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First Cr(III)-SNS Complexes and Their Use as Highly Efficient Catalysts for the Trimerization of Ethylene to 1-Hexene

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The selective trimerization of ethylene to 1-hexene is an area of much recent interest¹ due to the importance of this comonomer in the production of polyethylene. The trimerization route largely avoids the production of unwanted olefins that conventional transition metal oligomerization processes produce. We have recently communicated that Cr(III) complexes of tridentate PNP ligands (I), along with MAO cocatalyst, are highly active and selective catalysts for this transformation.² However, the high cost of secondary alkyl phosphine precursors for the synthesis of these ligands makes their use in a potential technical process difficult. Added to this, the toxicity of phosphines and their sensitivity toward oxidation, which makes inert atmosphere techniques necessary for ligand synthesis, represent serious drawbacks for this and other^{1d,3} phosphine-containing systems. In trying to increase the attractiveness of this system, we therefore became interested in alternatives that could replace the phosphorus donor in these ligands, while still maintaining the essential attributes of the donor set. For this purpose, it occurred to us that the thioether donor group may be suitable.4



In principle, an appropriately chosen thioether group should be able to mimic a phosphine group in many circumstances. In the PNP system (I) with Cr as the metal center, it is thought that the phosphine arms operate as soft donor ligands which are capable of facile association—dissociation equilibria, and from this respect the donor properties of thioether groups should be similar. In this report, we detail the synthesis of new SNS complexes of Cr and their use as highly active catalysts for the selective trimerization of ethylene to 1-hexene.

Previous results with PNP ligands I revealed that alkyl groups with a low steric demand on phosphorus give the most active catalysts; we therefore targeted SNS ligands with like substitution. Ligands II–V were prepared by a literature method⁵ that allows simple large-scale benchtop synthesis in high yield, using technical solvents and inexpensive reagents. This ease of synthesis is in contrast to the preparation of ligands I.⁶ Most importantly, the dramatically lower cost of this ligand makes it superior in terms of potential technical application. When reacted with CrCl₃(thf)₃, the immediate formation of complexes 1-4 was observed, which were isolated as blue-green powders in 87-96% yield (Scheme 1).



Complexes 1-4 represent new additions to a rare class of complexes that display Cr^{III} -thioether bonding.^{7,8}

Initial catalytic tests to probe the activity of the complexes were carried out in a 75 mL autoclave, immersed in a oil bath heated to 80 °C. The results of this catalytic testing of 1-3 for ethylene trimerization are given in Table 1.

Along with MAO as cocatalyst, all complexes gave rise to highly active and selective catalysts for the trimerization of ethylene to 1-hexene. Table 1 shows that over a 30 min run, TOFs (of ethylene conversion) of between ca. 75 000 and 95 000 were obtained with total C_6 selectivities of 93–94% (entries 1–3). Furthermore, the hexene fraction was composed of over 99.3% 1-hexene in each case. The methyl-substituted and ethyl-substituted complexes gave rise to catalysts with the same activity and selectivity, while complex **3** was significantly more active than the complexes with shorter alkyl chains. It should be noted here that the procatalyst **3** was noticeably more soluble in toluene than were **1** and **2**, and an activity contribution from this effect cannot be ruled out.

After these initial tests, complexes **2** and **4** were taken for further optimization, and the results are shown in Table 2. These reactions were carried out in a 300 mL Parr autoclave fitted with a gas entraining stirrer and internal temperature control, allowing the temperature to be maintained at close to 85 (complex **2**) and 90 °C (complex **4**) during the reaction. Results using complex **2** reveal that very low concentrations of catalyst in this system led to extremely high activities and unparalleled selectivity toward C₆. For instance, with 280 equiv of MAO, an activity of 160 840 g/g of Cr/h was obtained (TOF = 298 900), with a selectivity toward C₆ of 98.4%, of which 99.7% was 1-hexene. Trimerization is best conducted at an ethylene pressure of 30–50 bar. At higher pressure (70 bar), no increase in activity results, but a greater amount of polymer is formed (entry 6).

Results using the more soluble complex **4** reveal that by using similar pressures, temperatures, and chromium concentrations, we could achieve high catalyst activity in the presence of a very low amount of MAO (30-100 equiv). This, as alluded to earlier, may in part be due to the enhanced solubility in toluene that the longer alkyl chain affords. The ability of the catalyst to operate at low cocatalyst loadings becomes crucially important in the potential

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entry	run time	PE	hexenes	1-hexene	TON	TOF
(complex)	(min)	(wt %)	(wt %)	(wt %) ^b		(h ⁻¹) ^c
$ \begin{array}{r} 1 (1) \\ 2 (2) \\ 3 (3) \\ 4 (1) \\ 5 (2) \end{array} $	30	0.11	94	99.7	38 530	77 050
	30	0.66	94	99.7	37 630	75 260
	30	0.97	93	99.3	47 730	95 470
	60	0.32	95	99.8	49 400	49 400
	60	0.27	95	99.7	59 780	59 780
6 (3)	60	0.50	93	99.7	59 220	59 220

^a Conditions: 11.0-12.0 µmol of complex, 600-650 MAO, 25 mL of toluene, 40 bar of ethylene, 80 °C. ^b Selectivity for 1-hexene as a percentage of total C₆ fraction. ^c TOF of ethylene conversion averaged over complete run.

Table 2. Ethylene Trimerization with 2 and 4^a

entry	$\mu \mathrm{mol}$ of Cr	equiv of MAO	pressure (bar)	PE (wt %)	C ₆ (wt %)	1-C ₆ (wt %)	TOF (h ⁻¹)	productivity (g/g of Cr/h)
1 (2)	4.6	280	30	0.16	98.4	99.7	298 900	160 840
2 (2)	4.3	120	30	0.38	97.1	99.8	104 870	56 260
3 (2)	12.0	200	50	0.10	98.0	99.7	211 820	113 950
4 (2)	20.0	120	30	0.14	96.6	99.6	113 550	61 060
5 (2)	20.0	280	30	0.14	96.7	99.6	190 560	102 470
6 (2)	20.0	120	70	1.15	96.4	99.7	86 480	46 660
7 (4)	12	100	45	0.30	97.2	99.7	263 757	142 035
8 (4)	12	30	45	1.51	97.4	99.7	147 619	82 654
9 (4)	8	50	45	1.11	98.7	99.8	153 482	85 950

^a Conditions: 100 mL of toluene, 30 min.



Figure 1. Molecular structure of 2. Selected bond distances (Å) and angles (deg): Cr-N 2.1059(18), Cr-S1 2.4508(7), Cr-S2 2.4556(7), Cr-Cl1 2.2985(8), Cr-Cl2 2.3184(7), Cr-Cl3 2.3167(7), N-Cr-S1 83.07(5), N-Cr-S2 82.90(5), S1-Cr-Cl1 97.20(2), S2-Cr-Cl1 96.85(2), N-Cr-Cl1 179.71(5), N-Cr-Cl2 85.82(6), N-Cr-Cl3 88.64(6).

industrial use of this and other systems. The results presented in Table 2 show that the complexes give activity comparable to those of the best trimerization systems available, but that significantly enhanced selectivity is achieved. While trimerization systems of like high activity^{1b,d} give <93% selectivity to C₆, the very high selectivities obtained with this system represent an important advance in terms of process economy.

There are very few examples of structurally characterized thioether complexes of CrIII,7 and, in all but one,8 the thioether donor forms part of a macrocyclic ring. Single crystals of 2 suitable for X-ray diffraction studies were grown by slow evaporation of a nitromethane solution of the complex. The molecular structure of 2, along with selected bond lengths and angles, is shown in Figure $1.^{9}$ It is instructive to compare the ligand bonding parameters of 2 with those in the closely related PNP-Cr trimerization catalyst $CrCl_3$ { $HN(CH_2CH_2PPh_2)_2$ }, which incorporates ligand **I**.² In both complexes, the Cr displays the expected octahedral coordination geometry, with the tridentate ligand coordinated in a meridonal fasion. The chelate bite angles of the SNS ligand in 2 [83.07(5)°, 82.90(5)°] compare similarly to those in the PNP complex [81.08(8)°, 82.07(8)°]. The Cr-S distances [2.4508(7), 2.4556(7)

Å] are likewise similar to the Cr-P distances [2.4660(12), 2.4678(12) Å] and indicate a similar degree of donor-Cr bonding. The Cr–N distance in 2 [2.1059(18) Å] is somewhat shorter than that in the PNP analogue [2.139(3) Å], but overall it can be said that the metal-ligand bonding in 2 and the PNP analogue is very similar. This supports our supposition that the thioether group can make an effective substitute for the phosphine donor group in certain circumstances.

In summary, we have developed highly efficient new catalysts for the trimerization of ethylene which are characterized by a simple and inexpensive synthesis. This, coupled with the high activity, excellent selectivity, and performance in the presence of low amounts of MAO, means that the potential of this system being employed to produce 1-hexene on a large scale is promising. The high cost of ligand is often a limiting factor in the application of new homogeneous catalysts based on phosphine ligands; however, we have demonstrated here that thioether donor groups can make effective substitutes. The application of sulfur-based ligands in homogeneous catalysis has recently been reviewed.⁴ This report showed that, on the whole, sulfur ligands have received very little attention, and the instances where catalysis has been studied with sulfur-based ligands have almost exclusively involved late transition metals. We have shown here for the first time the positive effect sulfur ligands are capable of having on an early transition metal for olefin oligomerization. While it appears sulfur-based ancillary ligands have, to an extent, been overlooked, these ligands have great potential in many types of homogeneous catalysis, and this aspect of their chemistry is under further investigation.

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Supporting Information Available: Crystallographic data, in CIF format, for structure 2. Preparation of 1-4 and X-ray structure determination (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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