5708 *Organometallics* **2008,** *27,* 5708–5711

Preparation and Characterization of a Switchable Single-Component Chromium Trimerization Catalyst

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Received June 17, 2008

Reaction of [(Ar)NPN(*t*-Bu)]$_2$Cr (**2**) with Me$_3$Al afforded {[(Ar)NP(Me)N(*t*-Bu)]AlMe$_2$}Cr{[(Ar)NP(Me)(AlMe$_3$)N(*t*-Bu)]AlMe(μ-Me)} (**3**), in which the ligand's P atom has been alkylated and one AlR$_2$ residue retained by the chelating framework. One of the two ligands also retained an additional Me$_3$Al unit via coordination to the alkylated P atom. Complex **3** provides the first case of a selective ethylene trimerization catalyst with high activity and excellent selectivity, producing 1-hexene upon exposure to ethylene at 80 °C. Furthermore, upon treatment with MAO, complex **3** acts as a nonselective catalyst, producing a statistical mixture of oligomers with the highest ever observed activity. In addition, upon treatment with [(*i*-Bu)$_2$Al]$_2$O, the complex acts as a highly active polymerization catalyst.

Introduction

Catalytic selective ethylene trimerization and tetramerization are fascinating processes increasingly attracting interest from both industrial and academic standpoints.[1] The mechanism through which the selective trimerization[2] is accomplished is conceptually different from that of a regular polymerization.[3] The ring-expansion mechanism, commonly accepted by workers in the field,[2g,h] implies in fact a redox process, during which oxidative addition of the metal center to the ethylene double bond is followed by two subsequent insertions. The reductive elimination of the seven-membered ring, generated during the insertions, affords 1-hexene and restores the metal coordinative vacancy as well as the original low-valent configuration. In this event, the availability of d electrons seems to be a requirement for this catalytic cycle.

The most selective and active ethylene oligomerization catalysts remain those based on chromium,[4−6] where trivalent complexes are by far the most frequently reported catalyst precursors.[1b] This is despite its trivalent state being well known as rather inert and certainly not inclined toward oxidative addition. For this reason, it is also believed that a primary function of the alane activator is to reduce the metal toward a lower oxidation state.[7] Recent mechanistic work[8] on the most selective and active catalytic systems has revealed a rather dynamic and somewhat contradictory behavior from the metal oxidation state point of view, which, as a matter of fact, has not yet been conclusively identified. The situation is further complicated by the fact that some of the chromium catalysts display extremely high activity but produce instead a statistical distribution of oligomers.[9] Therefore, questions arise as to which mechanism the frequently observed formation of a Schultz−Flory distribution of oligomers may belong to: namely, the nonredox polymerization-type mechanism or the redox trimerization-type

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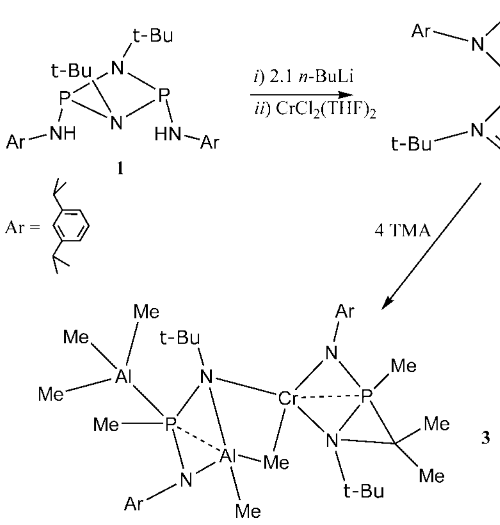
10.1021/om800563w CCC: $40.75

Scheme 1



mechanism, where the intermediate metallacycle ring is sufficiently stable to allow further expansion by a few subsequent insertions.[10] Or is it a completely separate mechanism? Addressing these issues is of course central to the rational design of much wanted trimerization and tetramerization catalysts. One possible strategy is to attempt to isolate intermediates of the catalytic cycle capable of acting as single-component catalysts. These species would in fact reveal the metal electronic configuration and steric environment and, thus, provide critical information for process improvement and future catalyst design.

We have recently discovered a catalytic system based on the (*t*-Bu)NPN(*t*-Bu) ligand system, which switches selectivity from polymerization to a nonselective oligomerization and even selective trimerization depending on the particular nature of the alane activator.[11] By replacing one of the ligand's *t*-Bu groups with an aryl substituent, we have now succeeded in obtaining high activity[10,12] for the nonselective ethylene oligomerization and, most of all, isolated the first ever single-component selective trimerization chromium catalyst. To the best of our knowledge, these findings are precedented by only one claim in the patent literature describing a lower-activity single-component trimerization catalyst based on vanadium.[1d]

Results and Discussion

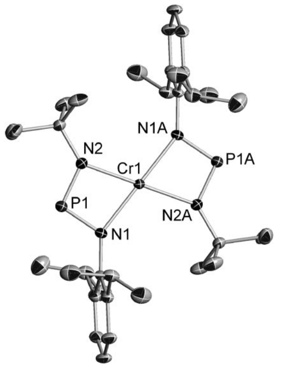


Figure 1. Thermal ellipsoid plot of **2** with ellipsoids drawn at the 50% probability level.

Table 1. Crystal Data and Structure Analysis Results

formula	$C_{32}H_{52}CrN_4P_2$,	$C_{41}H_{78}Al_3CrN_4P_2$
M_w	606.72	821.95
space group	monoclinic, *P*2(1)/*n*	monoclinic, *P*2(1)/*n*
a (Å)	9.201(9)	18.9199(16)
b (Å)	21.91(2)	14.7620(12)
c (Å)	9.597(9)	18.1352(15)
β (deg)	113.947(11)	102.7670(10)
V (Å^3)	1768(3)	4939.9(7)
Z	2	2
radiation	0.781	0.781
T (K)	203(2)	203(2)
D_{calcd} (g cm^{-3})	1.140	1.105
μ_{calcd} (mm^{-1})	0.439	0.379
F_{000}	652	1780
R, $R_w{}^{2a}$	0.0559, 0.1350	0.0648, 0.1383
GoF	1.039	1.069

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

The reaction of [(Ar)N(H)PN(*t*-Bu)]$_2$ (**1**)[13] with *n*-BuLi followed by reaction with $CrCl_2(THF)_2$ afforded the divalent [(Ar)NPN(*t*-Bu)]$_2$Cr (**2**), where the ligand system **1** underwent a dimer to monomer dissociation generating two (Ar)NPN(*t*-Bu) monoanions (Scheme 1). The affinity of divalent chromium for square-planar ligand fields as dictated by the d^4 electronic configuration is most probably the driving force behind this unusual behavior. The structure of **2** is very similar to that of the earlier reported divalent [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr[11] and does not show any relevant feature other than a divalent chromium center in the much expected square-planar environment defined by the four nitrogen atoms of the two NPN anions (Figure 1, Tables 1, 2).

Following our interest in the behavior of chromium complexes with aluminum alkyls,[8,9] we have reacted **2** with a diverse series of alanes using several different stoichiometric ratios. Whereas the reaction of the [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr system with several alanes afforded crystalline products,[11] to this end, only treatment of **2** with 4 equiv of $Al(CH_3)_3$ gave material in good yield that could be characterized by X-ray single-crystal diffraction and was found to be the novel {[(Ar)NP(Me)N(*t*-Bu)]AlMe$_2$}-Cr{[(Ar)NP(Me)(AlMe$_3$)N(*t*-Bu)]AlMe(μ-Me)} (**3**) (Scheme 1).

A similar product was also obtained when [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr was treated with $Al(CH_3)_3$.[11] The primary role of the alane activators appears to have been the alkylation of the P atom. The resulting (Ar)NP(R)N(*t*-Bu) dianion binds to the AlMe$_2$ residue via the two N donor atoms, forming an {MeP[N(*t*-Bu)][N(Ar)]AlMe$_2$}$^-$ anion that is attached to the chromium metal via a nitrogen and a phosphorus atom (Figure 2). In the second ligand in **3** the alkylated phosphorus atom coordinates to an additional AlMe$_3$, which prevents it from binding to chromium. As a result, one of the two aluminum methyl groups of the AlMe$_2$ residue occupies the fourth coordination site of the distorted square-planar chromium atom.

Complex **3** is a single-component trimerization catalyst exclusively producing 1-hexene. Its activity is of the same order of magnitude as that of other selective systems recently reported, such as the Sasol's [SNS]CrCl$_3$ system.[5c] The selectivity also depends on temperature. Namely, at 80 °C 1-hexene is no longer

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Table 2. Selected Bond Distances (Å) and Angles (deg)

2	3
Cr(1)−N(1) 2.114(3)	Cr(1)−N(3) 2.144(4)
Cr(1)−N(2) 2.086(3)	Cr(1)−N(4) 2.125(4)
N(1)−P(1) 1.628(3)	Cr(1)−C(38) 2.289(6)
N(2)−P(1) 1.612(3)	Cr(1)−P(2) 2.4035(16)
N(1)−Cr(1)−N(2) 71.02(13)	N(4)−Al(2) 2.026(4)
N(1)−Cr(1)−N(2a) 108.98(13)	N(2)−Al(2) 1.899(4)
N(2)−Cr(2a)−N(1a) 179.998(1)	Cr(1)−Al(4) 2.8098(18)
	Al(2)−P(2) 2.627(2)
	P(2)−N(2) 1.659(4)
	P(2)−N(4) 1.717(4)
	Al(4)−P(1) 2.634(2)
	Al(4)−N(3) 1.951(4)
	Al(4)−N(1) 1.845(4)
	P(1)−N(3) 1.746(4)
	P(1)−N(1) 1.674(4)
	N(4)−Cr(1)−N(3) 165.94(16)
	N(4)−Cr(1)−C(38) 98.89(19)
	N(3)−Cr(1)−C(38) 90.15(19)
	N(4)−Cr(1)−P(2) 44.03(11)
	N(3)−Cr(1)−P(2) 127.78(12)
	C(38)−Cr(1)−P(2) 142.07(16)
	Al(4)−C(38)−Cr(1) 79.9(2)
	Cr(1)···Al(4) 2.8098(18)

produced and polymer is formed instead. A similar behavior was observed by de Wet-Roos and co-workers for Sasol's PNP-type tetramerization catalyst system.[14] At room temperature, the catalytic activity drops and the activity is marginal. Reaction times up to 10 h at typical reaction temperature (50 °C) did not improve the productivity of 1-hexene, indicating rapid catalyst deactivation (in less than 30 min). Interestingly, the analogue of **3** with only nitrogen-*t*-Bu substituents, $\{[\mathrm{MeP}\{\mathrm{N}(t\text{-Bu})\}_2]\mathrm{AlMe}_2\}\mathrm{Cr}\{[\mathrm{MeP}(\mathrm{AlMe}_3)\{\mathrm{N}\ (t\text{-Bu})\}_2]\mathrm{AlMe}(\mu\text{-Me})\}$, afforded polyethylene already at 50 °C.[11] This is assumed to be due to a lower stabilizing ability of *t*-Bu substituents versus aryl substituents. Upon addition of aluminum-based cocatalysts, the selectivity of complex **3** shows a dramatic switch. In the case of treatment with MAO, a statistical distribution of oligomers with an enormous increment of activity was observed.[10,12] Upon activation with $[(t\text{-Bu})_2\mathrm{Al}]_2\mathrm{O}$, the catalyst selectivity switches to ethylene polymerization instead. With $\mathrm{Al}(i\text{-Bu})_3$ as cocatalyst, no oligomers and only a small amount of polymer is formed. The switch of catalytic behavior from selective to nonselective oligomerization is intriguing given that the ligand and the initiating alkyl function (methyl) are the same for the two processes in this case. The fact that at elevated temperature **3** becomes an ethylene polymerization catalyst indicates that it is rather facile to switch between the two different processes.

Explaining or simply rationalizing this intriguing behavior is not an easy task at this early stage. We speculate that the difference of reactivity (trimerization, oligomerization, and polymerization) as a function of the presence/absence and nature of the alane is to be ascribed to three different species.

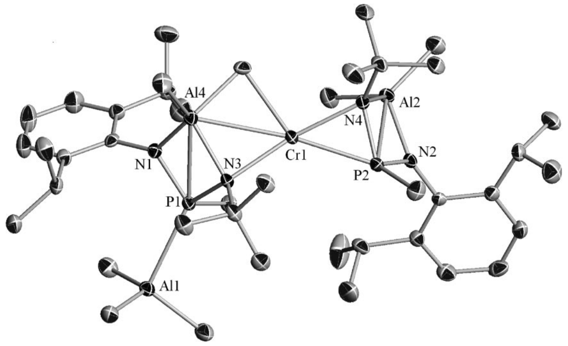

Figure 2. Thermal ellipsoid plot of **3** with ellipsoids drawn at the 50% probability level.

In conclusion, we have reported a single-component catalyst selectively producing 1-hexene with good activity. It is interesting to observe that this species contains chromium in its divalent state, as it is unlikely that the divalent state enables the selective trimerization process.[7c,11] Therefore, complex **3** can best be regarded as a self-activating catalyst precursor. Further work to elucidate the oxidation state of the true active species and the origin of the switching of the catalytic selectivity of this highly fascinating system is in progress.

Experimental Part

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. Ligand **1** was prepared according to a literature procedure.[12] Samples for magnetic susceptibility were preweighed inside a drybox equipped with an analytical balance and measured on a Johnson Matthey magnetic susceptibility balance. Data for X-ray crystal structure determination were collected with a Bruker diffractometer equipped with a 1K Smart CCD area detector. $\mathrm{CrCl_2(THF)_2}$ was prepared according to standard procedures. The reagents DIBAC (Aldrich), TMA (Aldrich), TIBA (Aldrich), TIBAO (Aldrich), and MAO (Chemtura) were used as received.

Preparation of [(Ar)NPN(t-Bu)]₂Cr (2). A solution of *cis*-{(2,6-diisopropylpheny)(H)NP[(*μ*-N)(*t*-Bu)]$_2$PN(H)(2,6-diisopropylpheny)} (**1**) (0.556 g, 1 mmol) in THF (20 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 0 °C. The mixture was allowed to stir at room temperature for 20 h. The resulting solution was added to a suspension of $\mathrm{CrCl_2\cdot 2THF}$ (0.268 g, 1 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature overnight. The solvent was evaporated *in vacuo* and the residue redissolved in toluene (10 mL). The resulting suspension was centrifuged, and the solution was stored at −30 °C. Brown crystals separated over four days and were filtered, washed with cold hexanes (10 mL), and dried *in vacuo* to give analytically pure **2** (0.355 g, 59%). [$\mu_{\mathrm{eff}} = 4.96\ \mu_{\mathrm{B}}$.] Anal. Calcd (Found) for $\mathrm{C_{32}H_{52}CrN_4P_2}$: C 63.35 (63.28), H 8.64 (8.59); N 9.23 (9.19).

Preparation of $\{[(\mathrm{Ar})\mathrm{NP(Me)N}(t\text{-Bu})]\mathrm{AlMe_2}\}\mathrm{Cr}\{[(\mathrm{Ar})\mathrm{NP(Me)}(\mathrm{AlMe_3})\mathrm{N}(t\text{-Bu})]\mathrm{AlMe}(\mu\text{-Me})\}$ (3). A solution of **2** (0.606 g, 1 mmol) in toluene (20 mL) was treated with trimethyl aluminum (0.288 g, 4 mmol) at room temperature and stirred for 10 min. Storing the resulting solution at −30 °C for 5 days afforded small purple crystals of **3**, which were filtered and washed with cold hexanes (5 mL) and dried *in vacuo* (0.455 g, 55%). [$\mu_{\mathrm{eff}} = 4.98\ \mu_{\mathrm{B}}$.] Anal. Calcd (Found) for $\mathrm{C_{41}H_{78}Al_3CrN_4P_2}$: C 59.91 (59.87); H 9.57 (9.55), N 6.82 (6.78).

Polymerizations and Oligomerizations. Catalytic runs were carried out in a 200 mL high-pressure Büchi reactor containing a heating/cooling jacket. A preweighed amount of catalyst was dissolved in 10 mL of toluene under $\mathrm{N_2}$ and injected into the preheated reactor already charged with cocatalyst and toluene (total volume 100 mL). Solutions were heated using a thermostatic bath and charged with ethylene, maintaining the pressure throughout the run. The oligo/polymerizations were quenched by venting the reactor (after cooling to 5 °C for oligomerizations) and addition of EtOH and HCl. The resulting polymer was isolated by filtration, sonicated with an acidified ethanol solution, rinsed, and thoroughly dried prior to mass determination. Oligomers were analyzed using GC and ^{1}H NMR. Molecular weight and molecular weight distributions of the resulting polymers were determined by gel permeation chromatography on a PL-GPC210 equipped with a RI

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Table 3. Oligomerization and Polymerization Results for Complex 3 with and without Cocatalysts[a]

cat.	cat. (μ-mol)	cocat.	Al:Cr	PE (g)	oligom. (g)	activity ($g \cdot mmol^{-1} \cdot h^{-1}$)	$C_6 =$ %	$C_8 =$ %	$C_{10} =$ %	$C_{12} =$ %	$C_{14} =$ %	$C_{16} =$ %	$C_{18} =$ %	α
3	10				3	600	99.9							
3[b]	10				0.5	100	99.9							
3[c]	10			3.9		780								
3	10	MAO	2000	0.4	85	17 000	39.0	27.6	15.7	8.7	4.8	2.9	1.4	0.55
3	10	$[(t\text{-Bu})_2Al]_2O$	1000	10.5[d]	2	400	9.9							
3	10	$Al(t\text{-Bu})_3$	1000	1.2		240								
$(SNS)CrCl_3$	10	MAO	1000	0.2	7	1400	≥98	2						
$(SNS)CrCl_3$	10	MAO	300	0.4	6	1200	≥98	2						

[a] Conditions: 100 mL of toluene, 35 bar of ethylene, reaction temperature 50 °C, reaction time 30 min. [b] Reaction temperature 25 °C. [c] Reaction temperature 80 °C. [d] The SEC of the polyethylene shows a bimodal distribution with an M_w for the main peak at 1.3×10^6 $g \cdot mol^{-1}$ and the M_w for the smaller peak at 12 000 $g \cdot mol^{-1}$.

and viscosity detector and a 3 × PLgel 10 μm Mixed-B column set at 135 °C using 1,2,4-trichlorobenzene as solvent. The molecular weight of the polyethylenes was referenced to polystyrene (M_w = 65500, PDI = 1.02) standards.

X-ray Crystallography. Suitable crystals were selected, mounted on a thin, glass fiber with paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1 k CCD diffractometer. Data collection was performed with three batch runs at $\phi = 0.00°$ (600 frames), at $\phi = 120.00°$ deg (600 frames), and at $\phi = 240.00°$ (600 frames). Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. The systematic absences and unit-cell parameters were consistent for the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.12 program library. Relevant crystal data and bond distances and angles are given in Tables 1 and 2 respectively.

Acknowledgment. This work was supported by the Natural Science and Engineering Council of Canada (NSERC) and by the Dutch Polymer Institute.

Supporting Information Available: Complete crystallographic data (as a CIF file) for complexes **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800563W