ORGANOMETALLICS

Highly Active Ethylene Oligomerization Catalysts

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Supporting Information

ABSTRACT: Reaction of RN(H)PBr(Ph)₂N(H)R [R = *t*-Bu, *i*-Pr, Ph] with two equivalents of *n*-BuLi followed by reaction with $CrCl_2(THF)_2$ afforded the divalent chromium complexes $[(t-Bu)NP(Ph)_2-N(t-Bu)]Cr(\mu^2-Cl)_2Li(THF)_2$ (1), $[(i-Pr)NP(Ph)_2N(i-Pr)]Cr(\mu^2-Cl)_2Li(THF)_2$ (2), and $[\{[(Ph)-NP(Ph)_2N(Ph)]Cr\}_2(\mu^2-Cl)_3][Li(DME)_3]$ (3). The trivalent analogue of 1, $\{[(t-Bu)NP(Ph)_2-N(t-Bu)]Cr(\mu^2-Cl)_3(\mu^3-Cl)_2\}$ {Li (THF)_2} (4), was obtained in a similar manner via treatment of the double deprotonated ligand with $CrCl_3(THF)_3$. Both reactions of the *divalent* 1 or *trivalent* 4 with AlMe₃ yielded the *trivalent* and cationic complex { $[(t-Bu)NP(Ph)_2N(t-Bu)]_2Cr$ }{ $(Me_3Al)_2Cl$ ·toluene (5). Upon activation with MAO, 1–3 produced unprecedented and potentially useful catalytic systems for nonselective ethylene oligomerization devoid of polymer. Divalent chromium is clearly the species responsible for the catalytic behavior, ruling out that nonselective oligomerization proceeds via a redox metallacycle mechanism. The absence of polymer in combination with the record activity makes 1 competitive with the best performing industrially used systems.



■ INTRODUCTION

A considerable amount of research effort has been dedicated both recently and in the past to nonselective ethylene oligomerization with the aim of improving the comprehension of this industrially relevant catalytic process.^{1–5} The mixtures of linear alpha olefins (LAO) produced by this process are in fact valuable commodity chemicals for a range of industrial and household applications depending on their molar mass distribution (detergents, surfactants, cosmetics, etc.).⁶

A nonselective oligomerization is closely reminiscent of a polymerization randomly truncated at the early stages of the chain growth (Cossee—Arlman mechanism).⁷ The commonly accepted Cossee—Arlman chain-growth mechanism does not require a change of the metal oxidation state during the catalytic cycle. In some cases however, the redox metallacycle mechanism proposed for selective tri- and tetramerization⁸ may also be ensued by nonselective systems.⁹ This is in the event that the two crucial steps, further ring expansion and reductive elimination, possess comparable activation barriers.¹⁰ Obviously, the possibility of discriminating between the two steps is central to obtain a general statistical oligomerization versus a selective process.

Trivalent chromium catalyst precursors constitute catalytic systems for both selective^{11-15,16a} and nonselective ethylene oligomerization¹² and also account for an important class of ethylene polymerization catalysts.¹³ The versatility of this element is likely to be ascribed to the large number of oxidation states available but most of all to the redox dynamism of the organochromium derivatives.¹⁴ More specifically, the trivalent state is normally used to feed the metal into the catalytic cycle.

Alkylating agents can then reduce the metal center to either the di- or monovalent state, each with its own distinctive catalytic behavior.¹⁴ What is remarkable is that the original trivalent state may also be regenerated during the catalytic cycles via simple disproportionation.¹⁵ Further reduction to the zerovalent state may also occur during the catalytic cycle, eventually affording metallic chromium or inert complexes with consequent catalyst deactivation. The easy interconversion of the three catalytically active oxidation states (+I, +II, and +III) and their occasional coexistence within the catalytic cycle explains the frequent occurrence of much unwanted polymer during the production of LAO and/or the occasional enrichment of the S–F distribution of α -olefins in 1-hexene and/or 1-octene.^{110-s,12-16}

The nature of the ligand plays a central role in stabilizing a particular oxidation state and consequently in determining the catalytic behavior. Previous work from our lab on an anionic ligand system based on the NPN framework of trivalent phosphorus has clearly indicated that this ligand frame is versatile for catalytic purposes, having allowed isolation of rare species and switchable catalytic systems.¹⁷ In addition, we observed that it provides a reversal of the PNP motif of the unique Sasol catalytic tetramerization system.^{16b,c,17,18} However, its chemistry appeared to be distinctively different. During the activation process of its chromium derivatives, the ligand-P atom was always attacked by the alkylating agent used for catalyst activation.¹⁷

 Received:
 March 17, 2011

 Published:
 May 27, 2011

	1	2	3	4	5	
formula	C35H52Cl2CrLiN2O2P	C ₂₈ H ₄₄ Cl ₂ CrLiN ₂ O _{2.5} P	$C_{64}H_{80}Cl_3Cr_2LiN_4O_8P_2$ $C_{48}H_{72}Cl_5Cr_2LiN_4O_2P_2$		C53H82Al2ClCrN4P2	
$M_{ m w}$	693.60	609.46	1312.55	1087.23	978.58	
space group	monoclinic, $P2(1)/n$	triclinic, P1	monoclinic, C2/c	triclinic, P1	monoclinic, C2/c	
a (Å)	9.911(2)	11.552(3)	28.944(3) 12.2348(19)		13.8861(12)	
b (Å)	16.784(3)	12.374(3)	14.4854(15)	15) 12.872(2)		
c (Å)	22.967(5)	14.246(3)	22.613(2)	18.296(3)	18.7679(16)	
α (deg)	90	67.528(4)	90	71.893(3)	90	
β (deg)	91.307(3)	75.972(5)	128.525(2)	85.406(3)	105.589(2)	
γ (deg)	90	70.253(4)	90	87.256(3)	90	
$V(Å^3)$	3819.7(13)	1756.1(7)	7417.4(13)	2729.1(7)	5796.4(9)	
Ζ	4	2	4	2	4	
radiation	0.71073	0.71073	0.71073	0.71073	0.71073	
T(K)	201(2)	200(2)	200(2)	200(2)	200(2)	
$D_{ m calcd}~({ m g~cm}^{-3})$	1.206	1.153	1.175	1.323	1.121	
$\mu_{ m calcd}~(m mm^{-1})$	0.512	0.549	0.493	0.741	0.364	
F ₀₀₀	1472	644	2752	1140	2100	
R , wR^2	0.0769, 0.2267	0.0774, 0.1621	0.0738, 0.1651	0.0839, 0.1859	0.0866, 0.2002	
GoF	1.037	1.022	1.011	0.989	1.082	

aluminum residues, in the end enabling the formation of singlecomponent and switchable ethylene oligomerization and polymerization catalysts. It was argued that eliminating the possibility of alkylation at the phosphorus atom might afford a different catalytic behavior. By oxidizing the P atom to the pentavalent state we have now obtained the first polymer-free highly active oligomerization system. Herein we describe our findings.

EXPERIMENTAL SECTION

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. The liquid reaction mixtures were analyzed by using a CP 9000 gas chromatograph equipped with a 30 mL \times 0.32 mm i.d., capillary CP-Volamine column and a FID detector. All single-point experiments were performed in duplicate. The yields were determined by ¹H NMR spectroscopy (Varian Mercury 400 MHz spectrometer). Samples for magnetic susceptibility were preweighed inside a VAC drybox equipped with an analytical balance and measured on a Johnson Matthey magnetic susceptibility balance. Elemental analyses were 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. Methylaluminoxane (MAO, 10% in toluene) was purchased from Aldrich. MMAO and PMAO were purchased from Akzo-Nobel. Ligands (t-Bu)N(H)PBr- $(Ph)_2N(H)(t-Bu), (i-Pr)N(H)PBr(Ph)_2N(H)(i-Pr), and PhN(H)PBr (Ph)_2N(H)Ph$ were prepared according to literature procedures.¹⁹

Preparation of $[(t-Bu)NP(Ph)_2N(t-Bu)]Cr(\mu^2-Cl)_2Li(THF)_2$ (1). A solution of *t*-BuN(H)PBr(Ph)_2N(H)*t*-Bu (0.41 g, 1.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25 °C, and the mixture was stirred at room temperature for 24 h. The resulting clear yellow solution was added to a suspension of $CrCl_2(THF)_2$ (0.27 g, 1.0 mmol) in THF (5 mL), and stirring was continued at room temperature overnight, affording a green solution. The solvent was removed *in vacuo*, and the residue redissolved in toluene (10 mL). The mixture was centrifuged, and the supernatant reduced to 4 mL and stored at -35 °C for 2 days. The resulting blue crystals of 1 were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* (0.39 g, 0.56 mmol, 65%). $\mu_{\rm eff}$ = 4.89 $\mu_{\rm B}.$ Anal. Calcd (found) for C_{28}H_{44}Cl_2CrLiN_2O_2P: C 55.91 (55.88), H 7.37 (7.21), N 4.66 (4.64).

Preparation of [(*i*-Pr)NP(Ph)₂N(*i*-Pr)]Cr(μ^2 -Cl)₂Li(THF)₂ (2). A solution of *i*-PrN(H)PBr(Ph)₂N(H)*i*-Pr (0.38 g, 1.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25 °C. After stirring for 24 h at room temperature, the clear yellow solution was added to a suspension of CrCl₂(THF)₂ (0.27 g, 1.0 mmol) in THF (5 mL). Stirring was continued at room temperature overnight, affording a green solution. The solvent was removed *in vacuo*, and the residue redissolved in toluene (10 mL). After centrifugation, the supernatant was concentrated to 4 mL and stored at -35 °C for 3 days. The resulting blue crystals of **2** were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* (0.30 g, 0.49 mmol, 51%). $\mu_{eff} = 4.91 \mu_{B}$. Anal. Calcd (found) for C₂₆H₄₀Cl₂CrLiN₂O₂P: C 54.46 (54.39), H 7.03 (7.07), N 4.89 (4.93).

Preparation of [{[(**Ph**)**NP**(**Ph**)₂**N**(**Ph**)]**Cr**}₂(μ^2 -**Cl**)₃][**Li**(**DME**)₃] (3). A solution of PhN(H)PBr(Ph)₂N(H)Ph (0.45 g, 1.0 mmol) in dimethoxyethane (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25 °C. The mixture was stirred at room temperature for 24 h, affording a clear yellow solution. A suspension of CrCl₂(THF)₂ (0.27 g, 1.0 mmol) in dimethoxyethane (5 mL) was then added. The reaction mixture was stirred at room temperature overnight, affording a green solution. The solvent was removed *in vacuo*, and the residue redissolved in toluene (10 mL). After centrifugation, the supernatant was evaporated to 4 mL and stored at -35 °C for three days. The resulting blue crystals of 3 were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* (0.35 g, 0.27 mmol, 55%). $\mu_{eff} = 4.97 \mu_{B}$. Anal. Calcd (found) for C₆₀H₇₀Cl₃Cr₂LiN₄O₆P₂: C 58.95 (58.90), H 5.77 (5.68), N 5.58 (5.51).

Preparation of {[(*t*-Bu)NP(Ph)₂N(*t*-Bu)]Cr}₂(μ^2 -Cl)₃(μ^3 -Cl)₂{Li-(THF)₂} (4). A solution of *t*-BuN(H)PBr(Ph)₂N(H)*t*-Bu (0.41 g, 1.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25 °C. The mixture was stirred at room temperature for 24 h, affording a clear yellow solution. After addition of a suspension of CrCl₃(THF)₃ (0.37 g, 1.0 mmol) in THF (5 mL) the mixture was stirred at room temperature overnight, giving a purple solution. The solvent was removed *in vacuo*, and the residue redissolved in dimethoxyethane (10 mL). After centrifugation, the supernatant was concentrated to 4 mL and stored at -35 °C for 3 days. Purple crystals of 4 were

Scheme 1



filtered and washed with cold hexanes (10 mL) and dried *in vacuo* (0.40 g, 0.36 mmol, 36%). μ_{eff} = 3.82 μ_{B} . Anal. Calcd (found) for $C_{48}H_{72}Cl_5Cr_2LiN_4O_2P_2$: C 53.02 (53.00), H 6.67 (6.59), N 5.15 (5.09).

Preparation of {[(*t*-Bu)NP(Ph)₂N(*t*-Bu)]₂Cr} {(Me₃Al)₂Cl} • toluene (5). *Method A*. A solution of *t*-BuN(H)PBr(Ph)₂N(H)*t*-Bu (0.41 g, 1.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25 °C. The mixture was stirred at room temperature for 24 h, affording a clear yellow solution. After the addition of a suspension of CrCl₂(THF)₂ (0.27 g, 1.0 mmol) in THF (5 mL), the reaction mixture was stirred at room temperature overnight, affording a green solution. The solvent was removed *in vacuo*, and the residue redissolved in toluene (10 mL). Neat AlMe₃ (0.36 g, 5 mmol) was added slowly at -35 °C, and the resulting mixture stirred for 1 h at room temperature. The suspension was centrifuged, and the supernatant concentrated to 4 mL and stored at -35 °C for 3 days. Brown-red crystals of **5** were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* to give 0.15 g (0.17 mmol, 18%). $\mu_{eff} = 3.89 \ \mu_{B}$. Anal. Calcd (found) for C₅₃H₈₂Al₂ClCrN₄P₂: C 64.99 (63.40), H 8.38 (8.01), N 5.72 (5.87).

Method B. The same procedure as method A was followed except using $CrCl_3(THF)_3$ (0.37 g, 1 mmol), producing 0.59 g of the product (73%).

Polymerization and Oligomerization Results. Catalytic runs were carried out in 200 mL high-pressure Büchi reactors containing a heating/cooling jacket. A preweighed amount of catalyst was dissolved in 100 mL of toluene under N_2 prior to loading the reaction vessel. Solutions were heated using a thermostatic bath and charged with ethylene, maintaining the pressure throughout the run. The reaction mixtures of the oligomerization runs were cooled to 0 °C prior to releasing the overpressure and quenching with EtOH and HCl. Activity was measured by NMR by integrating the resonances of the vinyl protons against the toluene solvent methyl group. Results of catalytic runs are given in Table 1.

X-ray Crystallography. Suitable crystals were selected, mounted on a thin, glass fibers with paraffin oil, and cooled to the data collection temperature. Data collection was performed with three batch runs at phi = 0.00 deg (600 frames), at phi = 120.00 deg (600 frames), and at phi = 240.00 deg (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 with the exception of uncoordinated solvent lattice molecules. Complex 1: the toluene lattice molecule was refined isotropically due to the low quality of the data. Complex 2: the THF solvent molecules in the lattice were refined isotropically due to the quality of data and solvent partial occupancy coupled with disorder. Complex 3: the DME solvent molecules in the lattice were refined isotropically due to the quality of data and partial occupancy. Complex 4: one of the two THF molecules coordinated to lithium showed disorder of two vicinal C atoms, producing an artificially short C-C distance. The disorder unfortunately could not be modeled, and therefore the geometry was restrained. Complex 5: the toluene solvent molecules in the lattice were refined isotropically due to the quality of data and solvent partial occupancy coupled with disorder. The [(Me₃Al)₂Cl] counteranion was also disordered over two positions with equal occupancy. 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 are given in Table 1, while bond distances and angles are given in the Supporting Information.

RESULTS AND DISCUSSION

The three ligands RN(H)PBr(Ph)₂N(H)R (R = *t*-Bu, *i*-Pr, Ph), bearing pentavalent phosphorus, were prepared according to an existing literature procedure.¹⁹ These species were subjected to double deprotonation with *n*-butyllithium and reacted with an equimolar amount of CrCl₂(THF)₂ (Scheme 1). The structures of the corresponding divalent complexes [(*t*-Bu)NP(Ph)₂N(*t*-Bu)]-Cr(μ^2 -Cl)₂Li(THF)₂ (1), [(*i*-Pr)NP(Ph)₂N(*i*-Pr)]Cr(μ^2 -Cl)₂Li-(THF)₂ (2), and [{[(Ph)NP(Ph)₂N(Ph)]Cr}₂(μ^2 -Cl)₃][Li-(DME)₃] (3) were authenticated by crystal structure analyses (Figure 1). Complexes 1 and 2 showed closely related geometries with the metal in the standard square-planar coordination geometry, the ligand chelating the chromium atom in a bidentate fashion and with two chlorine atoms bridging a THF-solvated lithium



Figure 1. Selected bond distances (Å) and angles (deg): 1 Cr1–N1 2.053(4), Cr1–N2 2.052(4), Cr1–Cl2 2.4363(14), Cr1–Cl1 2.4556(15); N2–Cr1–N1 72.44(18), N2–Cr1–Cl1 156.66(14), N2–Cr1–Cl2 103.18(14), Cl2–Cr1–Cl1 90.41(5); **2** Cr1–N1 2.038(8), Cr1–N2 2.061(8), Cr1–Cl1 2.385(3), Cr1–Cl2 2.399(3), N1–Cr1–N2 71.5(3), N1–Cr1–Cl1 98.4(2), N1–Cr1–Cl2 169.7(3), Cl1–Cr1–Cl2 91.09(11); 3 Cr1–N1 2.065(5), Cr1–N2 2.088(6), Cr1–Cl1 2.434(2), Cr1–Cl2 2.688(2), Cr1–P1 2.749(2); N1–Cr1–N2 70.9(2), N1–Cr1–Cl1 97.53(17), N2–Cr1–Cl1 160.84(17), Cl1–Cr1–Cl2 82.23(6).



Figure 2. Selected bond distances (Å) and angles (deg) of 4: Cr1–N2 1.995(8), Cr1–Cl1 2.343(3), Cr1–Cl3 2.440(3); N2–Cr1–N1 73.4(3), N2–Cr1–Cl 198.2(2), N2–Cr1–Cl3 94.5(2), Cl1–Cr1–Cl2 87.86(11), Cl1–Cr1–Cl3 163.64(10), Cr2–Cl2–Cr1 83.72(10), Cr1–Cl3–Cr2 82.99(9).

countercation. Complex **3** is instead dimeric, with three chlorine atoms bridging the two transition metals. The chromium atom displays a square-pyramidal coordination geometry that, albeit not very common, is precedented.²⁰ A solvated lithium countercation unconnected with the dimeric unit is also present in the lattice.

The trivalent analogue of **1** was obtained in a similar manner via treatment of the double-deprotonated ligand with CrCl₃(THF)₃. The corresponding trivalent {[(*t*-Bu)NP(Ph)₂N(*t*-Bu)]Cr(μ^2 -Cl)₃(μ^3 -Cl)₂}{Li(THF)₂} (4) was obtained as a purple crystalline mass (Scheme 1). The structure was elucidated by X-ray diffraction (Figure 2), showing the dinuclear complex containing two trivalent chromium atoms with an overall face-sharing bioctahedral structure. The bridging interaction between the two metal centers is realized through the facially oriented chlorine of the distorted octahedral geometry of each chromium center. One partially solvated lithium cation is retained as a part of a trimetallic cluster structure being bridged to the two transition metals by four chlorine atoms.

As described below, all the complexes display an interesting catalytic activity upon activation by methylaluminoxane. We have



Figure 3. Selected bond distances (Å) and angles (deg) for the cationic part of 5: Cr(1)-N(1a) 1.966(4), Cr(1)-N(2a) 1.969(5), N(1a)-Cr(1)-N(1) 73.9(3), N(1a)-Cr(1)-N(2) 132.34(18), N(1)-Cr(1)-N(2a) 126.8(2).

thus attempted the isolation of the catalytically active species by reacting the complexes with MAO. The reactions proved to be difficult, invariably affording intractable materials. Therefore, treatment with simple AlMe₃ was considered being the next step to obtain at least some information about the outcome of the interaction of the transition metal with the activator. The reaction of the *divalent* **1** with five equivalents of AlMe₃ afforded the *trivalent* and cationic complex {[(*t*-Bu)NP(Ph)₂N(*t*-Bu)]₂-Cr}{(Me₃Al)₂Cl} · (toluene) (**5**) as a crystalline product (Scheme 1). The same species could also be obtained upon treatment of the trivalent **4** with AlMe₃, thus providing two alternate syntheses for the same species.

The connectivity of **5** was revealed by an X-ray crystal structure and comprises a trivalent chromium center in a distorted tetrahedral environment defined by two ligand systems (Figure 3). One $[(Me_3Al)_2Cl]^{(-)}$ counteranion, unconnected to the chromium-containing unit, is also present in the lattice, thus conclusively assigning the trivalent state to the metal. The magnetic moment of **5** was in the expected range for the high-spin d³ electronic configuration of trivalent chromium.

The formation of 5 from 1 implies two separate processes: ligand scrambling and oxidation of the metal center. The acquisition by the chromium center of a second ligand during the reaction (ligand scrambling) in turn indicates that a second chromium-containing species must have been generated. Table 2. Ethylene Oligomerization Results^a

catalyst	co-catalyst (equiv)	co-cat: Cr	alkenes (mL)	activity (g/mmolCr/h)	C ₆ (mol %)	C ₈ (mol %)	C ₁₀ (mol %)	C ₁₂ (mol %)	C ₁₄ (mol %)	C ₁₆ (mol %)	C ₁₈ (mol %)
1	МАО	100	80	5600	33	25	18	11	9	3	1
1	MAO	500	208	14 560	40	31	15	9	4	1	0
1	MAO	1000	120	8400	37	26	18	11	5	2	1
1^{b}	MAO	500	14	980	51	40	6	2	1	0	0
1 ^c	MAO	500	20	1400	23	21	18	15	11	8	4
1^d	MMAO	500	0	0	0	0	0	0	0	0	0
1	PMAO	500	144	10 080	37	23	17	11	7	4	1
1	DMAO ^e	500	240	16 800	36	26	17	11	6	3	1
1	DMAO ^e	1000	348	24 360	33	30	16	11	6	3	1
1	DMAO ^e	2000	420	29 400	42	30	14	9	4	1	0
2	MAO	500	112	7840	31	30	16	10	7	4	2
3	MAO	500	100	7000	35	25	18	11	7	3	1
4	MAO	500	16	1120	25	27	20	14	8	4	2
5	MAO	500	0	0	0	0	0	0	0	0	0
^a Conditio	ns: 100 mL of	toluene, loa	ding 10 µm	ol of complex. 35	bar of ethy	lene, reactio	on temperat	ure 60 °C.	reaction tim	$b = 60 \text{ min.}^{b}$	T = 20 °C.

^{*c*} T = 100 °C. ^{*d*} 100 mL of methylcyclohexane. ^{*e*} DMAO = AlMe₃-depleted MAO.

Instead, the oxidation of the metal center during the reaction with an alkyl aluminum reagent is, at least in principle, surprising since these activators are known to act as reducing agents¹⁴ and certainly not as oxidants. On the other hand, recent work^{15,21} has indicated that the reoxidation of the chromium center in the presence of alkyl aluminum reagent is indeed possible via disproportionation as one of the distinctive aspects of the redox dynamism of chromium. This process is the direct result of the interaction of the metal center with the alkyl aluminum activator. In the present case, the additional ligand necessary for the formation of 5 can simply be provided by the low-valent partner of the disproportionation of 1 on the way to form metallic chromium. Instead, the formation of 5 from 4 has a more straightforward explanation since the oxidation state remained unchanged. However, given the acquisition of the additional ligand and that the reduction of the trivalent center to the divalent state during the reaction with activators is widely documented,¹⁴ it is tempting to suggest that the reaction proceeds with initial reduction of 4 to a divalent congener followed by similar disproportionation to that observed in the case of 1.

When activated with methylaluminoxane, 1 yielded a very large amount of pure oligomers with a minor excess of 1-hexene and 1-octene (Table 2). Interestingly, 1-butene was observed only in traces. Increasing the Al:Cr ratio resulted in a tremendous increase of catalytic activity as well as in a significant increment of the selectivity toward 1-hexene and 1-octene. The optimization was reached with an Al:Cr ratio of about 500 since larger excess decreased the activity as well as the selectivity. A similar rise in catalytic activity with increasing Al:Cr ratios was also observed for the original NPN system containing a trivalent phosphorus.^{17a} In that case the selectivity was, however, unchanged. Temperatures higher or lower than 60 °C visibly decreased the activity. At low temperature, the lower activity was accompanied by a considerable increase of selectivity (91% 1-hexene/1-octene and 9% heavier oligomers). Outstanding features of this catalytic system are the complete absence of polymer and the purity of the oligomers, which are both highly desirable from an industrial standpoint. The use of different aluminoxane activators afforded variable activities. The most productive run was obtained with

AlMe₃-depleted MAO (DMAO), which afforded an activity comparable to the highest ever observed for a LAO catalyst obtained with late transition metals²² (420 mL of polymer-free mixture of oligomers from 10 μ mol of catalyst per hour). Interestingly, the high activity was also accompanied by a significant enrichment in 1-hexene and 1-octene, the two most important α -olefinic oligomers (Table 2).

The replacement of the *t*-Bu substituents by *i*-Pr or Ph groups gave a noticeable decrease of both activity and selectivity, although the overall catalytic activity still remained quite acceptable. The fact that the large steric bulk of the *t*-Bu groups may play a central role in significantly enriching the oligomeric mixture in 1-hexene and 1-octene is intriguing. If the excess of these two oligomers is generated by a Cr(I) intermediate via a ring expansion mechanism, this would be of course in addition to the Cossee–Arlman mechanism, presumably operated by Cr(II) and which produces the large amount of oligomers. We therefore speculate that the bulky substituents of 1 prevent dimeric aggregation of the monovalent chromium, thus hindering its disproportionation but also decreasing the catalytic activity. In other words, the ligand's steric bulk might lend some stability to highly reactive Cr(I) intermediates. However, the absence of 1-butene in significant amount encourages the idea that the oligomer distribution may be generated by a ring-expansion mechanism.9 In such an event, one must assume that the presence of *t*-Bu groups somehow renders faster the reductive elimination of the seven- and nine-membered rings with respect to that of larger rings.

We have also attempted to utilize methylcyclohexane as solvent for the catalytic run since toluene is known to occasionally have a poisoning effect on trimerization catalysts.^{14b} In turn this has required the usage of MMAO for solubility reasons. The observed lack of catalytic behavior is likely to be ascribed to the strongly reducing *i*-Bu groups present in this particular activator most probably decomposing the catalyst to metallic chromium. The trivalent 4 displays only marginal catalytic activity compared to the divalent 1.

In conclusion, in this work we have discovered an unprecedented and potentially useful catalytic system for nonselective ethylene oligomerization devoid of polymer. This feature, in combination with the near to record activity of 1, makes the catalyst competitive with the best performing industrial systems. The general lack of selectivity and the chemical behavior of the complexes reported above altogether suggest that the most active catalytically active species may contain divalent chromium. In this event, the nonselective oligomerization would not proceed through a ring-expansion mechanism. It is worth reminding that divalent chromium, according to the current status of its chemistry, does not possess the reducing potential sufficient for coupling two ethylene molecules into a metallacycle. At this stage it is tempting to propose that the excess of 1-hexene and 1-octene observed in a few instances is likely to be generated by a monovalent chromium species produced in parallel to Cr(II) as a result of the redox dynamism. The subtle effect of ligand substituents in determining the appearance of the excess of these two oligomers, together with the exceedingly high activity, encourages further attempts to transform these systems into highly active and truly selective oligomerization catalysts.

ASSOCIATED CONTENT

Supporting Information. Complete crystallographic data for the complexes reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org

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ACKNOWLEDGMENT

This work was supported by NSERC and Basell Polyole-fine GmbH.

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