Isolation of a Hexanuclear Chromium Cluster with a Tetrahedral Hydridic Core and Its Catalytic Behavior for Ethylene Oligomerization

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ABSTRACT: A chromium complex [2-(NHCH₂PPh₂)C₅H₄N]CrCl₃·THF₂ (1) of the ligand PyNHCH₂PPh₂ has been synthesized, characterized, and examined for its catalytic behavior toward ethylene oligomerization. When complex 1 was treated with (i-Bu)₃Al, an unprecedented divalent polyhydride chromium cluster μ₅⁻₅⁻₅⁻₅⁻₅⁻N,N,P-{[2-(NCH₂PPh₂)C₅H₄N]⁻·Cr(μ-H)}₄[(μ-Cl)Cr(μ-Cl)Al(i-Bu)₃Cl] (2) was obtained. The complex contains a Cr₄H₄ core, which is expected to be diamagnetic, and which remains coordinated to two additional divalent high-spin Cr atoms via bridging interactions. Two aluminate residues remain bonded to the peripheral chromium atoms. The structure, magnetism, and electronic configuration are herein discussed.

INTRODUCTION

The Cr−Cr interaction in dimetallic units is probably the most unique and intriguing feature that can be encountered in M−M bond chemistry. Low-valent chromium has provided in fact the shortest ever found intermetallic contacts, initially leading to the conclusion that such interactions should be strong.3 However, a large body of work both theoretical1 and experimental1,4 has clearly highlighted the paradoxical weakness of such interactions.5 In turn, this hinted that ligand features (chelating geometry, bite, steric interactions, etc.) rather than M−M bond strength may be the factors at play in determining the extent of the Cr−Cr separation.1b,3f,6

The two oxidation states occasionally displaying this intriguing behavior are the monovalent1b,6,7 and divalent ones.8 The monovalent state is particularly noticeable in the sense that it has produced record short Cr−Cr bonds,1j thought to be quintuple. However, DFT work has also shown that there is the possibility for singlet open-shell AF-coupled configurations and which may reduce the formal M−M bond order.1d,3d,9

Interestingly, both Cr(II) and Cr(I) play an important role in catalytic ethylene oligomerization, and it is still debated whether selective catalytic oligomerization to either tri- or tetramerization should be ascribed to the monovalent state.10 In any event, the ligand system must be able to prevent formation of strong Cr−Cr interactions which may introduce excessive stability and ultimately obliterate the catalytic behavior. Thus, assuming that monovalent chromium is truly responsible for selective oligomerization, it was argued that ligands capable of holding two metal centers at appropriate distance might be the winning key to produce highly desirable selective tetramerization catalysts.11 Such catalysts remain to date exceedingly rare.12

The employment of ligands based on phosphorus or sulfur donor atoms appears to be mandatory if mononuclear and monovalent species of sufficiently long lifetime to initiate a catalytic cycle are being targeted. In addition, amino- and pyridine functionalities may also help to obtain selective catalytic systems. Following the work of McGuinness,13 Wass,14 and Rosenthal,15 we have also developed ligand systems based on those functionalities. Of primary interest to us was the isolation of catalytically active species, generated by the direct interaction of trivalent chromium precursors with aluminates.16

For the present work, we have selected a 2-[N(H)-CH₂PPh₂]C₅H₄N ligand with the hope of generating multinuclear species hopefully containing the chromium metal in lower oxidation states.17 By using a strongly reducing (i-Bu)₃Al activator in combination with the particular framework of the above ligand, we anticipated the possibility of forming dimetallic structures, which might help us to understand the role of the Cr−Cr interaction in terms or either favoring or disfavoring ethylene oligomerization.

Herein we describe the isolation and characterization of an unprecedented Cr(II) hydride hexachromium cluster with a diamagnetic tetrahedral core and two peripheral paramagnetic centers. It is worth noting that although there are precedents for Cr-hydrides in the literature,18 information remains scarce.

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**RESULTS AND DISCUSSION**

Treatment of CrCl₃(THF)₃ with the amino-phosphine ligand derivative 2-[N(H)CH₂PPh₂]C₅H₄N in THF afforded the corresponding paramagnetic adduct [2-[N(H)CH₂PPh₂]C₅H₄N]CrCl₃(THF)·THF (1) (Scheme 1).

![Scheme 1](image_url)

Complex 1 features a trivalent chromium atom in a distorted octahedral arrangement surrounded by three chlorines (Figure 1) [Cr(1)−Cl(1) = 2.301(2) Å, Cr(1)−Cl(2) = 2.304(2) Å, Cl(3)−Cr(1)−Cl(3) = 86.22(16)°]. An additional molecule of THF was also found in the lattice.

![Figure 1](image_url)

Table 1. Ethylene Catalyzed Oligomerization Reactions of 1–2a

| catalyst | alkene (g) | PE (g) | activity (g/g Cr h) | C₄ | C₆ | C₈ | C₁₀ | C₁₂ | C₁₄ | C₁₆ | C₁₈ | α<sub>av</sub> |
|----------|-----------|--------|---------------------|----|----|----|----|----|----|----|----|----|-------------|
| 1        | 36        | 3.2    | 55 654              | 11 | 14 | 16 | 15 | 14 | 12 | 10 | 8  | 0.76        |
| 2        | 22        | 2.1    | 43 913              | 4  | 13 | 19 | 18 | 15 | 13 | 10 | 8  | 0.78        |

*a*Conditions: 100 mL of toluene, loading 20 μmol of catalyst, 40 bar of ethylene, T = 80 °C, (Al:Cr) MAO = 500, reaction time 30 min.
paramagnetic cluster \([\text{Cp}^*\text{CrH}]_4\) also containing divalent chromium. That structure has a more symmetric core with hydrogen atoms capping each face of the coordination tetrahedron.\(^2\)

In complex 2, each dimetalllic core unit also retains one chloride atom approximately lying on the metal–metal vector \([\text{Cr}(2)–\text{Cl}(1) = 2.7040(15) \text{ Å, Cr}(1)–\text{Cr}(2)–\text{Cl}(1) = 168.38(6)°]\) (Figure 2). Two of the four deprotonated ligand nitrogen atoms, along with the two P atoms and the two pyridine N atoms not connected to the tetrahedral core as well as the two coaxial chlorine atoms, generate two square-planar pockets where two additional chromium atoms are accommodated \([\text{Cr}(3)–\text{Cl}(1) = 2.3691(16) \text{ Å, Cr}(3)–\text{Cl}(2) = 2.5957(19) \text{ Å, Cr}(3)–\text{P}(2) = 2.5490(16) \text{ Å, Cr}(1)–\text{N}(4) = 2.006(4) \text{ Å, Cr}(2)–\text{N}(3) = 2.026(4) \text{ Å, Cl}(1)–\text{Cr}(3)–\text{P}(2) = 87.90(5)°, \text{Cr}(2)–\text{Cr}(1)–\text{N}(4) = 95.01(13)°, \text{Cr}(2)–\text{Cr}(1)–\text{N}(1) = 107.03(13)°, \text{P}(2)–\text{Cr}(3)–\text{Cl}(2) = 108.55(6)°]\]. The coordination geometry around these two additional metal centers appears to be square-pyramidal since an additional coordination geometry around these two additional metal ions. That structure has a more symmetric core with hydrogen atoms capping each face of the coordination tetrahedron.\(^2\)

\[\begin{align*}
\text{Cr}(1)–\text{N}(1) = 2.091(4), \text{Cr}(2)–\text{P}(1) = 2.245(3), \text{Cl}(1) = 2.7040(15) \text{ Å, Cl}(1)–\text{Cr}(2)–\text{Cl}(1) = 168.38(6)°, \text{Cr}(1)–\text{Cr}(2)–\text{N}(3) = 94.00(18), \text{Cr}(1)–\text{Cr}(2)–\text{N}(3) = 95.27(12), \text{Cr}(1)–\text{Cr}(2)–\text{P}(1) = 91.38(5), \text{N}(3)–\text{Cr}(2)–\text{Cl}(1) = 92.67(12), \text{P}(1)–\text{Cr}(2)–\text{Cl}(1) = 97.51(5), \text{Cl}(1)–\text{Cr}(3)–\text{Cl}(2) = 89.74(6), \text{Cr}(3)–\text{Cl}(1)–\text{Cr}(2) = 79.57(5), \text{Al}(1)–\text{Cl}(2)–\text{Cr}(3) = 136.17(12), \text{Cl}(3)–\text{Al}(1)–\text{Cl}(2) = 102.61(13).\end{align*}\]

\[\begin{align*}
\text{Cl}(1) = 2.7040(15) \text{ Å, Cr}(1)–\text{Cr}(2)–\text{Cl}(1) = 168.38(6)°, \text{Cr}(1)–\text{Cr}(2)–\text{N}(3) = 94.00(18), \text{Cr}(1)–\text{Cr}(2)–\text{N}(3) = 95.27(12), \text{Cr}(1)–\text{Cr}(2)–\text{P}(1) = 91.38(5), \text{N}(3)–\text{Cr}(2)–\text{Cl}(1) = 92.67(12), \text{P}(1)–\text{Cr}(2)–\text{Cl}(1) = 97.51(5), \text{Cl}(1)–\text{Cr}(3)–\text{Cl}(2) = 89.74(6), \text{Cr}(3)–\text{Cl}(1)–\text{Cr}(2) = 79.57(5), \text{Al}(1)–\text{Cl}(2)–\text{Cr}(3) = 136.17(12), \text{Cl}(3)–\text{Al}(1)–\text{Cl}(2) = 102.61(13).\end{align*}\]

The susceptibility can originate from the inherent significant anisotropy as arising from mixing of the electronic ground state and low-lying electronic exited states in the \(d^4\) high-spin Cr(II) ions.

\[J = -3.47\]
\[g = 2.38\]

\[\begin{align*}
\chi(T) &= \chi_0 + \chi_1, \\
\chi_0 &= \chi_{\text{free}} - \chi_{\text{free}}^a, \\
\chi_1 &= \chi_{\text{diamag}}\text{ (diamagnetic).}
\end{align*}\]

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\chi_1 &= \chi_{\text{diamag}}\text{ (diamagnetic).}
\end{align*}\]

The \(\chi(T)\) vs \(H\) data (Figure 5) for \(I\) also shows similar behavior, where at high fields there is no saturation or overlay onto a single master curve. This confirms the presence of large magnetic anisotropy and/or low-lying excited states. To probe any single-molecule magnet (SMM) behavior, temperature dependence of the out-of-phase magnetic moment of 2 under an applied dc field of 10000 Oe.
(\(\chi^\prime\)) magnetic susceptibility was investigated. No temperature-dependent signal was observed thus precluding any SMM behavior.

The most appropriate method for studying the electronic structure of chromium clusters is probably CASSCF,\(^{22}\) including all Cr valence electrons in the active space. This method has been used for the study of chromium dimers,\(^{25,34}\) but would be completely unfeasible for our hexachromium cluster. As an alternative, several authors have used spin-restricted DFT methods.\(^{35,36}\) We feel this is not appropriate for our cluster either, in particular for the weaker interactions between the four core and the two outer Cr atoms, where weak ferromagnetic coupling might be expected. Therefore, we decided to use the spin-unrestricted DFT formalism (using broken-symmetry solutions for \(\chi^\prime\)) magnetic susceptibility was investigated. No temperature-dependent signal was observed thus precluding any SMM behavior.

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The cluster was built in two stages: initially, only the central Cr core was modeled (cluster A), and then the two terminal Cr fragments were added. This was helpful in understanding the interaction between the core and terminal Cr atoms. The dangling \(\eta^1\)-Cl\(_2\)AlBu\(_2\) anions were modeled by chlorides (cluster B) or deleted altogether (cluster \(C^{2+}\)). For core A, we considered the possibility of 0, 8, or 16 unpaired electrons. Coupling to the terminal Cr fragments led us to consider 0, 8, 16, and 24 unpaired electrons for B and \(C^{2+}\). All of these possibilities were individually optimized at the b3-lyp level,\(^{24,25,35,36}\) although in the following we will only discuss the lowest-energy state of each. The lowest-energy spin states (bold in Table 2) were then reoptimized using the tpssh\(^{25}\) and b-p\(^{25,35,36}\) functionals.

Calculations at the b3-lyp and tpsh level do not reproduce the extreme shortness of the Cr1–Cr2 bond found in 2 (for calculated bond lengths, see Table 3). On the other hand, b-p predicts even shorter bonds than those found in the X-ray structure. The large differences in calculated Cr–Cr distances obtained with different functionals reflect the “softness” of the Cr–Cr interaction. However, the bonding arrangement is roughly the same in all calculations. The distorted tetrahedral core of the molecule consists of two dimeric units \([(\text{CrI,Cr}2) (\text{Cr1A,Cr2A})]\). Within each unit, the Cr atoms are high-spin but AF coupled to each other. The degree of coupling is higher in the b-p structures, with their short Cr–Cr distances, and this is reflected in lower \(\langle S^2 \rangle\) values (included in Table 3). The two dimeric units are then more weakly F coupled to each other, which still leaves the core unit overall diamagnetic (see Figure 6, cluster A). Since within the core symmetry-related Cr atoms prefer to have parallel spins, one could expect that when the symmetry-related terminal Cr atoms (Cr3, Cr3A) are added these would also prefer to have their spins parallel. This is indeed what we find both B and \(C^{2+}\) have a preference for an \(S_z = 4\) “state”, and the spins of Cr3 and Cr3A are aligned with those of Cr1 and Cr1A (shown in Figure 6 for \(C^{2+}\)).

Chromium hydride clusters are rather rare. The only example relevant to the present context is the set of \([(\text{Cp}2\text{CH})_4]\) clusters reported by the group of Theopold.\(^{18,21}\) These clusters have a tetrahedral Cr\(_4\) core with hydrides assumed to be located on the faces of the tetrahedron; they are weakly paramagnetic. We have studied simplified model cluster \([(\text{CpCrH})_4]\) for comparison (see Tables 2 and 3), using the same methods as for A–C.
The drawback of using the spin-unrestricted formalism is that it makes a detailed analysis of the bonding situation difficult. Calculations indicate that an overall low-spin structure is preferred by a modest margin (10.6 kcal/mol, b3-lyp). As for model A, the $S_z = 0$ state is heavily spin-contaminated (see Table 3) and corresponds to four high-spin $C_2^\pi$ centers coupled ferromagnetically within pairs, and antiferromagnetically between pairs. Interestingly, optimization at the b3-lyp or tpssh level produces edge-bridging hydrides (approximate cluster symmetry $D_2$) rather than the symmetrically face-bridging hydrides observed experimentally (approximate cluster symmetry $T_b$), but all Cr–Cr contacts, whether bridged or unbridged, are rather similar. On the other hand, b-p calculations reproduce the face-bridging hydrides found in the X-ray structure but yield much more variation in the Cr–Cr distances (2.33–2.78 Å) than observed experimentally (2.61–2.68 Å). One could imagine that the real complexes reported by Theopold have fluxional hydrides and/or dynamic Cr–Cr distances, but it is equally possible that optimization within a proper spin state (avoiding the UKS artifact of two spin distances, but it is equally possible that optimization within a cluster symmetry $D_2$ level produces edge-bridging hydrides (approximate cluster symmetry $D_2$) rather than the symmetrically face-bridging hydrides observed experimentally (approximate cluster symmetry $T_b$), but all Cr–Cr contacts, whether bridged or unbridged, are rather similar. On the other hand, b-p calculations reproduce the face-bridging hydrides found in the X-ray structure but yield much more variation in the Cr–Cr distances (2.33–2.78 Å) than observed experimentally (2.61–2.68 Å). One could imagine that the real complexes reported by Theopold have fluxional hydrides and/or dynamic Cr–Cr distances, but it is equally possible that optimization within a proper spin state (avoiding the UKS artifact of two spin $\alpha$ and two spin $\beta$ chromium atoms) would lead to symmetric face-bridging hydrides and more similar Cr–Cr distances. In any case, it seems reasonable to conclude that the energy difference between edge-bridging and face-bridging hydrides is small for $[Cp'\text{CrH}]_4$, and probably also for 2.

The drawback of using the spin-unrestricted formalism is that it makes a detailed analysis of the bonding situation difficult. This is compounded by the fact that bridging hydrides are involved in the Cr1–Cr1′, Cr2–Cr2′, and Cr1–Cr2–Cr3 interactions. NBO analyses$^{27}$ of the three model clusters (at the BP86 level) consistently produce a triple bond for the short Cr1–Cr2 contact, as well as a nonbonding ("$LP$") electron at Cr2 and bonds of Cr1 and Cr2 to their N and P ligands. There is a slight difference in bonding picture between models B and $C^\pi$: analysis for the former produces a half Cr1–Cr3 bond and three Cr3-centered nonbonding electrons, whereas for the latter the analysis indicates four Cr3-centered nonbonding electrons and no Cr1–Cr3 bond. It should be noted here that in the analysis no discrete bonds to hydrogens were produced. While this analysis should be considered tentative (for all of the reasons mentioned above), a triple Cr1–Cr2 bond seems reasonable compared to results reported for Cr dimers.$^3$ In addition, the absence of multiple metal–metal bonding involving Cr3 appears to be consistent with the much larger bond lengths to the Cr atom.

Interestingly, complex 2 shows a catalytic behavior very similar to 1 where a lower amount of 1-butene and more 1-octene is the most noticeable difference (besides a decreased activity). It should also be reiterated that the previously reported divalent and paramagnetic $[(\mu-\text{i-Bu})\text{P}[\text{N}(\text{i-Bu})_2]_2\text{Al}(\text{i-Bu})_3]\text{Cr}(\mu-H)]_2$ is also a self-activating polymerization catalyst of high activity. In contrast, no such behavior was detected with 2, and the polymeric material appears to be only heavier oligomers with a $M_n$ centered over 366 g mol$^{-1}$. It is tempting to suggest at this stage that only the two peripheral Cr units of 2 are responsible for the catalytic behavior, while the central core, by being multiply bonded, does not produce any interaction with ethylene even under further activation conditions.

### EXPERIMENTAL SECTION

All reactions were carried out under inert atmosphere using Schlenk techniques or in a purified nitrogen-filled drybox. Solvents were dried using a purification system composed of aluminum oxide, GC–MS analysis of the oligomers was carried out with a Hewlett-Packard HP 5973 gas chromatograph using an Agilent DB1 column and dual FID and MS detector. Elemental analysis was carried out with a PerkinElmer 2400 CHN analyzer. Magnetic susceptibility measure-

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Table 3. Comparison of Calculated and Experimental Cr–Cr Distances

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<th>Cr2–Cr2′</th>
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Figure 6. Spin density plots for model clusters A and C$^{2+}$ (b-p results).
mements were performed with a Johnson Matthey balance at room temperature. The samples were powdered and weighed inside a drybox and transferred to sealed and calibrated tubes for measurements.

NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer at 300 K. Infrared spectra were recorded on an ABB Bomem FTIR instrument from Nujol mulls prepared in a VAC drybox. All chemical reagents were purchased from commercial sources and used as received. Tri-isobutyl aluminum was purchased from Strem and used as received. Methylaluminoxane (MAO, 20% in toluene) was purchased from Albermarle Corporation. TMS-depleted methylaluminoxane (DMAO) was prepared by removing all the volatiles from MAO in vacuo (2 mm Hg) and with moderate heating (40 °C) for 6 h.

A magnetic analysis was performed on a crushed polycrystalline sample of 2, wrapped in a polyethylene membrane sealed in a glovebox to prevent any sample degradation. The direct current (dc) magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T. Alternating current (ac) susceptibility measurements were carried out under an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. The magnetization data was collected at 100 K to check for ferromagnetic impurities which were found to be absent in 2. Diamagnetic corrections were applied for the sample holder and the core impurities which were found to be absent in 2. SQUID susceptibility measurements were carried out under an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz.

**Preparation of [2-(CH₂)₂NH][(CH₂)₃P]CrCl₃(THF) (1).** A solution of CrCl₃(THF) (0.375 g, 1.0 mmol) in THF (15 mL) was added to a solution of (CH₂)₃PCH₂NH(0.292 g, 1 mmol) in THF (5 mL). The color of the solution immediately changed to dark green. Green crystals of 1 were obtained by slow evaporation (0.26 g, 0.50 mmol, 50%). μ₂ = 3.81 μB. Anal. Calcd (%) for C₂₆H₃₃Cl₃CrN₂O₂P: C 50.64 (50.58), H 4.64 (4.61), μ₂ = 3.81 μB. Anal. Calcd (%) for C₆H₁₃Cl₃CrN₂O₂P: C 50.64 (50.58), H 4.64 (4.61), N 5.37 (5.32). IR (Nujol): ν_{30} = 3252 cm⁻¹.

**Preparation of [μ₂-C≡C(μ-N)₂(N-C₆H₅)(μ₂-C≡C(μ-N)₂(N-C₆H₅))Cr(μ-H)]₄[(μ-C≡C(μ-Cl)(μ-Cl)(μ-Cl)(μ-Cl)]₂(Al(μ-Bu)Cl)₂ (2).** A solution of PyNHCH₂PPh₂ (0.292 g, 1.0 mmol) in toluene (10 mL) was treated with CrCl₃(THF) (0.292 g, 1.0 mmol), and the mixture, in which a dark brown solution formed, stirred for 30 min. After it was warmed to room temperature overnight, a blue precipitate formed, filtered, washed with cold heptanes (10 mL), and dried in vacuo, affording 2 (0.538, 0.272 mmol, 27.2%). Anal. Calcd. (%) for C₆H₁₃₃Cl₃₆Cr₃N₂₀₅P: Found: C 53.48 (53.12), H 5.30 (5.26), N 5.67 (5.61).

**Chemical Degradation of 2.** Different amounts of hydrogen gas were introduced with a gas-tight volumetric syringe in tightly sealed vials filled with nitrogen gas. Once hydrogen gas was introduced, it was allowed to equilibrate at room temperature for 10 min after which a 1 mL sample of the gaseous mixture was injected into the GC with TC detector to obtain the calibration curve. Different amounts of the cluster sample were placed in vials under the same conditions. Degradation was carried out via addition of acetone/HCl (1/0.1 mL) causing visible gas evolution. The quantification of hydrogen was obtained by determining its concentration in the gas phase via GC analysis relative to the calibration curve.

**DFT Calculations.** All geometries were optimized without constraints, starting from the X-ray structure of 2, at the spin-unrestricted b3-LYP/6-31G(d,p)+ZPE level (using the Turbomole program) coupled to an external optimizer. The lowest-energy spin states of each of the model clusters A, B, and C were then reoptimized at the spin-unrestricted TPSSH and b3-LYP/6-31G(d,p)+ZPE level, still using the SV(P) basis set. Vibrational analyses (analytical frequencies) confirmed all optimized structures as local minima (no imaginary frequencies). NBO analyses on the b-p optimized structures were carried out with Gaussian09. The BP86/SVP functional, and the SV(P) basis set. Spin density plots were produced using Molden.
Inorganic Chemistry

the solvent unit. All carbon atoms for tolune solvent molecules were refined with isotropic approximation to avoid introducing excessive amount of constrains/restrains as well to preserve acceptable data to parameters ratio. In addition, the set of thermal parameters constrains (EADP), geometry (FLAT, DFIX) and rigid body restrains (AFIX 66), and geometry constrains (SADI) were used to maintain reasonable molecular geometrical and thermal motion values for solvent molecules.

For all the compounds, all hydrogen atom positions were calculated on the basis of the geometry of the related non-hydrogen atoms. All hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL 2013 program library.34

Ethylene Oligomerization. Oligomerizations were carried out in a 200 mL high-pressure Büchi reactor containing a heating/cooling jacket. A preweighted amount of catalyst was dissolved in tolune (10 mL) under nitrogen 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. Oligomerizations were quenched by cooling to 0 °C, releasing the pressure, and adding MeOH/HCl (80% MeOH solution). The total yield of oligomers was determined by 1H NMR by integrating the intensity of the olefinic signals giving crystallographic date for the solvent unit. All carbon atoms for toluene solvent molecules were determined by GC using an FID detector. The α value was measured with the C(n + 2)/Cn ratio for the range C6–C20. The insoluble polymeric solid was isolated by filtration and dried prior to measuring its mass.

ASSOCIATED CONTENT

Supporting Information
Tables and CIF files giving crystallographic date for 1–2. DFT calculation tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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