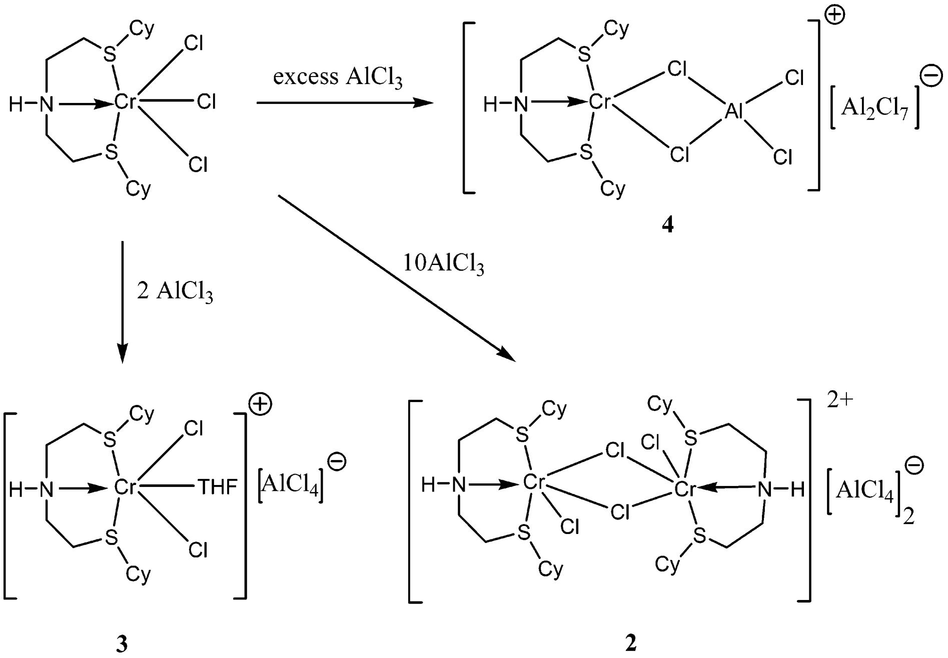
(12) See for example: (a) Foo, D. M.; Sinnema, P. J.; Twamley, B.; Shapiro, P. J. *Organometallics* **2002**, *21*, 1005. (b) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902. (c) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **2005**, *127*, 1082. (d) Kohn, R. D.; Haufe, M.; Kociok-Kohn, G.; Grimm, S.; Wasserschield, P.; Heim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4337. (e) Bazan, G. C.; Rogers, J. S.; Fang, C. C. *Organometallics* **2001**, *20*, 2059. (f) Rogers, J. S.; Bazan, G. C. *Chem. Commun.* **2000**, 1209.

Scheme 2



spectral features. As can be observed in Figure 2, the spectra of **1a** and **1b** display only minor differences. The complexity of the spectra would require an in-depth magnetic study to enable interpretation and simulation of the spectral features that are beyond the scope of this study. However, for the purpose of this work, it will suffice to observe the close spectral similarity, which substantiates the conclusion that even in the case of **1b**, two trivalent chromium species are part of a dinuclear species with an overall integer spin configuration. The room-temperature magnetic moment of **1a** [$\mu_{\mathrm{eff}} = 3.94\ \mu_{\mathrm{BM}}$ per chromium atom] is in the range expected for the high-spin d^3 electronic configuration of an octahedral Cr(III). **1b** has a comparable magnetic moment [$\mu_{\mathrm{eff}} = 3.93\ \mu_{\mathrm{BM}}$ per chromium atom] once the same formulation is assumed with the only difference consisting of the replacement of the Me_3AlCl counteranion with $1/n[MeAlOCl]_n$. We suspect that the polymeric nature of the counteranion is, in fact, most likely responsible for the lack of suitable crystallinity and very poor solubility. Finally, treatment of **1b** in THF with an excess of pyridine afforded a significant amount of $CrCl_3(pyridine)_3$ (Scheme 1). Although other ill-defined byproducts were also formed during this degradation, this experiment qualitatively confirms that complex **1b** also contains trivalent chromium. The IR spectrum of **1b** indicated that, even in this case, the ligand was not deprotonated at the nitrogen atom [$\nu_{\mathrm{N-H}} = 3191\ \mathrm{cm}^{-1}$]. The only significant spectral difference between the two species consists of the presence of a large and intense absorption at 580 cm^{-1} in the spectrum of **1b**, attributable to the Al−O−Al groups.

The behavior of $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_3$ with $AlCl_3$ (Scheme 2) indicates that cationization of the trivalent center is a trend in the reactivity of this catalyst precursor with Lewis acids. The reaction afforded three different cationic complexes, either monomeric or dimeric, depending on the amount of $AlCl_3$ employed. **2** (Figure 3) has the same structure as **1a** except for the replacement of the Me groups by chlorine in both the cationic and anionic moieties. The structure of **2** consists of a symmetry-generated ionic dimer very similar to **1a** (Figure 3). The dicationic unit is formed by two slightly distorted octahedral chromium atoms connected by two bridging chlorine atoms [Cr(1)−Cl(2) = 2.364(3) Å; Cr(1)−Cl(2a) = 2.391(3) Å] forming a planar Cr_2Cl_2 core [Cl(2)−Cr(1)−Cl(2a) = 84.81(9)°; Cr(1)−Cl(2)−Cr(1a) = 95.19(9)°]. The equatorial plane [Cl(2)−Cr(1)−N(1) = 173.9(2)°; Cl(2)−Cr(1)−Cl(1) = 94.34(10)°; N(1)−Cr(1)−Cl(1) = 91.7(2)°] around each chromium atom is defined by three chlorine atoms (two bridging and one terminally bonded) [Cr(1)−Cl(1) = 2.233(3) Å] and the ligand nitrogen atom [Cr(1)−N(1) = 2.057(7) Å]. The sulfur atoms of each ligand are placed on the two axial positions [Cr(1)−S(1) = 2.436(3) Å; Cr(1)−S(2) = 2.447(3) Å], and the

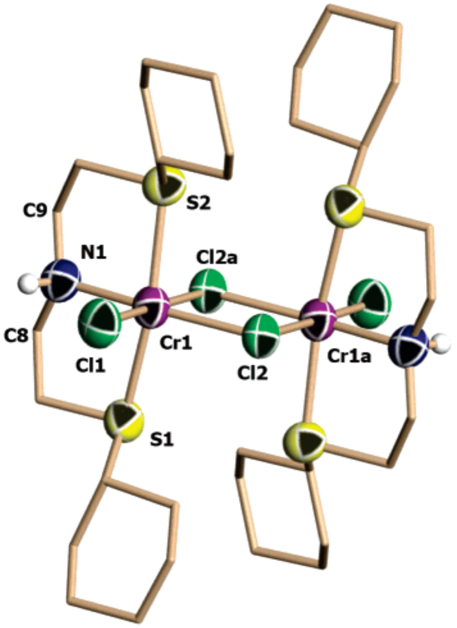


Figure 3. Drawing of the cationic part of **2**. The two $[AlCl_4]^-$ anions have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

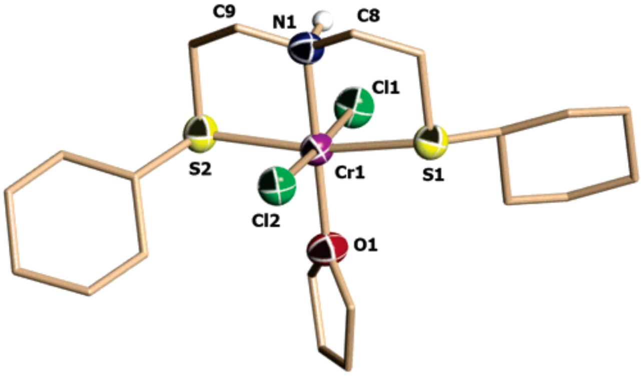


Figure 4. Drawing of the cationic part of **3**. The $AlCl_4$ counteranion has been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

protonation of the ligand nitrogen atom is emphasized by its pyramidal geometry [C(9)−N(1)−C(8) = 113.8(8)°; Cr(1)−N(1)−C(8) = 113.5(6)°; Cr(1)−N(1)−C(9) = 114.5(6)°]. Two tetrahedral $[AlCl_4]^-$ anions unconnected to the dicationic unit complete the structure.

3 is ionic with the cationic moiety consisting of an octahedral chromium atom counterbalanced by one $[AlCl_4]^-$ tetrahedral anion. The cationic unit (Figure 4) has the octahedral coordination geometry of the chromium atom defined by the ligand meridionally arranged [S(1)−Cr(1)−N(1) = 84.31(17)°; S(1)−Cr(1)−S(2) = 169.12(8)°; N(1)−Cr(1)−S(2) = 84.81(17)°]. The three residual coordination sites are occupied by the two trans-located chlorine atoms [Cr(1)−Cl(1) = 2.295(2) Å; Cr(1)−Cl(2) = 2.292(2) Å; Cl(1)−Cr(1)−Cl(2) = 177.12(9)°] and the oxygen atom of one THF molecule [Cr(1)−O(1) = 2.034(5) Å]. Despite the close similarity with the structure of **6**, the Cr−S distances [Cr(1)−S(1) = 2.440(2) Å; Cr(1)−S(2) = 2.443(2) Å] are substantially shorter in the bonding range as a result of the higher oxidation state in combination with the cationic charge for **3** compared to **6**. The nitrogen donor atom of the ligand [Cr(1)−N(1) = 2.068(6) Å] is sp^3 hybridized, as indicated by the out-of-plane arrangement with respect to the two neighboring carbon and chromium atoms [C(8)−N(1)−Cr(1) = 113.8(7)°, C(9)−N(1)−Cr(1) = 111.6(6)°; C(8)−N(1)−C(9) = 115.6(9)°].

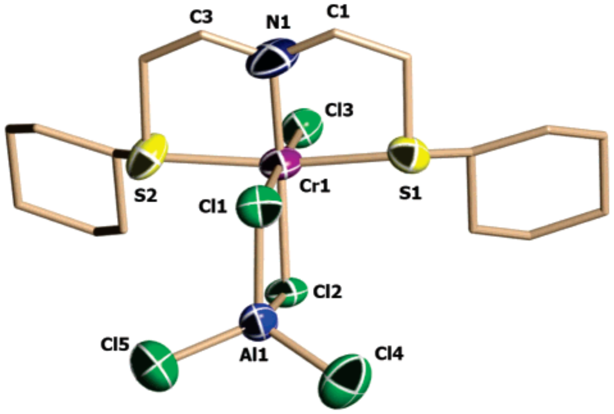
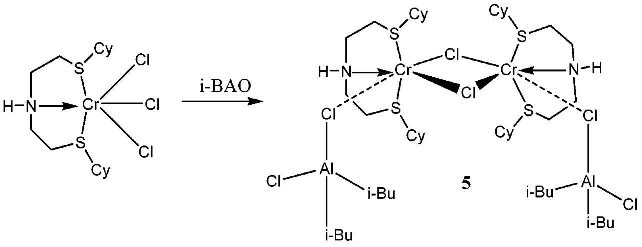


Figure 5. Drawing of the cationic part of **4**. The $[Al_2Cl_7]^-$ anion has been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Scheme 3



4 is a heterobimetallic cationic complex formed by one chromium atom in a regular octahedral coordination environment bridged by two chlorine atoms to a tetrahedral $AlCl_3$ residue (Figure 5). A heavily disordered $[Al_2Cl_7]^-$ anion completes the structure. The coordination environment of the chromium atom [Cl(3)−Cr(1)−Cl(1) = 178.20(13)°; Cl(2)−Cr(1)−N(1) = 170.6(4)°; Cl(2)−Cr(1)−Cl(3) = 95.41(12)°; N(1)−Cr(1)−Cl(1) = 87.7(4)°] is defined by the chlorine atom bridging the aluminum center [Cr(1)−Cl(1) = 2.218(5) Å; Cr(1)−Cl(2) = 2.247(5) Å], one terminal chlorine atom [Cr(1)−Cl(3) = 2.229(3) Å], and the N atom of the ligand system [Cr(1)−N(1) = 2.058(10) Å]. The two sulfur atoms are located on the axial positions [Cr(1)−S(1) = 2.447(4) Å; Cr(1)−S(2) = 2.464(4) Å; S(1)−Cr(1)−S(2) = 166.16(12)°; S(1)−Cr(1)−N(1) = 85.0(3)°; S(1)−Cr(1)−Cl(1) = 85.00(11)°]. The aluminum moiety displays the typical tetrahedral coordination geometry [Cl(1)−Al−Cl(2) = 93.36(16)°); Cl(4)−Al−Cl(5) = 118.7(2)°] with two terminally bonded chlorine atoms [Al(1)−Cl(4) = 2.088(5) Å; Al(1)−Cl(5) = 2.080(5) Å] and the other two bridging the chromium center [Al(1)−Cl(1) = 2.218(5) Å; Al(1)−Cl(2) = 2.247(5) Å]. The $CrAlCl_2$ core is coplanar with the N atom and terminally bonded chlorine atom bonded to chromium [torsion angles: Al(1)−Cl(2)−Cr(1)−Cl(1) = −3.80(14)°; Al−Cl(2)−Cr−N(1) = 2(2)°]. The protonation of the nitrogen atom is evident from the pyramidal geometry of the nitrogen atom [Cr(1)−N(1)−C(1) = 114.8(9)°; Cr(1)−N(1)−C(3) = 116.1(11)°; C(1)−N(1)−C(3) = 122.0(13)°].

Unfortunately, **4** could not be isolated in analytically pure form, thus preventing its full characterization and meaningful catalytic activity testing.

The remarkable thermal stability of **1a** and **1b** *in pure toluene* encourages the idea that, different from the PNP[9] and tripyrrolide catalysts,[10] the oligomerization might be initiated by a trivalent organo-chromium species[2i,n] before the catalyst decomposes in the presence of the large excess of activator required by the catalytic cycle. However, this idea is in contrast with the result of the reaction of $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_3$ catalyst precursor with isobutyl alumoxane [*i*-BAO]. The reaction did not produce the analogue of **1** but yielded instead the new *divalent* species **5** (Scheme 3).

The structure of **5** appears to be very similar to **1a**, the only difference arising from the absence of the terminally bonded methyl groups (Figure 6). As a result, the coordination geometry around each of the two metal centers is square pyramidal [Cl(1)−Cr(1)−S(1) = 97.66(7)°; Cl(1)−Cr(1)−S(2) = 97.07(7)°; N(1)−Cr(1)−S(1) = 82.74(17)°; N(1)−Cr(1)−S(2) = 82.45(17)°] with the basal plane defined by one of the two bridging chlorines [Cr(1)−Cl(1) = 2.3486(19) Å], the ligand nitrogen [Cr(1)−N(1) = 2.134(5) Å], and the two sulfur atoms [Cr(1)−S(1) = 2.519(2) Å, Cr(1)−S(2) = 2.511(2) Å]. The second bridging chlorine is located on the axial position [Cr(1)−Cl(1a) = 2.714(2) Å; Cl(1a)−Cr(1)−N(1) = 87.57(16)°; Cl(1a)−Cr(1)−S(1) = 87.05(7)°; Cl(1a)−Cr(1)−S(2) = 88.74(7)°; Cl(1a)−Cr(1)−Cl(1) = 91.30(6)°]. The chromium atom shows little

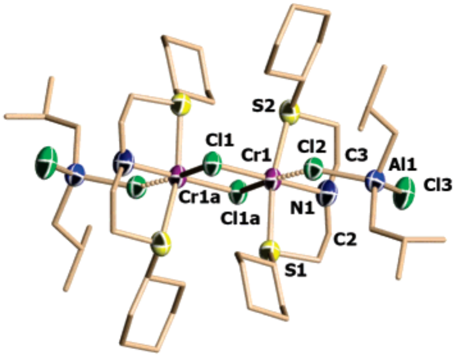


Figure 6. Drawing of **5** with thermal ellipsoids drawn at the 30% probability level.

deviation from the basal plane [Cl(1)−Cr(1)−N(1) = 178.79(16)°; S(1)−Cr(1)−S(2) = 164.76(7)°]. Even in this case, the presence of the proton on the nitrogen atom is indicated by the deviation from the planarity of the N atom [C(2)−N(1)−C(3) = 114.8(6)°; C(2)−N(1)−Cr(1) = 112.8(4)°; C(3)−N(1)−Cr(1) = 111.7(4)°]. Two [*i*-Bu_2AlCl_2] anions complete the structure. One of the two chlorine atoms of the aluminate unit is loosely coordinated to the chromium atom [Cr(1)−Cl(2) = 2.794(2) Å] occupying the sixth position of an ideal octahedron centered on chromium.

The dicationic, dinuclear structure of **5** is closely reminiscent of that of **1a** apart from the absence of the alkyl group attached to chromium, the lower oxidation state, and the loose coordination of the [*i*-Bu_2AlCl_2] counteranion. The fact that, similar to other catalytic systems,[9,10] a divalent species has been formed suggests that **1a** and **1b** may also follow the same reduction pathway during the catalytic cycle. On the other hand, the isobutyl group is more susceptible to reductive elimination than the Me group. Therefore, the spontaneous room-temperature reduction leading to **5** is not particularly surprising. Even in this case, the ligand system was not deprotonated [ν_{N-H}: 3169 cm^{-1}].

Due to the their similarity in terms of ligand arrangement, cationic nature, and dinuclear structure, **1a** and **5** provide a suitable system to compare the effect of the metal oxidation state on catalytic activity and selectivity. While in combination with MAO and under the usual reaction conditions (1000 equiv MAO), **2** and **3** display the same selectivity as **1a**, **1b**, and [$CySCH_2CH_2N(H)CH_2CH_2SCy$]$CrCl_3$, thus suggesting that they can all be precursors to the same catalytically active species (Table 3). The substantial fluctuation of activity observed among these complexes can be ascribed to a combination of different solubility and poor stability in the presence of an excess of MAO. In other words, a less soluble complex would generate a lower concentration of catalyst in solution, given the rather rapid degradation that occurs in the presence of high concentration of cocatalyst. The decrease of activity observed with higher loadings of MAO in the case of **1a**, **1b**, and **5** is most probably the result of catalyst decomposition. As shown in Table 3, the catalytic activity of **5** is somewhat between **1a** and **1b**. Given the fluctuation of activity observed among the trivalent species, the lower activity is not particularly informative. The most striking feature is that, in the presence of a lower loading of MAO, **5** *has the same selectivity* as all the other trivalent precursors. Furthermore, an increase of MAO loading affords for both **1a** and **5** a similar loss of selectivity in favor of a Schulz−Flory distribution. These observations strongly suggest that *both Cr(III) and Cr(II) complexes are precursors to the same catalytically active species most likely containing chromium in the divalent state*. Decomposition or ligand dissociation prior to decomposition (vide infra) could be responsible for the loss of selectivity. **1b** is instead more resilient. The fact that selectivity is preserved with a higher loading of MAO (possibly only the first sign of selectivity loss starts to show at 2000 equiv) can only be ascribed to the nature of the counteranion. In other words, the alumoxane counteranion, though not preventing reduction of the metal center to the divalent state, may somehow improve the robustness of ligand coordination and the stability of the catalytically active species.

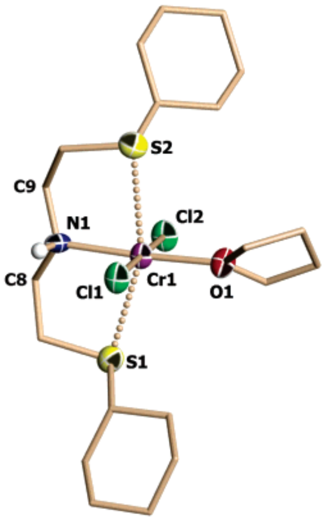
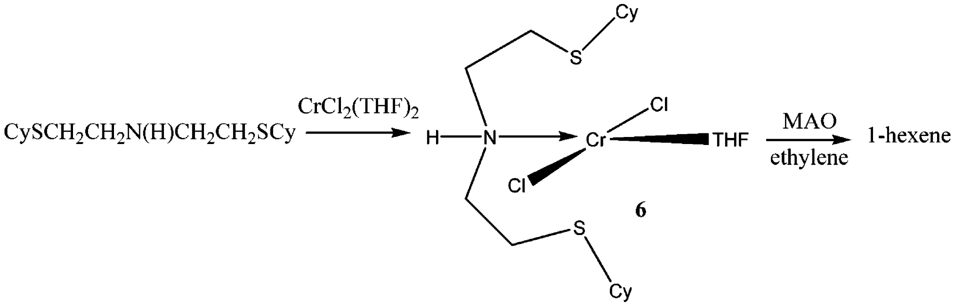


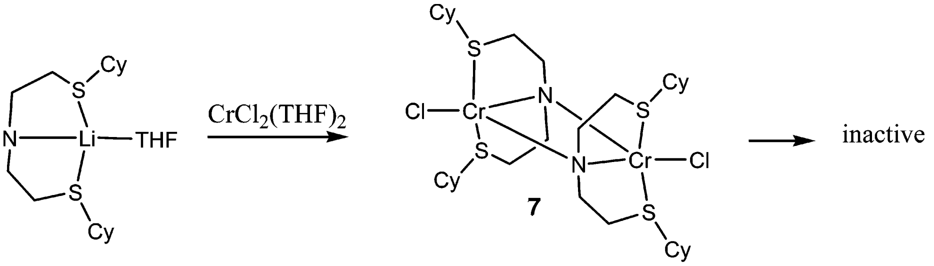
Figure 7. Drawing of **6**. Thermal ellipsoids are drawn at the 30% probability level.

In an attempt to substantiate these working hypotheses, the noncationic Cr(II) complex [$CySCH_2CH_2N(H)CH_2CH_2SCy$]$CrCl_2$(THF) (**6**) was prepared and fully characterized (Scheme 4).

Scheme 4



Scheme 5



6 is a monomer (Figure 7) with the chromium atom in the center of a regular square plane [N(1)−Cr(1)−Cl(1) = 87.6(2)°; N(1)−Cr(1)−Cl(2) = 92.0(2)°; O(1)−Cr(1)−Cl(1) = 90.00(18)°; O(1)−Cr(1)−Cl(2) = 90.49(18)°] defined by the nitrogen atom of the ligand [Cr−N(1) = 2.142(7) Å], two chlorines in trans to each other [Cr−Cl(1) = 2.405(3) Å; Cr−Cl(2) = 2.372(3) Å; Cl(1)−Cr(1)−Cl(2) = 178.49(11)°], and one coordinated molecule of THF [Cr(1)−O(1) = 2.098(6) Å]. The two sulfur atoms are located on the axis of the ideal octahedron centered on chromium. However, the two Cr−S distances [Cr(1)]..S(1) = 2.846(6) Å, Cr(1)..S(2) = 2.840(6) Å] are beyond the normal bonding range. The nitrogen atom of the ligand appears also to carry the proton, as indicated by its pyramidal arrangement [C(8)−N(1)−C(9) = 110.5(6)°; C(8)−N(1)−Cr(1) = 114.3(5)°; C(9)−N(1)−Cr(1) = 112.2(5)°].

Besides the expected square-planar coordination environment expected for the d^4 electronic configuration [$\mu_{\mathrm{eff}} = 4.86\ \mu_{\mathrm{B}}$], **6** shows a curious positioning of the two sulfur donor atoms, which are placed on the axial positions of the ideal octahedral geometry centered on chromium. However, there is a very strong axial elongation that places the S−Cr distances outside the normal bonding range. The fact that the ligand coordination in this neutral divalent chromium may be labile is further suggested by the fact that, during the preparation of **6**, unreacted $CrCl_2(THF)_2$ was always present in the reaction mixtures, unless using a very large excess of ligand. Conversely, in the divalent **5**, the ligand appears to be fully coordinated as a probable result of the cationic nature. **6** shows comparable activity and the same selectivity as **1b,** thus reiterating that the trivalent species is simply a precursor to a divalent complex. The substantially better selectivity of **6** at 1000 equiv of MAO compared to **5** (when **5** has already lost some of its selectivity) is in agreement with the hypothesis that MAO-based counteranions are beneficial for ligand retention.

Another important parameter of this remarkable catalytic system is whether the possible deprotonation of the ligand may play any part in the catalytic system. As clearly indicated by the crystal structures and the IR spectra of all the complexes, the N−H function of the SNS ligand remained unreacted during the reaction with the aluminum alkylating agents. This suggests that the Al−R function does not have sufficient basicity to deprotonate the ligand. Nonetheless, the possibility that deprotonation may occur in the presence of a large excess of alkylating agent cannot be ruled out a priori. Because the $CySCH_2CH_2N(H)CH_2CH_2SCy$ ligand can be readily deprotonated by MeLi or *n*-BuLi, and given that the divalent state is the precursor to the catalytically active divalent state, we have reacted the deprotonated ligand with $CrCl_2(THF)_2$ and obtained the dinuclear complex **7** (Scheme 5).

7 is also a symmetry-generated dimer (Figure 8) where the bridging interaction is realized through the deprotonated nitrogen atoms of two ligands forming a planar Cr_2N_2 core [Cr(1)−N(1) = 2.071(3) Å; Cr(1a)−N(1) = 2.093(3) Å; N(1)−Cr(1)−N(1a) = 88.61(11)°; Cr(1)−N(1)−Cr(1a) = 91.39(11)°]. The coordination geometry of each of the two identical chromium atoms is regular trigonal bipyramidal. The equatorial plane is defined by the two sulfur atoms [Cr(1)−S(1) = 2.6948(17) Å; Cr(1)−S(2) = 2.5359(17) Å] of the same ligand and the bridging nitrogen atom [Cr(1)−N(1a) = 2.093(3) Å] of the second ligand attached to the other chromium atom [S(1)−Cr(1)−N(1a) = 104.93(8)°; S(1)−Cr(1)−S(2) = 96.20(5)°; S(2)−Cr(1)−N(1a) = 154.52(8)°]. The terminally bonded chlorine [Cr(1)−Cl(1) = 2.3581(16) Å] and the nitrogen atoms [Cr(1)−N(1) = 2.071(3) Å] of the ligand coordinated to the chromium atoms are located on the axial positions [N(1)−Cr(1)−Cl(1) = 176.29(8)°].

The dinuclear structure of **7** with the two high-spin coordinatively saturated Cr(II) centers in a trigonal bipyramidal coordination environment is probably very robust and, by not being disrupted by the MAO activator, accounts for the observed *complete lack of oligomerization activity* under the usual reaction conditions. Accordingly, no decomposition or color change was observed when **7** was treated with a large excess of MAO and TMA.

In conclusion, we have attempted to isolate intermediate species formed by the reaction of tri- and divalent chromium $CySCH_2CH_2N(H)CH_2CH_2SCy$ complexes with aluminum activators. Unfortunately, this work did not unveil the structure of the catalytically active species, which would have been the starting point to understanding the marvelous selectivity of this system. Nonetheless, it was possible to obtain some useful information. Our findings indicate that, in line with the other catalytic systems analyzed before,[9,10] *the trivalent oxidation state is a precursor to a Cr(II) species which, in turn, is a precursor to the catalytically active species.* Cationization of the metal

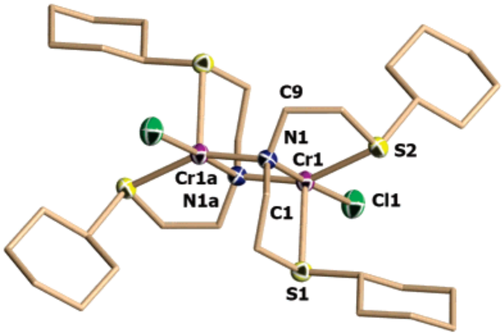


Figure 8. Drawing of **7**. Thermal ellipsoids are drawn at the 30% probability level.

center seems to be a *leit-motif* in the reactivity of these Cr(III) and Cr(II) complexes of this neutral ligand system with aluminum-based Lewis acids. In turn, the cationization is certainly beneficial to improve the retention of the ligand system, which is not deprotonated as a result of the interaction with the cocatalyst. At this stage, it is tempting to speculate that a cationic Cr(II) species, probably carrying an alkyl group and a partly coordinating alumoxane anion, is the active catalyst. Further synthetic efforts in this direction are in progress.

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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.

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