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Highly Selective Chromium(III) Ethylene Trimerization Catalysts with [NON] and [NSN] Heteroscorpionate Ligands

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Summary: Cr(III) complexes with [NON] and [NSN] heteroscorpionate ligands derived from bis(pyrazol-1-yl)methane have been prepared, which are active for ethylene trimerization to 1-hexene with high selectivity. Structural studies have established the coordination of the ether or thioether pendant group, which leads to a bicyclic metallaheterocycle flanked by pyrazoyl rings.

The oligomerization of ethylene typically gives a broad distribution of α-olefins which requires fractional distillation of the products to give relatively low yields of the desired fractions.[1] In view of the importance of 1-hexene in the production of linear low-density polyethylene (LLDPE), there is a critical need to develop a methodology for selective trimerization of ethylene to 1-hexene.[2] Although this was first achieved with Cr-based catalysts in 1977,[3] there are very few highly active and selective catalysts for this conversion and they include the Phillips pyrrolide,[4] the BP diphosphine,[5] and the Sasol mixed heteroatomic[6] systems.

The mechanism of this selective catalytic oligomerization is generally considered to involve metallacyclic intermediates. Oxidative addition of two ethylene molecules to the metal followed by ethylene insertion yields a metallacycloheptane entity.[7] Considerable debate, however, remains concerning the catalytic initiation, the metal oxidation state, the nature of the chain growth and termination steps, and, perhaps most importantly, the interplay of these factors in determining oligomer selection.[8] Although it is clear that the selectivity is sensitive to the ligand environment of the metal, details of such dependence remain largely speculative. It is therefore important to explore a variety of ligand designs and examine the catalytic efficiency and selectivity of the corresponding metal complexes. Our interest in heterofunctional, especially hemilabile, ligands is stimulated by their catalytic relevance.[9] Accordingly, the recent use of neutral heteroscorpionate ligands derived from bis(pyrazol-1-yl)methane has attracted our attention because they are adpatable to a range of metals, can be sterically and electronically tuned, and constitute multidentate hybrid ligands.[10] We report herein a novel Cr(III) catalytic system with hitherto unknown heteroscorpionate pyrazolyl ligands of the type Pz_2CHCH_2XR (Pz = pyrazol-l-yl, X = O, S, R = alkyl, aryl) (Scheme 1). Notwithstanding the large number of known heteroscorpionates, very few contain an ether or thioether pendant functional group, and such examples include anisolyl

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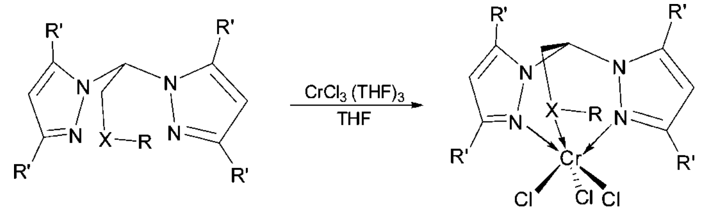
Scheme 1. Synthesis of the Cr(III) Precatalysts 1−8



1: X = S; R' = Me; R = Me
2: X = S; R' = Me; R = CH_2Ph
3: X = S; R' = Me; R = Decyl
4: X = O; R' = Me; R = Et
5: X = O; R' = Me; R = ^{i}Pr
6: X = O; R' = Me; R = Hexyl
7: X = O; R' = Me; R = Ph
8: X = O; R' = H; R = Hexyl

Table 1. Ethylene Trimerization with Complexes 1−8[a]

entry (complex)	amt (wt %)						activity (g/((g of Cr) h))
	PE	C_6	C_8	C_{10}	$\geq C_{12}$	1-C_6	
1 (**1**)	<0.1	96.3	1.7	0.5	1.4	99.2	2800
2 (**2**)	<0.1	94.7	5.2	0	0	96.1	1050
3 (**3**)	<0.1	95.1	4.7	0.1	0	97.2	3900
4 (**4**)	<0.1	97.3	0.7	1.3	0.6	99.3	5400
5 (**5**)	<0.1	96.1	2.0	1.3	0.5	97.9	2700
6 (**6**)	<0.1	98.9	0.6	0.3	0.1	99.6	16200
7 (**6**)[b]	<0.1	97.1	0.4	1.1	1.3	99.3	9100
8 (**6**)[c]	<0.1	98.1	0.5	0.7	0.6	99.5	21000
9 (**7**)	<0.1	96.8	0.3	0.5	2.3	99.0	11300
10 (**8**)	51.7	41.3	0.8	1.6	4.6	99.5	10200

[a] Conditions: 2.0 μmol of complex, 200 equiv of MAO, 25 bar of ethylene, 6 mL of toluene, 80 °C, 20 min. The results shown are representative of at least duplicated experiments. [b] 60 min. [c] 80 mL of toluene.

($MeOC_6H_4$),[11] benzyl ether,[10a] and 2-thienyl groups.[12] At variance with such related ligand designs,[13] we placed a functionalized pendant arm on the spacer link between the pyrazolyl moieties and avoided the presence of a coordinatively more inhibitive heteroatom directly on the link. The combination in a ligand framework of an ether or thioether function with tunable pyrazole rings could also allow easy stereoelectronic modifications, which is highly desirable in the study of ligand effect on selectivity. Upon activation with excess methylaluminoxane (MAO), our catalysts generally exhibit considerable activity and selectivity for ethylene trimerization.

The hybrid pyrazolyl ligands were prepared by heating a mixture of the appropriate acetal with 2 equiv of pyrazole in the presence of *p*-toluenesulfonic acid using a modified literature procedure.[14] Treatment of the appropriate pyrazolyl ligands with [$CrCl_3(THF)_3$] in THF afforded the corresponding Cr(III) complexes in good yields (85−91%) (Scheme 1).

The catalytic performances of the thioether complexes **1**−**3** toward ethylene trimerization are summarized in Table 1. With MAO, these precatalysts are highly selective toward trimerization (total C_6 selectivities >94.7%) to 1-hexene (>96.1%) with activities of 1050−3900 g/((g of Cr) h) (entries 1−3). The ether analogue **4** is even more active and selective (entry 4). Whereas the beneficial role of a soft donor[6b] such as S (as in thioether) or P (in phosphine) has been documented, e.g. in the Sasol mixed-donor systems, the effect of a harder donor (such as N or O) is less established.

The exceptional performance of **4** prompted a more thorough investigation of other ether derivatives. At 80 °C under 25 bar ethylene and in the presence of 200 equiv of MAO, all of them (notably **4**, **6**, and **7**) give almost exclusively hexenes with remarkable selectivity for 1-hexene (entries 4−9). The highest activity of 16 200 g/((g of Cr) h) was found in **6**, which has a long hexyl chain protruding from the pendant group. It also gives a high selectivity of 98.9% (entry 6). This could be attributed to a better solubility in toluene compared to that of **4**, which has a shorter ethyl chain. A similar trend has been observed for the Sasol mixed heteroatomic SNS Cr systems, in which the *n*-decyl-substituted precatalyst [$CrCl_3\{HN(CH_2CH_2S^{n}decyl)_2\}$] is significantly more active than those with shorter alkyl chains.[6b] Introduction of bulkier substituents on the chalcogen (compare entries 5 and 4 and compare entries 2 and 1) lowers the catalyst activity. For **6**, the activity is higher when the reaction is performed under higher dilution (compare entries 8 and 6). Replacement of the alkyl by an aryl group has no significant influence in either the activity or the selectivty (compare entries 9 and 4, 6). In the ether-based system, replacement of the methyl group on the pyrazole rings by hydrogen decreases significantly the selectivity toward hexenes and favors the formation of polyethylene (PE) (compare entries 10 and 4−6). With a longer reaction time of 1 h, the activity of **6** decreases by a factor of 2 (compare entries 7 and 6), which suggests a shorter catalyst lifetime. The activities are in general

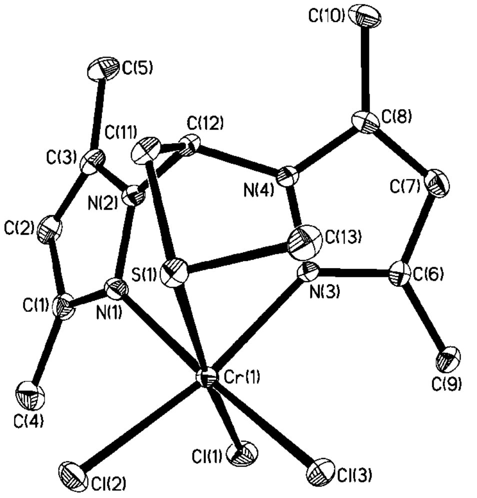


Figure 1. Molecular structure of **1** (30% probability ellipsoids, H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Cr−N(1) = 2.102(2), Cr−N(3) = 2.096(2), Cr−S = 2.4808(7), Cr−Cl(1) = 2.2784(7), Cr−Cl(3) = 2.3175(7), Cr−Cl(2) = 2.3183(8); N(3)−Cr−N(1) = 84.10(7), N(3)−Cr−Cl(1) = 91.87(6), N(1)−Cr−Cl(3) = 174.38(6), Cl(1)−Cr−Cl(3) = 93.36(3), N(3)−Cr−Cl(2) = 169.15(5), Cl(1)−Cr−Cl(2) = 97.71(3), N(1)−Cr−S = 89.01(6), Cl(1)−Cr−S = 176.07(3).

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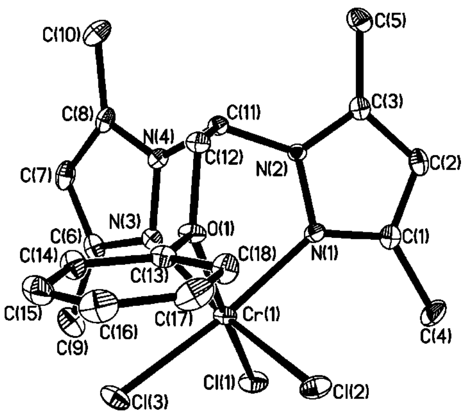

Figure 2. Molecular structure of **7**·MeCN (30% probability ellipsoids, MeCN and H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Cr−N(1) = 2.076(3), Cr−N(3) = 2.089(3), Cr−O = 2.131(3), Cr−Cl(1) = 2.269(1), Cr−Cl(3) = 2.293(1), Cr−Cl(2) = 2.296(1); N(1)−Cr−N(3) = 85.2(1), N(3)−Cr−Cl(1) = 91.05(9), Cl(1)−Cr−Cl(3) = 94.68(5), N(1)−Cr−Cl(3) = 173.35(9), Cl(1)−Cr−Cl(2) = 96.63(5), N(3)−Cr−Cl(2) = 170.79(9), O−Cr−Cl(1) = 172.49(8), N(1)−Cr−O = 85.0(1).

significant (1050−21 000 g/((g of Cr) h)) under 25 bar of ethylene pressure but are lower than those of the Cr-PNP ethylene trimerization system developed by McGuinness and Wasserscheid et al. (312−37 400 g/((g of Cr) h)), which was run under a higher (40 bar) ethylene pressure.[6a] The Cr(III) pyrazolyl ethylene oligomerization system developed by Carpentier and Casagrande et al. also achieved higher activities in the range of 1834−70 664 g/((g of Cr) h) under 20 bar of gas pressure.[13]

In order to establish the coordination mode of the heteroscorpionate ligands, complexes **1** and **7** were selected for structural analysis by single-crystal X-ray diffraction. As there is no example of a structurally characterized thioether or ether Cr complex with a bis(pyrazol-1-yl)methane heteroscorpionate ligand, it was important to establish the denticity and ligation function of these generally perceived weak donors. Both complexes display a distorted-octahedral geometry, with the Cr atom facially capped by the tridentate heteroscorpionate ligand and with coordination of all three donor atoms (Figures 1 and 2). Coordination of the ether or thioether function enables the formation of a metallabicyclic structure with two connected six-membered rings, flanked by two pyrazoyl rings. This offers an explanation for the high stability of the complexes. The Cr−N bond lengths span a relatively narrow range (2.096(2), 2.102(2) Å for **1** and 2.076(3), 2.089(3) Å for **7**). The Cr−S bond in **1** (2.4808(7) Å) is slightly longer than those in similar Cr(III) precatalysts such as [CrCl$_3${HN(CH$_2$CH$_2$SEt}$_2$] (Cr−S$_{av}$ = 2.453 Å), [CrCl$_3${2,6-bis(cyclohexylthiomethyl)pyridine}] (Cr−S$_{av}$ = 2.439 Å), and [CrCl$_3$L] (L = mixed PNS or SNS ligand, Cr−S = 2.403−2.456 Å).[15] This is consistent with the weak basicity of the thioether function. The Cr−O bond in **7** (2.131(3) Å) is also longer than those in related complexes, e.g. [CrCl$_3${bis[2-(3,5-dimethylpyrazolyl)ethyl)]amine}] (Cr−O = 2.076(1) Å), but shorter than that in [CrCl$_3${^{i}amyl-N(2-MeO-4-^{t}BuC$_6$H$_3$)$_2$P}$_2$] (Cr−O = 2.156(2) Å).[16]The Cr−Cl bonds trans to the thioether in **1** (2.2784(7) Å) and to the ether in **7** (2.269(1) Å) are significantly shorter than the other Cr−Cl bonds (2.3175(7), 2.3183(8) Å and 2.293(1), 2.296(1) Å, respectively). This, together with the potential hemilability of the hybrid ligand, could facilitate the entry of ethylene in the trimerization process.

The heteroscorpionate pyrazolyl ligands reported herein can be readily prepared from inexpensive materials. They are stable toward oxidation and hydrolysis. The one-step complexation at room temperature, giving high yields (85−91%), represents an additional advantage. Their excellent selectivity is generally comparable with that of the most efficient ethylene trimerization catalytic systems reported.[4−6] While the activity appears to be sensitive to the nature of the third donor (O or S), the selectivity difference is less pronounced. The presence of a hard donor atom (e.g., MeO ether group in the BP system[5] and NH amine in the Sasol system[6]) is an important element in these types of hybrid ligands to support olefin oligomerization. The use of two pyrazolyl groups in place of the common and generally softer phosphines and thioethers has given the current system some notable advantages. The fused and hybrid metallaheterocyclic ring structures adds stability in an inherently labile or hemilabile system. These hybrid tridentate ligands thus offer a mix of donor characters that could help the metal respond to changes throughout the catalytic cycle. These features could offer an explanation to the notable activity and high selectivity observed. Ongoing experiments are directed at the development of other hybrid ring systems, especially for the use of heterocycles to support olefin oligomerization.

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Supporting Information Available: Text and figure giving details of the syntheses and characterization data for all new compounds and CIF files giving X-ray crystallographic data for **1** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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