Catalyst Reactivation

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The Question of the Cr Oxidation State in the {Cr(SNS)} Catalyst for Selective Ethylene Trimerization: An Unanticipated Re-Oxidation Pathway**

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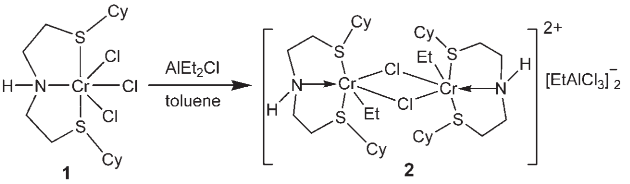
The steady growth of interest in selective ethylene oligomerization[1] is easily understood in view of the importance of linear α-olefins for a wide range of applications. In particular, clarifying the reaction mechanism and identifying the redox couple utilized by the catalytically active species is clearly central to the rational design of new and better catalysts. Among all the metals that are known to catalyze the process, chromium is currently the most preferred since it produces the best activity as well as selectivity.[2] The metallacyclic mechanism[1,3] has become the most favored explanation for the selectivity of the process, yet important questions, including the metal oxidation state,[4] remain unanswered.

Previous work from our group has attempted to address this issue by examining one of the most versatile catalytic systems reported to date, one which is able to selectively tetramerize ethylene. For example, we found that when the trivalent catalyst precursor of the remarkable PNP system ($PNP = Ph_2PN(R)PPh_2$)[5] was exposed to $AlMe_3$, reduction to Cr^{II} and formation of a cationic complex ensued.[6] Along the same lines, a comparative testing of two σ,π-donating tripyrrolide Cr^{III} and Cr^{II} complexes indicated that the Cr^{II} species was more active while producing an identical product distribution to the Cr^{III} complex.[7] These results led us to believe that Cr^{III} is reduced by the alkyl aluminum activator in the early stages of catalyst formation.

A more recent investigation of the highly selective Sasol SNS trimerization system ($SNS = RSCH_2CH_2N(H)CH_2CH_2SR$)[8] initially indicated that even this system follows the same trend.[9] The main supporting evidence for this was the isolation of a divalent, cationic species resulting from the reaction of $[(SNS)CrCl_3]$ (**1**) with isobutylaluminoxane (*i*BAO). On the other hand, the identical reaction of **1** with either methylaluminoxane (MAO) or $AlMe_3$ did not lead to Cr^{II}, but instead gave a thermally robust cationic organochromium(III) species. This result indicates that the SNS ligand system has an unanticipated ability to stabilize some organochromium(III) functions. This observation led us to question whether the Cr^{II} oxidation state is effective in the SNS system. In other words, could the exceptional stability of the cationic Cr^{III}–R function be related to the selectivity? This idea was initially discounted because the Cr^{II} precursors of this ligand system display the same selectivity as the Cr^{III} precursors and that oxidation of Cr^{II} to the trivalent state cannot normally be foreseen in the presence of reducing alkyl aluminum activators. On the other hand, a cationic Cr^{III} species has been shown to perform the trimerization reaction even in the absence of activator.[10]

Herein we propose an intriguing alternative mechanistic possibility based on further results obtained while studying the effects of aluminum-based activators on the {Cr(SNS)} system.

When complex **1** was treated with 10 equivalents of $AlEt_2Cl$ in toluene, the dicationic dimer $[\{(SNS)Cr(\mu\text{-}Cl)Et\}_2][AlEtCl_3]_2$ (**2**) was obtained with an 83% yield of crystalline material (Scheme 1). Surprisingly, the crystal structure (Figure 1) clearly indicated that the trivalent state is preserved in this ethylchromium species.[11] The lack of metal reduction in this case and the isolation of a cationic ethylchromium(III) species in good yield was quite unexpected given the inclination of 1) trivalent organochromium towards reduction and 2) the M–Et function towards β-hydride elimination.[12]



Scheme 1.

The organochromium complex **2** displays a remarkable thermal stability in both the solid state and boiling toluene, where it slowly starts to degrade after one hour under reflux. On the other hand, if **2** is left in an excess of alkylating agent (e.g. MAO, $AlMe_3$, $AlEt_3$), intractable degradation products form rapidly. Since no well-defined/isolatable Cr^{II} complexes were obtained from any of the above reactions, we deliberately attempted the preparation of divalent species by treating $[CrCl_2(thf)_2]$ with either $AlEtCl_2$ or $AlMe_3$ in the presence of SNS (reaction with $AlEt_2Cl$ or NEt_3 led only to intractable materials). In the first case, the reaction did not directly ethylate the Cr center, but rather produced the cationic, monomeric, square-planar complex **3** (Figure 2).

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Supporting Information for this article is available on the WWW under http://www.angewandte.org or from the author.

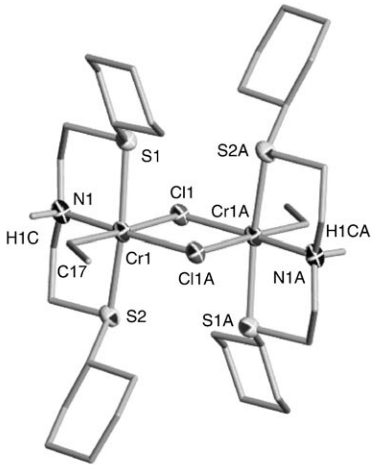


Figure 1. ORTEP view of **2** (thermal ellipsoids set at 30%); Al-containing counterions have been omitted for clarity. Relevant bond lengths [Å]: Cr1–S1 2.4654(14), Cr1–S2 2.4632(14), Cr1–N1 2.090(4), Cr1–Cl1 2.5529(13), Cr1–Cl1A 2.3574(13), Cr1–C17 2.108(5).

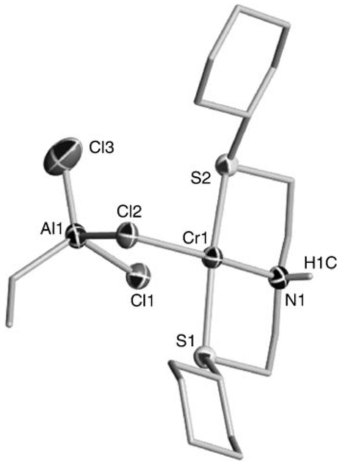
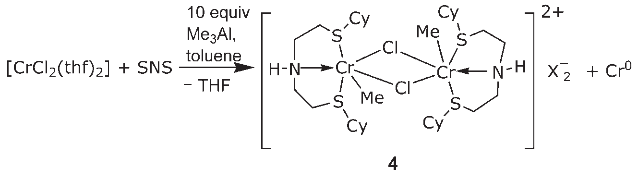


Figure 2. ORTEP view of complex **3** (thermal ellipsoids set at 30%); Al-containing counterions have been omitted for clarity. Relevant bond lengths [Å]: Cr1–S1 2.4828(18), Cr1–S2 2.4844(19), Cr1–N1 2.092(4), Cr1–Cl2 2.3974(17).

This Cr^{II} complex contains a chlorine atom bridging an $\{AlEtCl_2\}$ unit and is counter-balanced by an $[AlEtCl_3]^-$ ion. Thus, cationization also occurs in this case. When the same reaction was carried out with $AlMe_3$, the cationic Cr^{III} complex $[\{(SNS)Cr(\mu\text{-}Cl)Me\}_2][Al_2ClMe_6]_2$ (**4**)[9] was formed and subsequently isolated with a 32% yield of crystalline material. The oxidation of the metal center during the formation of **4** has no straightforward explanation given that an alkylating agent, such as $AlMe_3$, can hardly be regarded as an oxidizing agent. The only possibility of explaining this behavior is to propose that a disproportionation reaction may account for the re-oxidation of the metal center (Scheme 2). This proposal, in turn, implies that a species with a valence lower than two must be generated as a result of the formation of the trivalent **4**. The well-established stability of zero- and monovalent chromium–arene complexes[13] could well be a driving force for the disproportionation. However, we found no evidence for these species, although we did observe that a substantial amount of metallic chromium was invariably present in these reaction mixtures as a black, pyrophoric, and insoluble material. The X-ray fluorescence spectrum of this material confirmed the presence of Cr as the only heavy element while both the IR spectrum and combustion analysis showed the absence of organic functions. Furthermore, the EPR spectrum of the crude reaction mixture was found to be identical to that of an analytically pure sample of **4**,[9] thereby conclusively proving that **4** is the only EPR-active species formed during this unusual reaction.



Scheme 2. X = $[Me_6Al_2Cl]$.

Results of the catalytic testing for ethylene trimerization (30 μmol of catalyst at 50 °C, 35 bar of ethylene, 1 h of reaction time, and 1000 equiv of MAO in 150 mL of toluene) are summarized in Table 1. Upon activation with MAO, the Cr^{III} precursors afford high selectivity. The increase in activity with no change in selectivity observed for complexes **1**, **2**, and **4** follows the order Cl < Me < Et. It is tempting to suggest that this sequence might be related to the different ability of the dinuclear structure of these complexes to dissociate and form coordinatively unsaturated catalytically active species.

Table 1: Oligomerization results.

Catalyst	PE [g]	Activity [g (g Cr)$^{-1}$ h^{-1}]	Product [mol%]		
			C_6	C_8	C_{10}
Cr^{III}					
$[(SNS)CrCl_3]$ (**1**)	0.08	5824	> 98	trace	trace
$[\{(SNS)CrMeCl\}_2]^{2+}$ (**4**)	0.80	6903	> 98	trace	trace
$[\{(SNS)CrEtCl\}_2]^{2+}$ (**2**)	0.80	9383	> 98	trace	trace
Cr^{II}					
$[(SNS)Cr(ClAlEtCl_2)]^+$ (**3**)	0.64	2265	96.39	1.48	0.63

These observations clearly indicate that, contrary to what we previously thought, the Cr^{III} oxidation state delivers a more active and selective catalyst in the case of cationic SNS complexes. On the other hand, our previous work[9] has also shown that this particular system is not immune from reduction to the divalent state. However, we have now discovered that the alkyl aluminum activator may indirectly induce re-oxidation of Cr^{II} towards the more active and selective Cr^{III} catalyst precursor. This oxidation by an alkyl aluminum species is unprecedented and, to our knowledge, has never even been considered. It is therefore tempting to conclude that, in the case of the SNS ligand, the selective trimerization might be performed by a trivalent catalyst. When reduction occurs, the activity of the catalyst decreases and it loses selectivity. Nonetheless, a disproportionation pathway promoted by the aluminum activator may restore the highly active and selective trivalent state, clearly at the expense of the overall concentration of chromium. Ultimately, the chromium complex is irreversibly decomposed to metallic chromium, which, incidentally, offers a reasonable explanation for why these thermally robust trivalent organochromium complexes decompose in the presence of an excess of activator. The possibility that a lower valent chromium species may be responsible for the high catalytic activity and selectivity cannot, in principle, be excluded at this stage. However, in the absence of evidence for stable mono- or zerovalent Cr complexes of this ligand system, this possibility remains, as yet, unsubstantiated. Finally, these results indicate that the N–H group of the ligand backbone is unaffected by the alkylating agents or the Cr–R function under the conditions studied so far for this system.

Experimental Section

2: A mixture of [{CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy}CrCl$_3$] (0.503 g, 1.1 mmol) and AlEt$_2$Cl (1.32 g, 11 mmol) in toluene (15 mL) was stirred at 22 °C to give a dark green solution. After centrifugation and decantation, the resulting green solution was stored at −35 °C for one day. Green crystals of analytically pure **2** (0.570 g, 0.91 mmol, 83 %) were isolated from the solution. IR (nujol): $\nu_{N-H} = 3185\ cm^{-1}$. Elemental analysis (%) calcd for C$_{23.5}$H$_{45}$AlCl$_4$CrNS$_2$: C 45.05, H 7.24, N 2.24; found: C 45.41, H 7.63, N 2.01. $\mu_{eff} = 3.92\,\mu_B$.

3: A mixture of [CrCl$_2$(thf)$_2$] (0.250 g, 0.93 mmol), CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy (0.285 g, 0.95 mmol), and [AlEtCl$_2$] (1.2 g, 9.5 mmol) in toluene (15 mL) was stirred at 22 °C to give a blue solution. Crystals of **3** (0.521 g, 7.7 mmol, 82 %) formed over the course of three days at −35 °C. IR (nujol): $\nu_{N-H} = 3174\ cm^{-1}$. Elemental analysis (%) calcd for C$_{20}$H$_{41}$Al$_2$Cl$_6$CrNS$_2$: C 35.41, H 6.09, N 2.06; found: C 35.61, H 6.33, N 2.01. $\mu_{eff} = 4.83\,\mu_B$.

Cr^{II} oxidation: Preparation of **4**: A mixture of [CrCl$_2$(thf)$_2$] (0.122 g, 0.46 mmol) and CySCH$_2$CH$_2$N(H)CH$_2$CH$_2$SCy (0.138 g, 0.46 mmol) in toluene (5 mL) was stirred at 22 °C to give a blue suspension. AlMe$_3$ (0.329 g, 4.57 mmol) was added and green crystals precipitated immediately. After filtration of the green suspension the solution was stored at −35 °C for 1 h. Complex **4** (0.100 g, 0.15 mmol, 32 %) was isolated as green crystals by removing the mother liquor, washing with hexanes (2 × 5 mL), and drying in vacuo. IR (nujol): $\nu_{N-H} = 3181\ cm^{-1}$. Elemental analysis (%) calcd for C$_{30}$H$_{60}$Al$_2$Cl$_2$CrNS$_2$: C 53.32, H 8.95, N 2.07; found: C 53.41, H 8.73, N 2.01. $\mu_{eff} = 3.94\mu_B$. Pyrophoric, black, and insoluble metallic chromium separated from the mother liquor when it was left to stand at room temperature for a few hours.

Crystal data for **2**: C$_{23.50}$H$_{45}$AlCl$_4$CrNS$_2$, $M_r = 626.51$, monoclinic, $C2/c$, $a = 27.329(4)$, $b = 13.296(2)$, $c = 28.167(6)$ Å, $\beta = 124.302(2)°$, $V = 6462.2(17)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.288\ Mg\,m^{-3}$, $T = 202$ K, absorption coefficient 0.855 mm^{-1}, $F(000) = 2640$, 23795 reflections collected, 5486 independent reflections, GoF = 1.034, $R = 0.0605$ [$I > 2\sigma(I)$], $wR^2 = 0.1443$ [$I > 2\sigma(I)$].

Crystal data for **3**: C$_{20}$H$_{41}$Al$_2$Cl$_6$CrNS$_2$, $M = 678.32$, triclinic, $P\bar{1}$, $a = 11.836(3)$, $b = 12.263(5)$, $c = 12.733(3)$ Å, $\alpha = 75.302(7)°$, $\beta = 74.194(5)°$, $\gamma = 76.374(4)°$, $V = 1692.4(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.331\ Mg\,m^{-3}$, $T = 200.2$ K, absorption coefficient 0.998 mm^{-1}, $F(000) = 704$, 12890 reflections collected, 4792 independent reflections, GoF = 1.025, $R = 0.0621$ [$I > 2\sigma(I)$], $wR^2 = 0.1594$ [$I > 2\sigma(I)$].

CCDC-608869 (**2**) and CCDC-608870 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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