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Ethylene Trimerization with Cr−PNP and Cr−SNS Complexes: Effect of Ligand Structure, Metal Oxidation State, and Role of Activator on Catalysis

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Selected PNP and SNS ethylene trimerization ligands have been coordinated to Cr^{II} and Cr^{III}, and further reactions of these complexes have been studied. The ligands are easily deprotonated to afford monoanionic tridentate ligands. All prepared complexes gave ethylene trimerization catalysis with varying degrees of activity upon activation with both MAO and $AlR_3/B(C_6F_5)_3$. The results of this study show that the role of MAO during activation is one of deprotonation, Cr reduction, and cation generation. A $Cr^{II} \rightarrow Cr^{IV}$ cationic mechanism is suggested.

1. Introduction

While the trimerization of ethylene to 1-hexene has been known for many years,[1] this reaction has gained increased attention recently[2] due to the importance of 1-hexene in the production of linear low-density polyethylene (LLDPE). The trimerization route largely avoids the production of undesired olefins that conventional (full-range) olefin oligomerization processes produce. Perhaps the best known of the ethylene trimerization catalysts is the Chevron Phillips system that is based on pyrrolyl−Cr complexes, which was commercialized in Qatar during 2003.[3] However, a number of other highly active and selective systems based on Cr,[4−7] and also Ti,[8] have recently been disclosed both in the open literature and in corresponding patents. Additionally, an important advance is the selective tetramerization of ethylene to 1-octene, which we have recently reported for the first time.[9] 1-Octene is also an important comonomer used for the production of LLDPE.

We have previously reported on the use of Cr^{III}−PNP and −SNS complexes as highly selective and active systems for ethylene trimerization when activated with MAO.[10,11] The effects of central N-donor substitution, chelate ring size, and also changes to the tridentate donor set have been explored.[12] The most active systems arise with ligands of the type $(RSCH_2CH_2)_2$-NH, in which the S-donor is substituted with an *n*-alkyl group. It was also found that a secondary amine donor was essential for high activity, raising the possibility that the ligand is deprotonated during catalyst activation. However, the precise role of the cocatalyst, the mode of ligand binding, and the oxidation state of the metal during catalysis has hitherto not been studied.

The mechanism of ethylene trimerization is generally supposed to follow a metallacyclic route,[1] involving oxidative addition of two ethylene molecules to the metal followed by insertion of another to yield a metallacycloheptane species, although conclusive experimental evidence for this is limited. Jolly and co-workers[13] have isolated a chromacycloheptane species that liberates 1-hexene upon thermolysis, while Bercaw and co-workers, and our research group, used deuterium-labeled ethylene to probe the mechanism.[6,14] Additionally, Gibson and co-workers have recently provided evidence for large ring

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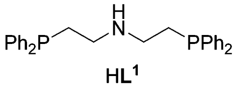
metallacycle intermediates in Schulz−Flory oligomerization.[15] These results provide good evidence for a mechanism based upon metallacycle formation. More extensive mechanistic studies have been carried out by theoretical methods on Cr,[16] Ta,[17] and Ti[18−20] based systems. These studies also support a metallacyclic mechanism. With regards to the formal oxidation state of the metal in Cr-catalyzed trimerization, there is evidence for both Cr^{I}/Cr^{III} [6,21] and Cr^{II}/Cr^{IV} [16,22,23] mechanisms, and it seems possible that the oxidation state of Cr in the catalytic cycle is ligand dependent.

Herein we report further studies on the PNP and SNS trimerization systems in which the nature of the ligand (neutral or anionic), effect of Cr oxidation state, and role of the cocatalyst are investigated. A number of new Cr^{II} and Cr^{III} complexes have been prepared and their reactivity has been studied. Evidence for a cationic Cr^{II}/Cr^{IV} mechanism in which the ligand is monoanonic is presented.

2. Results and Discussion

2.1. Ligands. While PNP and SNS ligands with a low steric demand give rise to the most active catalysts,[10] the aim of the present study was not to prepare highly active catalysts but rather to probe the mechanistic questions posed above. As the synthesis of complexes with lower coordination number was envisaged (see below), we chose to employ ligands with some degree of steric bulk, but not so much that catalysis is completely suppressed. Ligands H**L¹** and H**L²** were thus used in these studies, although highly active trimerization catalysts based on H**L³** and H**L⁴** have also been examined for comparative purposes.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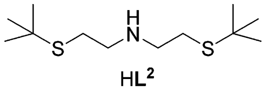
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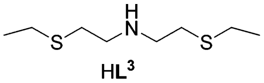
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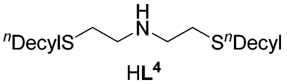

HL⁴

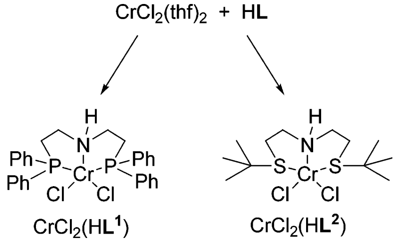
The preparation of $CrCl_3(HL^1)$, and subsequent ethylene trimerization upon activation with MAO, has been reported previously.[10] $CrCl_3(HL^2)$ was prepared in the same manner, and the results of ethylene trimerization reactions using both complexes are shown in Table 1. Entries 1 and 2 show that both complexes give comparable (moderate) activities, with good selectivity toward C_6. The introduction of bulky substituents has attenuated the activity of the SNS catalyst system, as expected. For comparison, a run conducted under comparable conditions with $CrCl_3(HL^3)$ is given in Table 1 (entry 3). It can be seen that less bulky ethyl-S substitution gives rise to a much higher activity.

Table 1. Ethylene Trimerization with Cr−PNP and Cr−SNS Complexes/MAO[a]

entry	catalyst	equiv MAO	PE (wt %)	C_6 (wt %)	selec 1-C_6 (wt %)[b]	TOF (h^{-1})[c]
1	$CrCl_3(HL^1)$	300	1.0	98.7	99.7	24 625
2	$CrCl_3(HL^2)$	150	1.1	98.5	99.8	27 625
3	$CrCl_3(HL^3)$	300	1.7	96.1	99.7	97 880
4	$CrCl_2(HL^1)$	300	1.9	72.2	98.5	26 060
5	$CrCl_2(HL^2)$	150	4.4	94.9	99.8	20 020
6	$[CrClL^1]_2$	300	2.2	79.8	98.5	14 465
7	$[CrClL^2]_2$	300	51.0	45.2	98.8	4785

[a] Conditions: 20 μmol of Cr, 100 mL of toluene, 80 °C, 30 min. [b] Selectivity to 1-hexene within C_6 fraction. [c] TOF = mol(ethylene)·mol(Cr)$^{-1}$·h^{-1}.

Scheme 1. Synthesis of $CrCl_2(HL^1)$ and $CrCl_2(HL^2)$



2.2. Effect of Chromium Oxidation State. Trimerization precatalysts of the PNP and SNS ligands studied here have previously been based exclusively on Cr^{III}, due mainly to the ready availability of the complex precursor, $CrCl_3(thf)_3$. It is possible that this oxidation state is not maintained during activation with MAO, reduction to a lower oxidation state being possible. To study the effect of using precatalysts containing Cr in a lower oxidation state, the complexes $CrCl_2(HL^1)$ and $CrCl_2(HL^2)$ were prepared in good yield (>70%) from $CrCl_2(thf)_2$ and the respective ligand (Scheme 1). The magnetic moments of blue $CrCl_2(HL^1)$ ($\mu_{eff} = 5.14\ \mu_B$) and pale blue-green $CrCl_2(HL^2)$ ($\mu_{eff} = 4.43\ \mu_B$) indicate both complexes are high-spin d^4. Both complexes are highly air and moisture sensitive. Additionally, $CrCl_2(HL^1)$ was found to react exothermically with CH_2Cl_2 to yield $CrCl_3(HL^1)$, presumably via a one-electron oxidation with radical generation,[24] although this was not investigated further.

Crystals of $CrCl_2(HL^1)$ suitable for an X-ray analysis were grown from hot MeCN, and the structure is shown in Figure 1. A square-pyramidal structure is displayed, with the ligand coordinated in a meridonal arrangement. The same mode of coordination was observed in Cr^{III} SNS and PNP complexes,[10,11] and with the exception of an extra chloride ligand in the sixth coordination site of $CrCl_3(HL^1)$, the chromium(II) complex exhibits comparable bond distances and angles (Figure 1). One interesting feature is the NH hydrogen bonding consisting of an intermolecular N−H···Cl bond (N−H···Cl(2′) 2.34(3) Å, N···Cl(2′) 3.17(4) Å, N−H···Cl(2′) 141(4)°) and an intramolecular N−H to apical chloride H-bond (H···Cl 2.71(4) Å, N···Cl 3.220(4) Å, N−H···Cl 113(3)°).

Ethylene trimerization results obtained with these Cr^{II} complexes are shown in Table 1, entries 4 and 5. The activities obtained with both are broadly similar to those obtained with the Cr^{III} congeners, although the selectivities to C_6 are somewhat lower for $CrCl_2(HL^1)$, this being due to the formation of some higher oligomers (C_8-C_{20}). Despite this difference, the results show that Cr^{II} precatalysts do give rise to the active species

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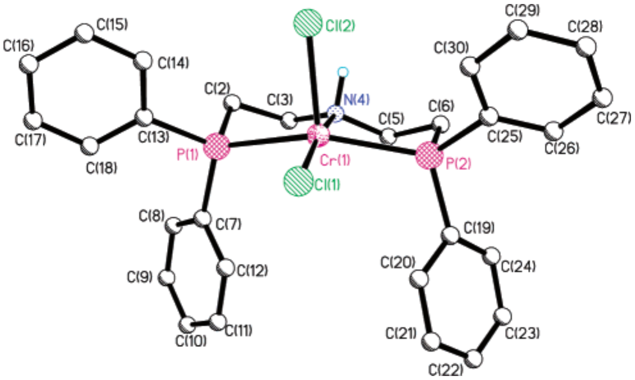


Figure 1. Molecular structure of $CrCl_2(H\mathbf{L}^1)$. Selected bond distances (Å) and angles (deg): Cr(1)−P(1) 2.4789(15); Cr(1)−P(2) 2.4684(14); Cr(1)−N(4) 2.168(4); Cr(1)−Cl(1) 2.3199(13); Cr(1)−Cl(2) 2.4642(14); P(1)−Cr(1)−N(4) 80.83(10); P(2)−Cr(1)−N(4) 81.02(10); P(1)−Cr(1)−P(2) 152.19(5).

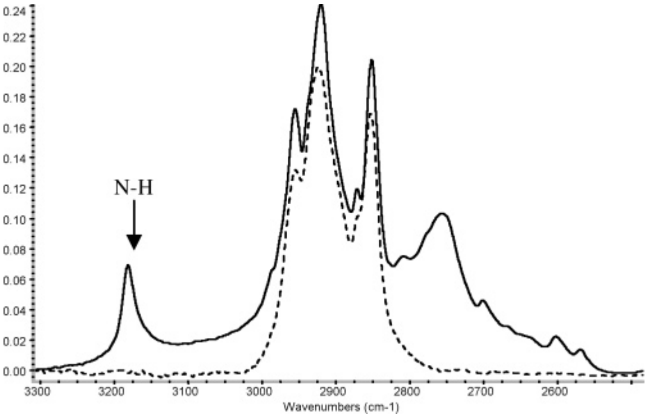


Figure 2. Infrared absorbance spectrum (KBr disk) in the ν(NH) region of $CrCl_3(H\mathbf{L}^4)$ before (—) and after (- - -) treatment with $LiCH_2SiMe_3$.

upon reaction with MAO. Assuming that MAO does not oxidize the Cr^{II} precatalyst, this suggests that, during activation, the Cr^{III} complexes are reduced to an oxidation state of II or lower.

2.3. Ligand Deprotonation. It has been shown that a secondary amine donor is essential to activity; substitution of an alkyl group for the proton results in greatly attenuated activity and selectivity.[12] One explanation for this is that the ligand is deprotonated during activation, yielding a monoanionic tridenate species. This has been investigated by reacting $CrCl_3(H\mathbf{L}^4)$ with $LiCH_2SiMe_3$, a more well-defined alkylating agent than MAO. $LiCH_2SiMe_3$ was chosen in order that an alkylated Cr complex might be isolated. Although we were unable to characterize the product from this reaction, IR spectroscopy clearly shows the disappearance of the strong N−H band at 3182 cm^{-1} (Figure 2). The same result was obtained with deprotonating agents DBU and DABCO (1,4-diazabicyclo(2.2.2)octane). On the basis of these results, it seems likely that MAO, or $AlMe_3$ contained therein, would deprotonate the SNS and PNP ligands during activation.

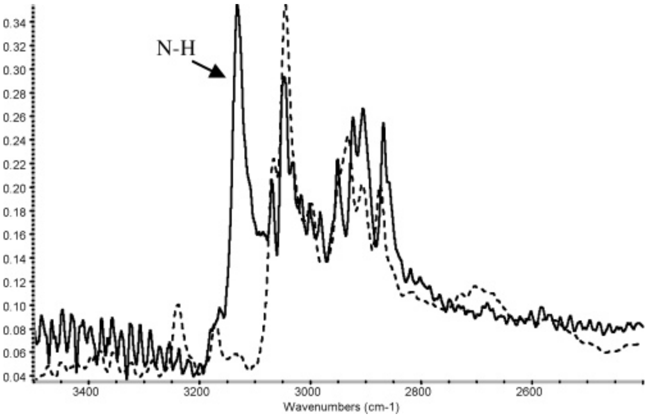
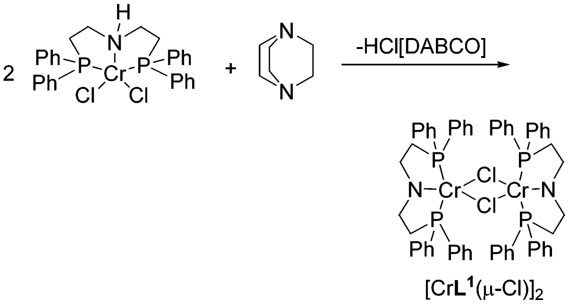


Figure 3. Infrared absorbance spectrum (KBr disk) in the ν(NH) region of $CrCl_2(H\mathbf{L}^1)$ (—) and $[Cr\mathbf{L}^1(\mu\text{-}Cl)]_2$ (- - -).

The coordination chemistry of the anionic ligand $-N(SiMe_2CH_2PPh_2)_2$ with Cr^{II} has been extensively studied by Fryzuk and co-workers in a number of reports.[25] These ligands are closely related to the SNS and PNP trimerization ligands, so we decided to investigate similar chemistry with deprotonated $\mathbf{L}^1$ and $\mathbf{L}^2$. Removal of HCl from $CrCl_2(H\mathbf{L}^1)$ with DABCO proceeded in ca. 50% yield to afford green-yellow $[Cr\mathbf{L}^1(\mu\text{-}Cl)]_2$ (reaction 1). Although a structural determination has not been carried out, a chloride-bridged dimeric structure is proposed on the basis of the structure of $\{Cr[N(SiMe_2CH_2PPh_2)_2](\mu\text{-}Cl)\}_2$ obtained by Fryzuk and the low magnetic moment of 3.79 μ_B per Cr, indicative of antiferromagnetic coupling. The complex can also be prepared in similar yield from the reaction of $Na\mathbf{L}^1$ and $CrCl_2(thf)_2$. In each case a toluene-insoluble purple product also formed, presumably a Cr complex formed by a side reaction (see below). The IR spectra of $CrCl_2(H\mathbf{L}^1)$ and $[Cr\mathbf{L}^1(\mu\text{-}Cl)]_2$ are compared in Figure 3, and again the disappearance of the ν(NH) band at 3132 cm^{-1} supports deprotonation.



(1)

Similarly, reaction of $Li\mathbf{L}^2$ with $CrCl_2(thf)_2$ afforded $[CrCl\mathbf{L}^2]_2$ as dark blue-purple crystals in 59% yield. The magnetic moment of 2.82 μ_B is consistent with either a low-spin d^4 metal center or a dinuclear structure with spin coupling. An X-ray analysis of the complex reveals an unusual dinuclear structure in which the amide donor bridges two Cr centers (Figure 4), with each Cr in a geometry that is midway between square-pyramidal and trigonal-bipyramidal. The Cr−Cr distance of 2.9381(11) Å is indicative of some degree of interaction between the metal centers. The Cr−N distances (2.076(3), 2.071(2) Å) are consistent with Cr−N single bonds. The ligand coordinates in a facial manner, as opposed to the meridonal coordination observed for $H\mathbf{L}^1$ and $H\mathbf{L}^2$. The possibility of this mode of coordination during catalysis has been speculated upon previously[10] (both facial and meridonal modes of coordination have been observed for $-N(SiMe_2CH_2PPh_2)_2$).[25] Evidently, the steric bulk at S is insufficient to prevent dinuclear complex formation. However, it is also interesting to note a large elongation of the Cr−S distances (2.6854(12), 2.5655(10) Å) in this complex relative to those in $CrCl_3(H\mathbf{L}^3)$ (2.4508(7), 2.4556(7) Å). It may be that steric congestion is relieved by elongation of the Cr−S bonds, thus allowing the dinuclear structure to form. The

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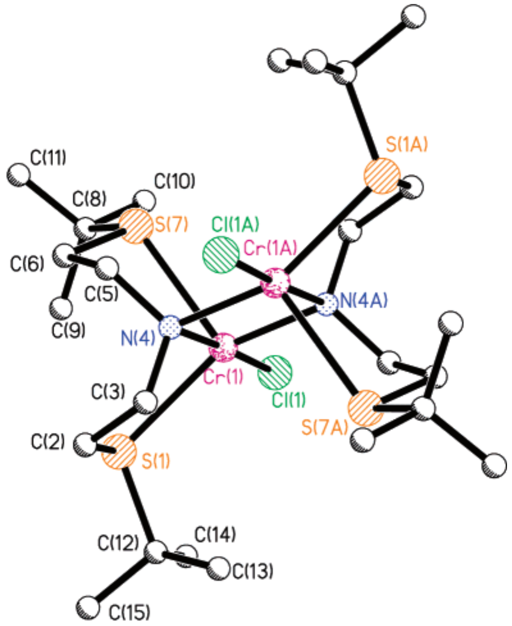

Figure 4. Molecular structure of $[CrCl\mathbf{L}^2]_2$. Selected bond distances (Å) and angles (deg): Cr(1)−S(1) 2.5655(10); Cr(1)−S(7) 2.6854(12); Cr(1)−N(4) 2.076(3); N(4)−Cr(1A) 2.071(2); Cr(1)−Cr(1A) 2.9381(11); Cr(1)−Cl(1) 2.3584(11); S(1)−Cr(1)−S(7) 98.30(4); S(1)−Cr(1)−N(4) 81.55(7); S(7)−Cr(1)−N(4) 80.16(8); N(4)−Cr(1)−Cl(1) 176.94(7); S(1)−Cr(1)−N(4A) 151.73(8); S(7)−Cr(1)−N(4A) 106.70(8); Cr(1)−N(4)−Cr(1A) 90.21(10).

catalytic relevance of such a structure remains uncertain. It is formed in the absence of other ligating compounds; however with ligands such as ethylene or sources of alkyl groups present, it may not form under catalytic conditions.

Both deprotonated Cr^{II} complexes are active for ethylene trimerization after treatment with MAO (Table 1, entries 6 and 7). The activity of $[Cr\mathbf{L}^1(\mu\text{-}Cl)]_2$ is around half of that of $CrCl_2(H\mathbf{L}^1)$, while the activity of $[CrCl\mathbf{L}^2]_2$ is greatly attenuated, relative to the precursor $CrCl_2(H\mathbf{L}^2)$, and a high proportion of polymer was formed. The poor performance of $[CrCl\mathbf{L}^2]_2$ may be due to the bimetallic nature of the precatalyst and bridging coordination of the SNS ligand. Despite this drop in activity, this result shows that the anionic SNS and PNP ligands can give rise to an active species and lends further support to such a mode of coordination during catalysis, resulting from cocatalyst-mediated deprotonation during activation.

The reaction of $Li\mathbf{L}^2$ with $CrCl_3(thf)_3$ was also carried out; however in this case we were unable to isolate the desired complex, $CrCl_2\mathbf{L}^2$. Instead, purple crystals of $[Cr(THF)_2Cl_2(\mu\text{-}Cl_2)Li(THF)_2]$ were obtained from THF solution, as identified by an X-ray structural analysis (see Supporting Information). While the fate of the ligand was not investigated, evidently the LiCl formed during the reaction has complexed to Cr.

2.4. Activation with $AlR_3/B(C_6F_5)_3$. Given the above observations, and the conclusion that the PNP and SNS ligands are deprotonated and monoanionic in the active species, two possible mechanisms for trimerization can be envisaged. A cycle made up of the formal oxidation states $Cr^{I} \rightarrow Cr^{III}$ would involve neutral species, whereas the couple $Cr^{II} \rightarrow Cr^{IV}$ would necessitate formally cationic active species (Scheme 2).

The use of MAO as a cocatalyst in olefin oligomerization and polymerization chemistry is normally thought to implicate a cationic active metal center.[26] Therefore, a cationic mechanism is favored for the SNS and PNP trimerization systems. The use of perfluoroaryl boranes, along with alkyl metal complexes or alkylating agents, has been shown to be a highly effective alternative to the use of MAO, in many instances allowing the characterization of well-defined cationic active species.[26,27] For this reason, the likelihood of a cationic active species has been investigated further by studying $AlR_3/B(C_6F_5)_3$ activation of the Cr−SNS and Cr−PNP systems. The addition of 1 equiv of $B(C_6F_5)_3$ to the alkylated (using $AlMe_3$ or $AlEt_3$) Cr complex was employed. Such a mode of activation is successful with these systems, as shown in Table 2.

The results with $[Cr\mathbf{L}^1(\mu\text{-}Cl)]_2$ show that the amount of trialkylaluminum employed has a large effect on activity. With only 5 equiv of $AlMe_3$ a poor activity is obtained (entry 1), while 10 equiv gives rise to a high activity (notably, higher than when MAO is employed, see Table 1, entry 6). This suggests that a minimum loading of alkyl aluminum is required to fully alkylate the precatalyst and possibly to also act as a poison scavenger. It is notable that this method of activation can give rise to a very high *overall* selectivity (99.3 wt % 1-hexene in entry 2), the implication being that a single active site is formed. Entry 3, in which $B(C_6F_5)_3$ was omitted, shows that the Lewis acid is an essential component, as without it the activity is an order of magnitude less. $AlEt_3$ as the alkylating agent is as effective as $AlMe_3$ (entry 4), although more polyethylene is formed in this case. Employing more $AlEt_3$ (entry 5) does not lead to a significant increase in activity. This method of activation with the SNS complex $[CrCl\mathbf{L}^2]_2$ gave a disappointing selectivity (entry 6). As was found for MAO activation of this complex, a high proportion of polymer was formed.

The precatalysts in which the ligands are protonated are also active after $AlEt_3/B(C_6F_5)_3$ activation. Interestingly, in this case a higher amount of trialkyl aluminum is required to reach full activity. For instance, whereas $[Cr\mathbf{L}^1(\mu\text{-}Cl)]_2$ is fully active with 10 equiv of $AlEt_3$, $CrCl_2(H\mathbf{L}^1)$ requires 20 equiv (cf. entries 7 and 8). This trend seems to continue for the Cr^{III} precursor, $CrCl_3(H\mathbf{L}^1)$, which requires 30 equiv of $AlEt_3$ to reach full activity (entries 10 and 11). This seems to make sense, as extra alkyl aluminum should be required to fully alkylate the di- and trichlorides, deprotonate the nitrogen, and, in the case of Cr^{III}, reduce the metal center. However, it was also found that adding too much $AlEt_3$ leads to deactivation and poor selectivity (entry 12).

Similar results are achieved with $H\mathbf{L}^2$ complexes (entries 9, 13, and 14), although in general the activities and selectivities are lower than those obtained with the $H\mathbf{L}^1$ precatalysts. The method of activation also seems to have an effect on the results obtained. Whereas the normal method employed was to add the trialkyl aluminum to the Cr complex, followed by $B(C_6F_5)_3$ and addition to the reactor, when $AlEt_3$ was first introduced into the reactor, followed by a $Cr/B(C_6F_5)_3$ mixture, a reduced activity and high polymer content resulted ($CrCl_3(H\mathbf{L}^2)$, entry 15).

Finally, $AlEt_3/B(C_6F_5)_3$ activation was also tested along with the more active system $CrCl_3(H\mathbf{L}^3)$. Entries 16−18 show that, in contrast to when MAO is used, poor results were obtained when this complex was employed. Curiously, in this case when no prealkylation step was carried out (the $AlEt_3$ was added to the reactor prior to $Cr/B(C_6F_5)_3$), a much improved activity and selectivity resulted (entry 19). Even so, the activity of this catalyst with $AlEt_3/B(C_6F_5)_3$ activation was well below that obtained with MAO. It was again found for this catalyst that

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[26] Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391, and references therein.

[27] Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.

Scheme 2. Possible Mechanistic Cycles with Cr−SNS and Cr−PNP Complexes: Neutral ($Cr^{I} \rightarrow Cr^{III}$) and Cationic ($Cr^{II} \rightarrow Cr^{IV}$)

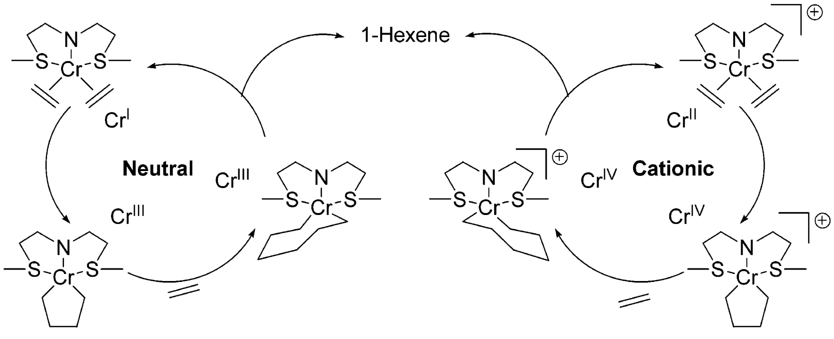

Table 2. Ethylene Trimerization with Cr−PNP and Cr−SNS Complexes/$AlR_3/B(C_6F_5)_3$[a]

entry	catalyst	AlR_3 (equiv)	PE (wt %)	C_6 (wt %)	selec 1-C_6 (wt %)[b]	TOF (h^{-1})
1	$[CrCl\mathbf{L}^1]_2$	$AlMe_3$ (5)	6.3	93.6	99.6	955
2	$[CrCl\mathbf{L}^1]_2$	$AlMe_3$ (10)	0.4	99.6	99.7	21 610
3[c]	$[CrCl\mathbf{L}^1]_2$	$AlMe_3$ (10)	1.7	98.3	99.8	2105
4	$[CrCl\mathbf{L}^1]_2$	$AlEt_3$ (10)	2.8	97.1	99.7	21 850
5	$[CrCl\mathbf{L}^1]_2$	$AlEt_3$ (20)	2.9	96.8	99.7	24 310
6	$[CrCl\mathbf{L}^2]_2$	$AlMe_3$ (5)	85.9	14.1	ca. 100	515
7	$CrCl_2(H\mathbf{L}^1)$	$AlEt_3$ (10)	4.6	95.3	99.2	2300
8	$CrCl_2(H\mathbf{L}^1)$	$AlEt_3$ (20)	0.9	98.9	99.6	41 810
9	$CrCl_2(H\mathbf{L}^2)$	$AlEt_3$ (20)	4.6	94.9	99.7	16 125
10	$CrCl_3(H\mathbf{L}^1)$	$AlEt_3$ (20)	2.5	97.2	99.6	21 160
11	$CrCl_3(H\mathbf{L}^1)$	$AlEt_3$ (30)	2.8	96.5	99.5	25 810
12	$CrCl_3(H\mathbf{L}^1)$	$AlEt_3$ (40)	22.8	76.2	99.5	8270
13	$CrCl_3(H\mathbf{L}^2)$	$AlEt_3$ (20)	10.1	89.3	99.7	10 205
14	$CrCl_3(H\mathbf{L}^2)$	$AlEt_3$ (30)	8.2	90.8	99.4	10 580
15[d]	$CrCl_3(H\mathbf{L}^2)$	$AlEt_3$ (30)	59.6	40.0	98.7	5325
16	$CrCl_3(H\mathbf{L}^3)$	$AlEt_3$ (20)	84.7	15.3	95.5	4630
17	$CrCl_3(H\mathbf{L}^3)$	$AlEt_3$ (30)	40.7	58.4	98.8	7535
18	$CrCl_3(H\mathbf{L}^3)$	$AlEt_3$ (100)	7.7	86.1	89.3	1160
19[d]	$CrCl_3(H\mathbf{L}^3)$	$AlEt_3$ (30)	1.3	97.8	99.5	29 390
20[d]	$CrCl_3(H\mathbf{L}^3)$	$AlEt_3$ (50)	4.0	93.4	95.5	1960

[a] Conditions: 20 μmol of Cr, 20 μmol of $B(C_6F_5)_3$, 100 mL of toluene, 80 °C, 30 min. [b] Selectivity to 1-hexene within C_6 fraction. [c] No $B(C_6F_5)_3$ added in run 3. [d] $AlEt_3$ added to reactor followed by $Cr/B(C_6F_5)_3$ solution, in runs 15, 19, and 20.

too much $AlEt_3$ leads to catalyst deactivation (entry 20). This effect may be related to the know propensity of perfluorophenyl borate anions and AlR_3 to undergo alkyl/aryl exchange, leading to catalyst deactivation.[28]

3. Conclusion

The coordination chemistry of selected PNP and SNS ligands with Cr^{III} and Cr^{II} has been studied, and the resulting complexes were evaluated for ethylene trimerization. The performance of monometallic Cr^{II} precatalysts is comparable with their Cr^{III} counterparts when MAO activation is used and somewhat better when $AlR_3/B(C_6F_5)_3$ is employed. These ligands are easily deprotonated, leading to monoanionic PNP and SNS complexes, which are also active trimerization precatalysts. The complexes can be activated with low amounts of AlR_3 followed by treatment with the alkyl-abstracting agent $B(C_6F_5)_3$, suggesting that a formally cationic active species is responsible for trimerization with these ligands. Although further mechanistic studies are necessary, these facts lead us to suggest a Cr^{II}−Cr^{IV} mechanistic cycle.[29] The role of MAO with $CrCl_3(H\mathbf{L})$ catalysts is thus to deprotonate the ligand, reduce the metal center, and facilitate cation generation.

It is interesting to note that while ligands with a low steric bulk, such as $\mathbf{L}^3$ and $\mathbf{L}^4$, provide the most active systems when MAO is used to activate the complexes, the use of the most sterically encumbered ligand tested in this study ($\mathbf{L}^1$) seems to be most suited to $AlEt_3/B(C_6F_5)_3$ activation. It is well known from olefin polymerization chemistry that cation−anion interactions play a significant role in catalysis, and it seems also for trimerization that the combination of activating agent and ligand must be tailored to obtain the best results. The use of $AlEt_3/B(C_6F_5)_3$ as an activating system is thus of more than just mechanistic interest. The use of MAO, or other $AlMe_3$-derived activators, represents a major cost-driver in the potential large-scale use of such a trimerization technology. The ability to utilize $AlEt_3$ (which is considerably cheaper) as a component of the activating system could therefore provide significant economic benefits, with respect to catalyst cost.

Our structural studies on these ligands and complexes seem to point to a high degree of flexibility in the way the ligand binds to the metal center. Both meridonal and facial type coordination have been observed, and the ability of the SNS ligand to bind with widely varying Cr−S distances is also noted. Such behavior has been postulated for other trimerization ligands. The pendant arene group in Ti trimerization systems is thought to moderate its coordination strength throughout the catalytic cycle,[18−20] while the pyrrolyl ligand of the Phillips catalyst does likewise by undergoing haptotropic shifts between η^1 and η^5 coordination.[16]

4. Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox, using solvents purified and dried by standard procedures. The synthesis of Cr^{III} PNP and SNS complexes has been reported previously.[10,11]

X-ray Crystallography. Data were collected on a Bruker SMART CCD diffractometer and were corrected for absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, *SHELXTL*; Bruker AXS: Madison WI, 2001, version 6.1).

$CrCl_2(H\mathbf{L}^1)$. $C_{28}H_{29}NP_2Cl_2Cr$, $M = 564.36$, blue plate, crystal size 0.1 × 0.1 × 0.01 mm, orthorhombic, *Pbca*, $a = 13.181(4)$ Å, $b = 17.030(5)$ Å, $c = 24.820(8)$ Å, $V = 5571(3)$ Å^3, $Z = 8$, $D_{calcd} = 1.346$ Mg m^{-3}; Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 0.735$ mm^{-1}, $T = 125(2)$ K; 36 107 data (5046 unique, $R_{int} = 0.1378$). $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.1185$, conventional R

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[28] Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908.

[29] We have conducted preliminary magnetic susceptibility studies using the Evans solution NMR method that further support a Cr(II) species upon activation and demonstrate that a similar minimum amount of alkylating agent is required to effect this change. When $CrCl_3(H\mathbf{L}^3)$ ($\mu_{eff} = 4.05\ \mu_B$) is treated with 10 equiv of MAO, the magnetic moment remains unchanged ($\mu_{eff} = 4.08\ \mu_B$), while treatment with 25 equiv of MAO leads to a magnetic moment of 2.95 μ_B, consistent with a low-spin Cr^{II} center (or Cr^{IV}).

$= 0.0600$ for F values of reflections with $F_o^2 > 2\sigma F_o^2$) [3244 observed reflections], $S = 1.031$ for 312 parameters. Residual electron density extremes were 0.775 and -0.458 e Å^{-3}.

[CrClL^2]$_2$. $C_{24}H_{52}N_2S_4Cl_2Cr_2$, $M = 671.82$, blue prism, crystal size 0.13 × 0.1 × 0.1 mm, triclinic, $P\bar{1}$, $a = 8.291(2)$ Å, $b = 9.907(3)$ Å, $c = 11.420(3)$ Å, $\alpha = 88.901(5)°$, $\beta = 70.838(5)°$, $\gamma = 68.979(5)°$ $V = 822.0(4)$ Å^3, $Z = 1$, $D_{calcd} = 1.357$ Mg m^{-3}; Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 1.094$ mm^{-1}, $T = 125(2)$ K, 5276 data (2925 unique, $R_{int} = 0.025$). $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.0670$, conventional $R = 0.0395$ for F values of reflections with $F_o^2 > 2\sigma F_o^2$) [2108 observed reflections], $S = 0.936$ for 155 parameters. Residual electron density extremes were 0.395 and -0.378 e Å^{-3}.

Cr(THF)$_2$Cl$_2$(μ-Cl)$_2$Li(THF)$_2$. $C_{16}H_{32}LiO_4Cl_4Cr$, $M = 489.16$, purple prism, crystal size 0.05 × 0.1 × 0.1 mm, monoclinic, $C2/c$, $a = 36.954(4)$ Å, $b = 10.2303(12)$ Å, $c = 19.885(2)$ Å, $\beta = 117.807(2)°$, $V = 6649.3(13)$ Å^3, $Z = 12$, $D_{calcd} = 1.466$ Mg m^{-3}; Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 1.016$ mm^{-1}, $T = 125(2)$ K, 18 443 data (6041 unique, $R_{int} = 0.047$). $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.1089$, conventional $R = 0.0441$ for F values of reflections with $F_o^2 > 2\sigma F_o^2$ [3926 observed reflections], $S = 0.936$ for 353 parameters. Residual electron density extremes were 0.371and -0.429 e Å^{-3}.

Trimerization. Ethylene trimerization was carried out in a 300 mL stainless steel reactor with mechanical stirring. The oven-dried vessel was purged with N_2 followed by ethylene and charged with 80 mL of toluene. After heating to 80 °C, MAO (AlR_3) was injected followed by a toluene (20 mL) solution of the catalyst. Alternatively, a solution of the catalyst that had been pretreated with AlR_3 followed by $B(C_6F_5)_3$ was added. After addition of Cr, the reactor was immediately charged with 40 bar of ethylene and maintained at this pressure for the duration of the reaction. After 30 min the reactor was cooled in an ice bath, the excess ethylene bled, and an internal standard added (nonane, 1000 μL). After quenching with MeOH followed by 10% HCl, the organic phase was analyzed by GC, while solids were filtered, washed, dried, and weighed.

CrCl$_2$(HL^1). A solution of $(Ph_2PCH_2CH_2)_2NH$ (1.748 g, 3.96 mmol) in 20 mL of THF was added to a suspension of $CrCl_2(thf)_2$ (1.00 g, 3.74 mmol) in 20 mL of THF. The solution was stirred for 2 h and the THF removed under vacuum. The product was recrystallized from 40 mL of hot acetonitrile to give blue crystals, which were suitable for X-ray analysis. Yield: 2.05 g (97%). $\mu_{eff} = 5.14$ μ_B.

CrCl$_2$(HL^2). A solution of $(^tBuSCH_2CH_2)_2NH$ (0.995 g, 3.99 mmol) in 20 mL of THF was added to a suspension of $CrCl_2(thf)_2$ (1.00 g, 3.73 mmol) in 20 mL of THF and stirred overnight. The solvent was removed under vacuum and the residue taken up in 60 mL of hot MeCN and filtered. Cooling to -18 °C gave light blue microneedles. After drying under vacuum a pale blue-green powder remained. Yield: 0.979 g (70%). Anal. Calcd for $C_{12}H_{27}S_2NCrCl_2$ (found): C, 38.70 (38.56); H, 7.31 (7.39); N, 3.76 (3.74). $\mu_{eff} = 4.43$ μ_B.

[CrL^1(μ-Cl)]$_2$. A solution of $CrCl_2(HL^1)$ (0.288 g, 0.510 mmol), prepared as above, in 15 mL of THF was treated with a THF solution of 1,4-diazabicyclo(2.2.2)octane (DABCO, 0.0294 g, 0.262 mmol). After stirring overnight the solution was filtered and the solvent removed under vacuum. The residue was taken up in toluene/THF (10 mL/10 mL) and filtered again. Removal of the solvent afforded a green-yellow solid. Yield: 0.146 g (54%). Anal. Calcd for $C_{28}H_{28}P_2NCrCl$ (found): C, 63.70 (63.89); H, 5.34 (5.41); N, 2.65 (2.73). $\mu_{eff} = 3.79$ μ_B/Cr (5.36 μ_B per dimer).

[CrL^{2}Cl]$_2$. A solution of $(^tBuSCH_2CH_2)_2NH$ (0.485 g, 1.94 mmol) in 10 mL of THF was treated with 1.3 mL of 1.6 M BuLi (2.1 mmol) and stirred for 1 h. The solution was then added to a suspension of $CrCl_2(thf)_2$ (0.495 g, 1.85 mmol) in 20 mL of THF. After stirring for 2 h the solvent was removed under vacuum and the residue taken up in 30 mL of toluene and filtered. The toluene was removed and the product washed with ether (3 × 5 mL) to give a dark purple powder. Yield: 0.366 g (59%). Anal. Calcd for $C_{12}H_{26}S_2NCrCl$ (found): C, 42.91 (42.85); H, 7.80 (7.67); N, 4.17 (4.00). $\mu_{eff} = 2.82$ μ_B/Cr (3.98 μ_B per dimer).

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Supporting Information Available: Crystallographic data, in CIF format, for structures reported. Preparation and crystal structure of $LiCrCl_2(\mu\text{-}Cl)_2(THF)_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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