Organometallics **2006,** *25,* 715−718

Isolation of a Cationic Chromium(II) Species in a Catalytic System for Ethylene Tri- and Tetramerization

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Received October 14, 2005

Treatment of the ethylene tetramerization catalyst precursor [PNP]$CrCl_3$ with Me_3Al afforded the new divalent catalyst precursor {$[PNP]_2Cr(m\text{-}Cl)AlMe_3$}$[ClAlMe_3]_{0.34}[Me_4Al]_{0.66}\cdot 0.125$(hexane)$\cdot 0.25$(toluene) (**1**). The formation of **1** implies reduction to the divalent state, cationization, and ligand scrambling. The fact that this species displays, upon activation with MAO, a catalytic activity similar to that of the trivalent precursor indicates that reduction of the metal to the divalent state is a step toward the formation of the actual catalytically active species. The failure of $CrCl_2(THF)_2$ to react with [PNP] indicates that cationization and acquisition of the second ligand and of a bridging $ClAlMe_3$ residue are central to the stabilization of this new divalent catalyst precursor.

Introduction

The ethylene trimerization process as reported in the Phillips patent literature,[1] which employs trivalent chromium under Ziegler−Natta type conditions, remains today not only a very useful and highly desirable process but also provides an intellectual challenge from the mechanistic point of view. The interest behind clarifying the mechanism of this fascinating catalytic process has been stimulated by the importance of gaining a better control over the selective production of C_6/C_8 oligomers above the typically observed Schulz−Flory distribution. In the recent literature there has been a strong revival of interest in this particular direction[2] and catalytic activity has been observed with several diversified metals.[3] A potent Ti-based switchable catalyst has been recently described.[4] However, the most preferred catalysts generally remain those based on chromium because of their high activity, thermal stability, and selectivity.[2]

The chromium catalyst precursors reported in the literature thus far have usually been based on *trivalent* chromium,[5] with very few exceptions.[1a,5e,6] However, while there is agreement that a non-Schulz−Flory type of tri- and tetramerization process involves a two-electron redox couple,[7] the oxidation state of the chromium species that actually starts the catalytic cycle remains unknown. The possibility that the reaction mechanism may proceed via an initial reduction to the divalent state and that the oligomerization is performed by the Cr(II)/Cr(IV) redox couple has been contemplated in the literature.[5f−k,8a−e] Different redox couples such as Cr(I)/Cr(III)[5c,e] and Cr(III)/Cr(V) have also been taken into consideration.[8f−h,9] However, a clearly

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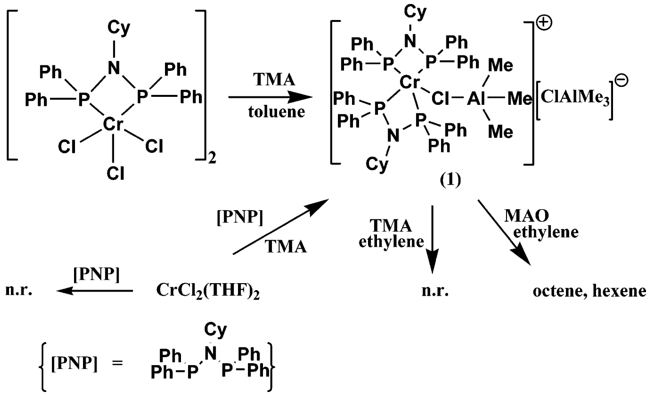
Scheme 1



defined Cr(II) complex capable of functioning as a catalyst precursor has been reported in only one case.[1a]

With the ultimate goal of gaining useful insight into the mechanism of the catalytic cycle, we have recently embarked on a project aimed at studying the interaction between trivalent chromium catalyst precursors with Al-based activators. In this first work, we have examined the reaction of one established trivalent chromium catalyst precursor, $[PNP]CrCl_3$ ($PNP = Ar_2PN(R)PAr_2$; $R = Cy$; $Ar = Ph$),[5f−g,k] with Al-based cocatalysts. The choice of this particular system was fostered by its outstanding activity and performance in terms of C_6/C_8 tunability. The wealth of data available on this catalytic system indicate that the [PNP] ligand indeed plays a dominant role in the structure of the catalytically active species. In other independent work, cationization of $[PNP]CrPh_3$ complexes *in the absence* of Al−alkyl activators also gave catalytically active species, realistically suggesting that the trivalent state may be in fact catalytically active.[9]

Results and Discussion

The reactions of $\{[PNP]CrCl_3\}_2$ with either MAO or TMA afforded solutions with identical blue colors. While in the first case attempted crystallization invariably afforded a resinous pyrophoric material, in the case of TMA a blue solid crystalline complex was isolated in 48% yield. The formulation of this crystalline complex as $\{(PNP)_2Cr(m\text{-}Cl)AlMe_3\}[ClAlMe_3]_{0.34}[Me_4Al]_{0.66}\cdot 0.125(\text{hexane})\cdot 0.25(\text{toluene})$ (**1**) was obtained by the X-ray crystal structure (Scheme 1).

Two ions make up complex **1** (Figure 1). The cation consists of a Cr atom placed in the center of a distorted trigonal bipyramid with two P atoms from two ligands occupying the axial positions. The three equatorial positions are defined by the remaining two P atoms and the chlorine atom, which in turn bridges a Me_3Al unit. One $ClAlMe_3$ counteranion, not connected with the Cr-containing cation, was present in the lattice. The $AlMe_3$ was equally disordered over two positions, while the chlorine atom was partially disordered with another methyl group.

Both the connectivity and the magnetic moment ($\mu_{eff} = 4.80$ μ_B) clearly indicate a Cr(II) oxidation state. Thus, complex **1** is a *cationic* Cr(II) complex and is comparable to the trivalent precursor in terms of overall catalytic activity (Table 1) under the same reaction and activation conditions.[5f,g,k] The only observed difference consists of a higher selectivity for C_8, which is not necessarily significant, due to the remarkable sensitivity of this catalytic system to the reaction conditions.[5k] Activation of **1** with TMA produced, in our experiments, neither oligomers nor polymer in significant amounts.

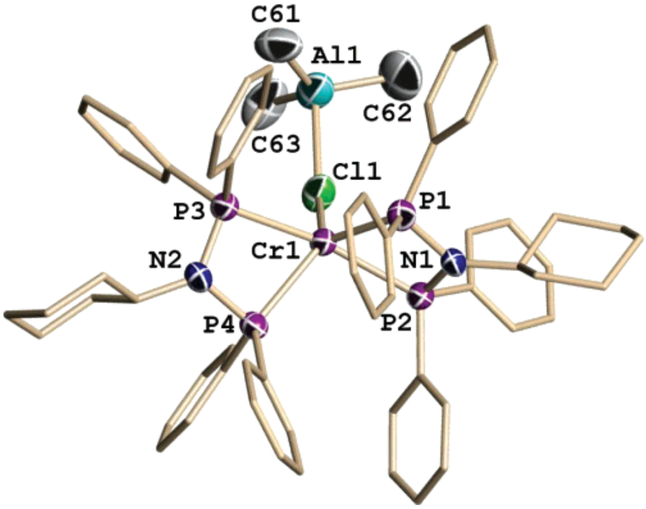


Figure 1. Plot of the Cr-containing cationic moiety of **1** with thermal ellipsoids of the non-carbon atoms drawn at the 30% probability level.

Table 1. Catalytic Activity Results[a]

cat.	activity (g/((g of Cr)/h))	amt of PE (g)	amt of C_6 (%)	amt of C_8 (%)	ref
$[PNP]CrCl_3$	8000	0.5	32.1	59.4	5f,g
1	8400	0.9	18.4	73.4	this work
blank	0.400	0.42	0	0	this work

[a] Conditions: 300 equiv of MAO, 30 bar, 65 °C, 30 μmol of catalyst, 150 mL total toluene volume. The blank reaction was carried out with $CrCl_2(THF)_2$.

In view of the isolation of **1** and of its catalytic activity, it seems reasonable to conclude that reduction of the metal center is a step toward the formation of the catalytically active species during the activation of the *trivalent* precursor. This is, of course, conceptually different from the case when activation of trivalent precursors is carried out with nonalkylating Lewis acids[8d,9] and where the oligomerization may well follow pathways involving higher-valent redox couples. In the present case, however, while oxidation of **1** is unlikely to occur during its activation with MAO, the possibility of further reduction toward even lower-valent species cannot in principle be excluded. The reduction of the metal center from the trivalent to the divalent state, as observed in the presence of alkylating agents during the formation of **1**, is not particularly surprising, given the behavior of organochromium compounds.[10] Although the Cr−C bond may occasionally display exceptional stability, as in the case of $PhCrCl_2(THF)_3$ and $MeCrBr_2(THF)_3$ (including toward hydrolytic media),[11] more often, trivalent organochromium complexes are characterized by a tendency to disproportionate toward tetra- and divalent species.[12] Also in line with the formation of **1**, a trivalent Cr bis-iminepyridine polymerization catalyst gave a divalent chromium aluminate species upon treatment with TMA.[13]

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A noticeable feature of complex **1** is that two [PNP] ligands instead of one are present in the coordination sphere of chromium. The ligand redistribution implies that at least 50% of the Cr(III) precursor has been converted to some other species which so far remains unknown. To our surprise, the [PNP] ligand does not react with $CrCl_2(THF)_2$ in THF or in toluene, even after a 12 h reflux. Nevertheless, a suspension of $CrCl_2(THF)_2$ with 2 equiv of [PNP] reacts in toluene and in the presence of excess of TMA to afford **1** in very good yield. This clearly indicates that *the presence of a second ligand in the coordination sphere of Cr and cationization by the Al cocatalysts are, together, central to the stability of the Cr(II) derivatives of the [PNP] ligand*. On the basis of the observation that an excess of MAO is necessary for the activation of **1**, it is tempting to speculate that perhaps a dicationic[14] $[(PNP)_2Cr]^{2+}$ complex, generated upon dissociation of the coordinated $ClAlMe_3$ residue, may be the actual catalytically active species. However, other hypotheses, involving the possibility of further abstraction of the [PNP] ligand from the "dormant" catalyst precursor **1**, cannot be ruled out at this stage.[5k]

A $ClAlMe_3$ residue was also retained in the coordination sphere of the Cr atom. Interestingly, the retention of this residue has been observed in the Phillips Cr(II) pyrrolide catalyst, where it seems to play an important role.[7d] Thus, even in the case of **1** the presence of this unit might be central to the tuning of the Lewis acidity of the chromium center.

In conclusion, we have now isolated a cationic, divalent Cr catalyst precursor upon treatment with Me_3Al of the trivalent $\{[PNP]CrCl_3\}_2$. The complex displays comparable or slightly improved catalytic activity with respect to the trivalent precursor. Its isolation and characterization do not provide definite answers to the important question about the Cr oxidation state in the actual catalytically active species. However, the study shows that in this particular system reduction of the metal to the divalent state does occur at least in the preliminary stage of the catalyst formation. The catalytic behavior of **1** and the failure of [PNP] to ligate to a $CrCl_2$ moiety in the absence of TMA also suggest that the acquisition of a second ligand and cationization are central to the stabilization of this divalent catalyst precursor.

Experimental Section

General Experimental Details. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. 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 1K Smart CCD area detector.

General Oligomerization Procedure. A Parr reactor was dried in an oven at 80 °C for 3 h prior to each run and then placed under vacuum for 30 min. The reactor was then charged with toluene, MAO, and 40 bar of ethylene and heated to 65 °C with stirring. 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 1 h, after which the temperature was rapidly reduced to 5 °C, the reactor was depressurized, and a mixture of MeOH/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. Yields 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.

Table 2. Crystal Data and Structure Analysis Results for 1

formula	$[(PNP)_2Cr(m\text{-}Cl)AlMe_3][ClAlMe_3]_{0.34}\text{-}Me_4Al]_{0.66}\cdot 0.125(hexane)\cdot 0.25(C_7H_8)$
mol wt	1226.51
cryst syst	triclinic
space group, Z	$P\bar{1}$, 2
a (Å)	12.366(2)
b (Å)	16.214(3)
c (Å)	21.347(4)
α (deg)	96.191(3)
β (deg)	106.453(3)
γ (deg)	91.839(3)
V (Å^3)	4072.0(12)
λ(Mo Kα) (Å)	0.710 73
T (K)	213(2)
D_{calcd} (g cm^{-3})	0.997
μ_{calcd} (cm^{-1})	0.3182
F_{000}	1294
R, R_w[a]	0.0781, 0.2015
GOF	1.035

[a] $R = \sum|F_o - F_c|/\sum F_o$; $R_w = [\sum(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1

Cr(1)−Cl(1)	2.3682(19)	Cl(1)−Al(1)	2.428(3)
Cr(1)−P(1)	2.5282(19)	Al(1)−C(61)	1.971(9)
Cr(1)−P(2)	2.4884(18)	Al(2)−Cl(2)	2.237(10)
Cr(1)−P(3)	2.4777(18)	Al(2)−C(75)	1.949(16)
Cr(1)−P(4)	2.5003(18)		
Cr(1)−Cl(1)−Al(1)	137.60(11)	P(2)−Cr(1)−P(4)	102.07(6)
P(1)−Cr(1)−P(2)	66.39(6)	P(3)−Cr(1)−P(4)	66.57(5)
P(1)−Cr(1)−P(3)	107.39(6)	Cl(1)−Cr(1)−P(1)	122.01(7)
P(1)−Cr(1)−P(4)	114.66(6)	Cl(1)−Cr(1)−P(2)	98.60(6)
P(2)−Cr(1)−P(3)	164.26(7)	Cl(1)−Cr(1)−P(3)	96.87(6)

Preparation of $\{(PNP)_2Cr(m\text{-}Cl)AlMe_3\}[ClAlMe_3]_{0.34}[Me_4Al]_{0.66}\cdot 0.125(hexane)\cdot 0.25(toluene)$ (1). Method A. A mixture of $\{[PNP]CrCl_3\}_2$ (PNP = $Ph_2PN(Cy)NPPh_2$; 1.70 g, 2.72 mmol) and TMA (1.96 g, 27.20 mmol) was stirred in toluene (15 mL). The color immediately changed from the initial purple-blue to bright green and then gradually to light blue over 5 min. After centrifugation of the solution and layering with hexane, crystals of analytically pure **1** (1.55 g, 48%) were grown upon allowing the mixture to stand at −35 °C over 2 days. Anal. Calcd (found) for $C_{69.16}H_{89.73}Al_2Cl_{1.34}CrN_2P_4$: C, 67.73 (67.38); H, 7.37 (7.31); N, 2.28 (2.14). μ_{eff} = 4.80 μ_B.

Method B. A suspension of $CrCl_2(THF)_2$ (56 mg, 0.21 mmol) and [PNP] (200 mg, 0.42 mmol) in toluene (15 mL) did not afford any color change, even upon refluxing the mixture. The addition of TMA (144 mg, 2.0 mmol) in toluene and stirring for 1 h at room temperature resulted in a color change, initially to brownish red and finally to light blue. The resulting solution was allowed to stand at room temperature for several hours, upon which **1** precipitated as a crystalline solid (230 mg, 0.19 mmol, 90%).

X-ray Crystallography. A suitable crystal was selected, mounted on a thin, glass fiber using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω scans at 0, 90, and 180° in ϕ. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere.

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[14] For an example of double activation, see: Chen, E. Y. X.; Kruper, W. J.; Roof, G.; Wilson, D. R. *J. Am. Chem. Soc.* **2001**, *123*, 745.

Semiempirical absorption corrections based on equivalent reflections were applied.[15] The diffraction data and unit-cell parameters were uniquely consistent with the reported space group $P\bar{1}$. No symmetry higher than triclinic was observed, and solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. The Me_3Al residue in the $ClAlMe_3$ counteranion was equally disordered over two positions, while the Cl atom was partially occupied by a CH_3 group (34 versus 66%, as suggested by the best refinement of the thermal parameters). All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHELXTL 6.12 program library (G. M. Sheldrick, Bruker AXS, Madison, WI, 2001). Relevant crystal data and selected bond distances and angles are reported in Tables 2 and 3, respectively.

Acknowledgment. This work was supported by the Natural Science and Engineering Council of Canada and by the Eindhoven University of Technology.

Supporting Information Available: Complete crystallographic data (as a CIF file) for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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