# Preparation and Characterization of a Reduced Chromium Complex via Vinyl Oxidative Coupling: Formation of a Self-Activating Catalyst for Selective Ethylene Trimerization

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S *Supporting Information*

ABSTRACT: Reaction of the divalent $[(t\text{-}Bu)NP(Ph)_2N(t\text{-}Bu)]CrCl_2Li(THF)_2$ (**1**) with 1 equiv of vinyl Grignard $(CH_2=CH)MgCl$ reproducibly afforded the triangulo $\{\pi\text{-}[(t\text{-}Bu)N-P(Ph)_2-N(t\text{-}Bu)]Cr\}_2(\mu,\mu',\eta^4,\eta^{4'}\text{-}C_4H_4)\{\sigma\text{-}[(t\text{-}Bu)N-P(Ph)_2-N(t\text{-}Bu)]Cr\}$ (**2**) containing a $\sigma\text{-}/\pi$-bonded butadiene-diyl unit. The diene-diyl moiety was generated by an oxidative coupling and deprotonation of two vinyl anions. The crystal structure revealed that of the three chromium atoms, each bearing one NPN ligand, two are perpendicularly bonded to the two sides of the π-system of the butadiene-diyl residue in a sort of inverted sandwich type of structure. The third is instead coplanar with the doubly deprotonated C_4 unit and σ-bonded to the two terminal carbon atoms. Despite the appearance as a Cr(II)/Cr(I) mixed valence species, DFT calculations have revealed that the structure of **2** consists of three divalent chromium atoms, while the additional electron resides on the π-system of the bridging organic residue. Complex **2** behaves as a single component selective catalyst for ethylene trimerization.
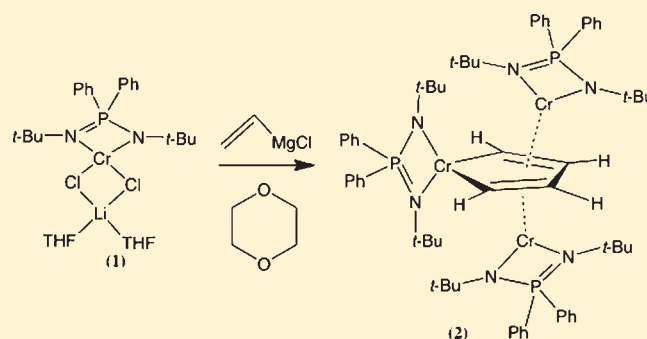
INTRODUCTION

Catalytic and selective ethylene trimerization is increasingly attracting the attention of academic researchers for the ongoing mechanistic debate[1] about the several aspects of this industrially relevant[2] and relatively rare process.[3] The current state of knowledge relies on the so-called ring expansion mechanism triggered by a transition metal (most often chromium) in a low oxidation state sufficiently reducing to perform the initial ethylene reductive coupling.[1,3,4] From recent studies in chromium-catalyzed selective tri- and tetramerization, it becomes apparent that the occurrence of selectivity in the catalytic process is directly related to the possibility of reaching the monovalent state.[5] There are substantial challenges, however. This particular oxidation state can be stabilized on chromium by π-systems (arene, cyclopentadienyls) and/or CO and for which a large family of compounds has today been established.[6] These species, however, are catalytically inert unless procedures are followed for the extraction of the strongly stabilizing carbonyl ligands.[6i,j] Asides from them, only less than a handful of monovalent compounds have been isolated and crystallographically authenticated. The common feature among all of these species is the clear evidence for a tremendous reducing power as indicated by the fact that these species form dinitrogen[7] and arene inverted sandwich compounds,[8] or quintupled bonded dichromium systems.[9] Therefore, it comes without surprise that the most

convenient path to monovalent chromium selective catalysts commonly consists of reducing tri- or divalent complexes in situ with the aid of an alkylating agent as an activator.

In the most selective chromium catalytic trimerization systems reported so far, the activation process is performed mainly by a large amount of MAO[2,3] or near to stoichiometric amount of TEAL/DEAC.[2a] It is well established that trivalent organochromium complexes may readily be reduced to the divalent state in the presence of alkyl aluminum reagents.[10] In this scenario, selective oligomerization does not occur, while instead polymerization or nonselective oligomerization (S—F distribution) is being observed.

In search for selective trimerization systems based on chromium, one possible strategy consists of bypassing the divalent state to reduce the trivalent precursor directly to the monovalent via a concerted two-electron reduction.[5d] This might be achieved via double alkylation of the transition metal center followed by two-electron reductive elimination of organic units (e.g., heavier alkanes or alkanes/alkenes mixtures). Organo-aluminum species, although effective so far, are not ideal for the purpose because they may embark in alkyl/halogen exchange equilibria with the transition metal, in turn often requiring the employment of a
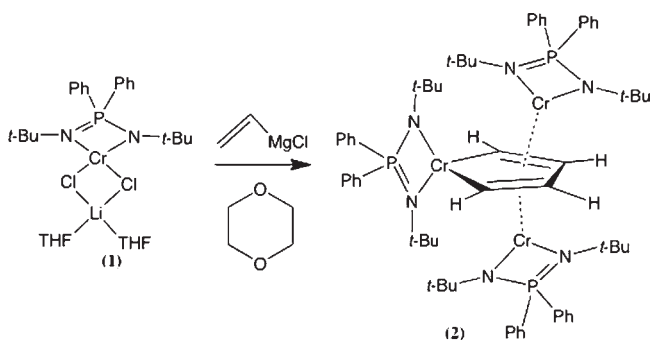
large amount of these dangerous and expensive chemicals. Even further, if during the dynamic alkyl exchange process, a substantial concentration of monoalkylated chromium species is generated, one-electron reduction to the stable divalent state may rapidly and irreversibly occur under the thermal conditions normally required by the catalytic cycle. In turn, this would negatively affect the selectivity by providing only S—F mixtures possibly enriched in 1-hexene depending on the extent of two- versus one-electron reduction.

Given this background, we are exploring the possibility of using stoichiometric amounts of organo-magnesium and -lithium derivatives for the purpose of cleanly generating catalytically active monovalent species. For this study, we have selected the vinyl-Grignard reagent with the purpose of performing alkylation and two-electron reduction of the metal center as discussed above.

As a substrate, we have focused on the recently prepared divalent $[(t\text{-Bu})NP(Ph)_2N(t\text{-Bu})]CrCl_2Li$.[11] A recent study from our lab has clearly identified its ready formation from a trivalent precursor in the presence of alkylating agents.[11] This catalyst only produces a S—F distribution of oligomers. This behavior clearly speaks for the initial reduction of the trivalent species to the divalent state that is obviously preserved throughout the catalytic cycle. The resiliency to reach the monovalent state made this substrate ideal for probing the effect of stronger alkylating and more reducing activators.

In this Article, we describe its reaction with $CH_2\!\!=\!\!CH\!-\!MgCl$ affording an oxidative coupling of two vinyl groups with formation of a reduced chromium complex storing additional spin density in a deprotonated butadiene residue. Its catalytic behavior as a single component selective trimerization catalyst is discussed.

■ RESULTS AND DISCUSSION

The reaction of divalent $[(t\text{-Bu})NP(Ph)_2N(t\text{-Bu})]CrCl_2Li\text{-}(THF)_2$ (**1**) with $CH_2\!\!=\!\!CH\!-\!MgCl$ reproducibly afforded the new trinuclear $\{\pi\text{-}[(t\text{-Bu})N\!-\!P(Ph)_2\!-\!N(t\text{-Bu})]Cr\}_2 (\mu,\mu',\eta^4,\eta^{4'}\text{-}C_4H_4)\{\sigma\text{-}[(t\text{-Bu})N\!-\!P(Ph)_2\!-\!N(t\text{-Bu})]Cr\}$ (**2**) (Scheme 1).

The trinuclear structure of **2** was revealed by an X-ray diffraction analysis and consists of three metal centers bridged by one butadiene-diyl unit (Figure 1). One metal center is coplanar with the C_4 unit and appears to be σ-bonded to the two terminal carbon atoms $[Cr(1)\!-\!C(32) = 2.128(3)$ Å$]$, thus forming a five-membered metallacycle. The coordination environment around this metal center is square-planar $[N(1)\!-\!Cr(1)\!-\!N(1a) = 71.5(2)°, N(1)\!-\!Cr(1)\!-\!C(32) = 107.5(1)°, N(1a)\!-\!Cr(1)\!-\!C(32a) = 107.5(1)°]$ with little deviation from the planarity and a narrower angle subtended by the two σ-bonded C atoms $[C(32)\!-\!Cr(1)\!-\!C(32a) = 73.7(2)°]$. The other two metal centers are symmetrically placed on the axis orthogonal to the plane of the C_4 unit with which they form a π-bonding interaction as indicated by the comparable values of the Cr—C distances $[Cr(2)\!-\!C(31) = 2.271(3)$ Å$, Cr(2)\!-\!C(32) = 2.174(3)$ Å$]$. The coordination geometry around each of the two metal centers may also be regarded as square-planar if considering only the two terminal C atoms as bonded to the metal center $[N(2)\!-\!Cr(2)\!-\!N(3) = 72.1(1)°, N(2)\!-\!Cr(2)\!-\!C(31) = 108.2(1)°, N(3)\!-\!Cr(2)\!-\!C(32a) = 106.4(1)°]$. The central and bridging C_4 unit has C—C distances $[C(32)\!-\!C(31) = 1.435(5)$ Å$, C(31)\!-\!C(31a) = 1.416(6)$ Å$]$ as to be expected for a π-bonded butadiene type of system.[12] The Cr···Cr distance between the σ- and π-bonded metals $[Cr(1)\!-\!Cr(2) = 2.4892(8)$ Å$]$ is considerably short and falls in what might be regarded as a metal—metal bonding range. The σ-/π-orientation of the metals to the same C_4 unit is somewhat reminiscent of the trinuclear Ru complex reported by Adams containing a fluorinated residue.[12e] Structures contains two transition metals π-bonded to similar or the same C_4 units have been also previously observed for both Cr[12f] and Ni.[12g]

The crystal structure was of sufficient quality to yield the position of the hydrogen atoms including those attached to the
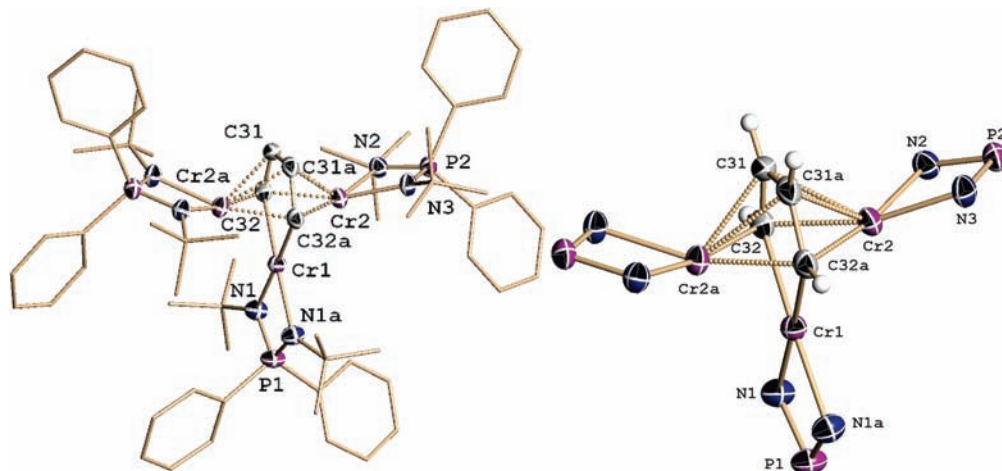
Scheme 1

Figure 1. Partial thermal ellipsoid plot for **2** (left) and simplified plot showing the position of the hydrogen atoms (right).

C_4 unit. Their position clearly suggested that the butadiene fragment is doubly deprotonated and is therefore in the form of a dianion. Attempts to degrade the complex with D_2O and to analyze the resulting mixture by NMR did not provide a definite answer in the sense that only partly deuterated butadiene oligomers have been identified. Fortunately, it was possible to obtain an informative ^1H NMR spectrum and which, despite the paramagnetism, showed a relatively minor line broadening in the normal range of ppm. The t-Bu groups showed a broad intense line at 1.02 ppm, while the phenyl groups gave two broad lines at 8.19 and 7.57. The butadiene-diyl moiety displays two poorly solved and broadened doublets of equal intensity at 7.95 and 7.43 ppm. All of the peaks integrate with the expected ratio. Finally, the MS-EI gave the parent peak and the fragmentation pattern as expected for the above formulation.

With three anionic NPN ligands, and one butadiene-diyl dianion, charge count considerations indicate that the complex should be regarded as a Cr(II)/Cr(I)/Cr(II) mixed valence species. To clarify the electronic structure of the complex, DFT calculations were undertaken using the atomic coordinates
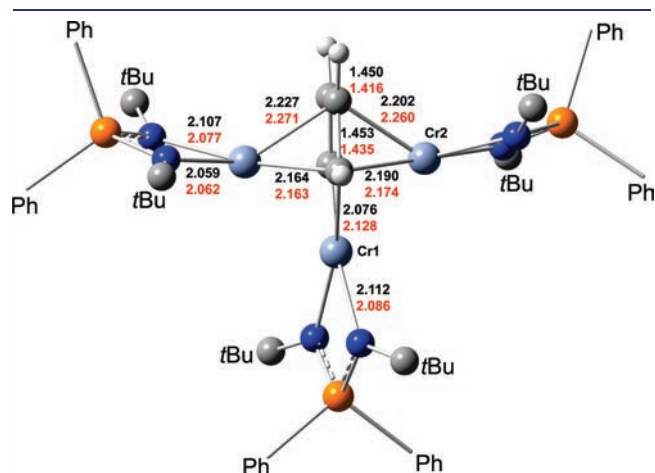

Figure 2. Optimized structure of **2** (at PBE/TZVP level). Calculated and experimental bond distances (Å) of selected bonds are shown in black and red, respectively.

as obtained from the crystal structure as a starting geometry. Geometry optimization calculations at the spin-unrestricted PBE level on the full structure of **2** yielded geometrical parameters in excellent agreement with the experimental values (Figure 2). The calculated C—C distances of the butadiene-diyl residue were only slightly longer for the central C—C bond and identical for the other two. The predicted Cr—Cr distances [2.46 and 3.46 Å for Cr1—Cr2 and Cr2—Cr2a, respectively] also were in very good agreement with the observed values [2.49 and 3.50]. Among the several possible spin states that have been used for calculation (Figure 3a), only that with three high-spin ($S = 2$) Cr(II) ions coupled through a butadiene-triyl monoradical ($S = 1/2$) trianion yielded the lowest energy and the best agreement between calculated and observed structural parameters, thus lending credibility to the formulation. In particular, the two chromium atoms π-bonded to the C_4 unit appear to be ferromagnetically coupled to each other and antiferromagnetically coupled to the third chromium ion σ-bonded to the C_4 unit. In turn, the C_4 moiety carries an additional electron in its π-system antiferromagnetically coupled to the two π-bonded Cr(II) ions and ferromagnetically coupled to the σ-bonded Cr(II) ion. With a total of, respectively, eight and five electrons antiferromagnetically coupled, the observed magnetic moment of three unpaired electrons per cluster unit was correctly predicted (Figure 3). The same ground electronic state was obtained by running the analogous calculations using the hybrid B3LYP instead of the PBE functional. The electronic interactions between the $[Cr2(L)]^+$ and $[(C_4H_4)Cr1(L)]^{2-}$ fragments in the structure **1** result in the net bond order of 2.62 between $[Cr2(L)]^+$ and $[(C_4H_4)Cr1(L)]^{2-}$. Both Cr2—C and Cr1—Cr2 covalent interactions contribute to the stabilization of the structure. The bond orders for individual Cr1—C bonds are in the 0.27—0.36 range, while the Mayer bond order for the Cr1—Cr2 interaction is 0.82. The calculated spin densities of the Cr atoms (3.18 on Cr1 and 3.26 on Cr2 from PBE calculations and 3.93 on Cr1 and 3.72 on Cr2 from B3LYP calculations) are consistent with the Cr(II) description for each metal in the structure. Lying 11.9 kcal mol^{-1} above the ground state is the next electronic state for **2**. It features two high-spin ($S = 2$) Cr(II) ions (Cr2 and Cr2a) coupled through a butadiene-triyl dianion with the intermediate spin ($S = 1$) Cr(I) ion (Cr1).
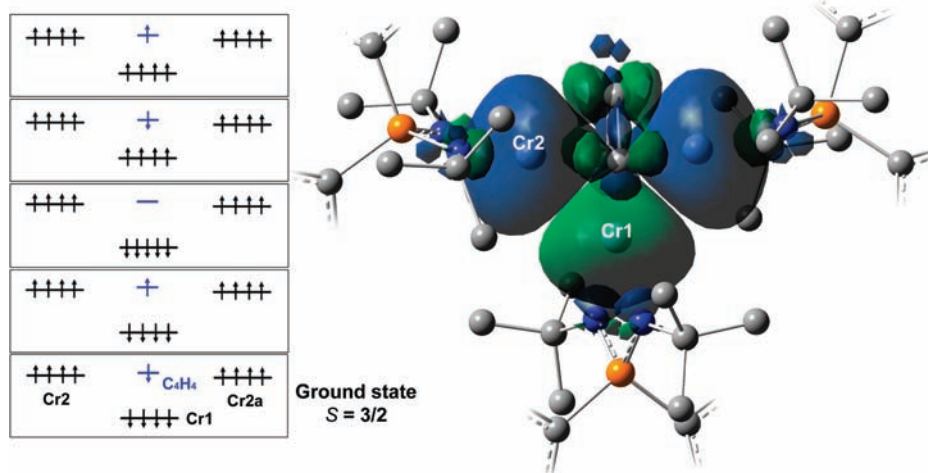

Figure 3. Left: Possible spin coupling situation for the electronic states of **2**. Right: Spin density of the ground electronic state of **2** (at the PBE/TZVP level). Isosurface contour value is 0.002 au.
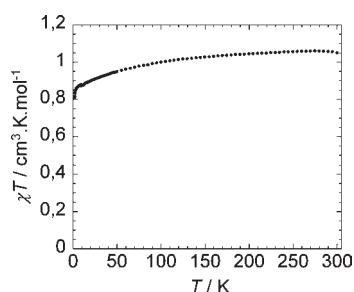
Figure 4. Temperature dependence of the χT product at 1000 Oe (with χ being the molar susceptibility per complex defined as M/H).

Figure 6. Temperature dependence of the χT product at 1000 Oe (with χ being the molar susceptibility per complex defined as M/H).
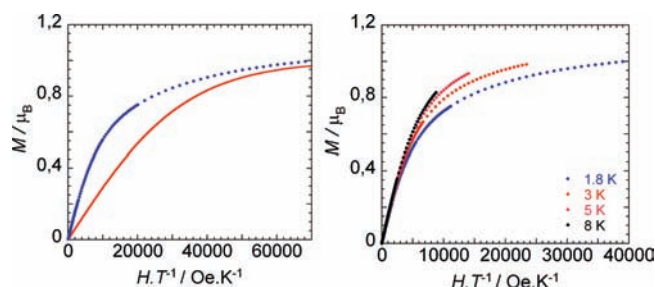

Figure 5. Left: Field dependence of the magnetization, M, between 1.8 and 8 K. Right: Field dependence of the magnetization at 1.8 K. The solid line corresponds to the Brillouin function for one $S = 1/2$ and $g = 2.0$.

Figure 7. Field dependence of the magnetization, M, between 1.8 and 8 K.

The magnetic susceptibility measurements were carried out on two differently prepared samples of **2** by 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. In the first sample, the crystallinity was removed via desolvation of the hexane lattice molecule in vacuo and under moderate heating. The second sample was instead highly crystalline, and special care was applied to make sure that no spontaneous desolvation occurred during the sample handling and preparation. The magnetization data for both samples collected at 100 K confirmed (Figure S1) the absence of ferromagnetic impurities as attested by the straight line at low fields.

The dc magnetic properties of the amorphous sample **2** were investigated under a 1000 Oe field in the temperature range 1.8−300 K. The plot of χT versus T revealed a gradual decrease upon lowering of the temperature (Figure 4). The slight negative deviation of χT product can be attributed to antiferromagnetic interaction between the spin carriers and/or presence of magnetic anisotropy. At room temperature, the experimental value of χT of 1.05 cm^3 K mol^{-1} is close to the value of 1.125 cm^3 K mol^{-1} expected for three uncoupled electrons [$S = 3/2, g = 2.0$]. The value of χT reached at 1.8 K is 0.80 cm^3 K mol^{-1}.

The magnetization was studied up to 7 T (Figure 5, left) at 1.8 K. As the field increased, the magnetization increases without real saturation up to 1.00 μB. An attempt to obtain a perfect fit for the data with a Brillouin function ($S = 1/2$ and $g = 2.0$) was not successful (Figure 5 left, solid red line). Although the low temperature susceptibility and magnetization data suggest a possible $S = 1/2$ ground state, the intensity of the magnetic interactions between the spin carriers is not known as well as the nonsaturation of the magnetization even at 1.8 K, and so it is difficult to precisely assign the spin ground state of the complex. Furthermore, the nonsuperposition of the different magnetization
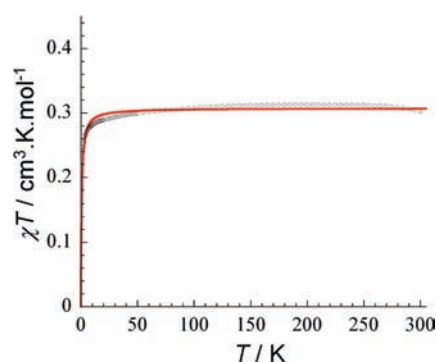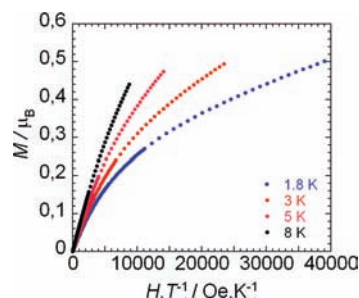
data on a single master curve as well as the nonsaturation of the magnetization suggest the possible presence of a magnetic anisotropy and/or low-lying excited states (Figure 5, right).

The behavior of the crystalline sample was surprisingly different. The dc magnetic properties were investigated under a 1000 Oe field in the temperature range 1.8−300 K (Figure 6). At room temperature, the experimental value of χT of 0.30 cm^3 K mol^{-1} is slightly lower than the value of 0.34 cm^3 K mol^{-1} expected for $S = 1/2$ ($g = 1.9$). The χT product remains roughly constant with decreasing temperature down to ~25 K, and then drops to a minimum value of 0.24 cm^3 K mol^{-1} at 1.8 K. The negative deviation of χT can be assigned to either intermolecular interaction between the molecules or magnetic anisotropy. The latter data can be fitted using a Curie−Weiss law leading to a small Weiss constant of $\theta = -0.65$ K (Figure 6, solid red line), which indicates the presence of a weak exchange interaction.

As shown in Figure 7 for the crystalline sample **2**, the low temperature magnetization measurements as a function of fields reveal a behavior similar to the desolvated batch. As before, the nonsaturation and the nonsuperposition of the different magnetization data on a single master curve suggest the possible presence of a magnetic anisotropy and/or low-lying excited states. Even though the presence of magnetic anisotropy might lead to the slow relaxation of the magnetization associated with a single-molecule magnet behavior due to the small spin ground state of the molecule, no such behavior was observed in the ac data.

In summary, the data can be fitted for both samples with a spin $S = 1/2$ Ci law at low temperature. However, while the spin state is preserved until room temperature in the crystalline sample, the amorphous one showed a spin increment to $S = 3/2$ as the

Scheme 2
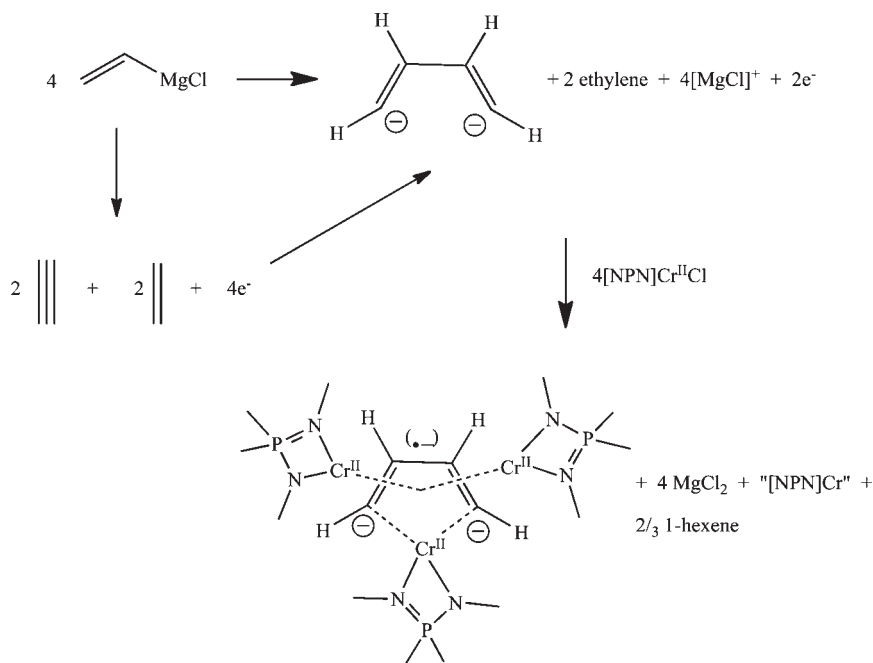
Table 1. Ethylene Oligomerization Results[a]

catalyst	cocatalyst (equiv)	vinylMgCl:Cr	alkenes (mL)	PE (g)	activity (g(alkene)/g(Cr)/h)[d]	C_6 (mol %)	C_8–C_{20} (mol %)
2[b]			4	0	1740	99.9	0
1[b]	CH_2CH_2MgCl	2	5	0	2175	99.9	0
1[c]	CH_2CH_2MgCl	2	9	0.8	3921	99.9	0

[a] Conditions: Loading 30 μmol of complex, 35 bar of ethylene, reaction temperature 80 °C, reaction time 60 min. [b] 100 mL of methylcyclohexane. [c] Room temperature. [d] Considering only one chromium per trimeric structure as active.

temperature reached room values. This marked difference of behavior indicates that the intermolecular interactions between the triangular clusters are probably significant. The lack of crystallinity in the desolvated sample and the consequent lack of order obviously affect the spin coupling within molecules, allowing one to reach the spin state $S = 3/2$ as predicted by the DFT calculation for **2** as a magnetically isolated system in the gas phase. In crystalline samples, the intermolecular magnetic coupling is instead maintained throughout the temperature variation.

The formation of **2** requires a sequence of events. The oxidative coupling of two vinyl anions implies loss of two electrons (Scheme 2). This process is widely known for second and third row late transition metals (Pt, Pd, Os, Rh) and for which, due to their enhanced inclination toward reductive elimination reactions, a broad range of applications has been developed.[13] The fact that in **2** a doubly deprotonated butadiene unit is present can be rationalized with at least two different arguments. In the first scenario, the coupling of two coordinated vinyls may give rise to a neutral butadiene unit that is in turn deprotonated by and additional 2 equiv of Grignard. From the formal point of view, the overall intervention of four vinyl units generates the C_4 dianion, two electrons, and two molecules of ethylene (Scheme 2). Alternatively, four coordinated vinyl anions may afford two molecules of acetylene, two of ethylene,

and four electrons.[14] In turn, coupling of two acetylenes with the intervention of two of the four electrons may afford the same C_4 dianion and products. In any of the two scenarios, the involvement of four Cr(II) starting complexes to afford **2** has to be assumed not only to trigger the vinyl coupling but also to balance the redox and stoichiometry of the reaction. Of the two electrons generated by the vinyl oxidative coupling, one is hosted in the C_4 unit, while the last could be used to reduce the fourth equivalent of chromium to some not yet identified low-valent species. Although its presence has to be admitted just for balancing the redox and stoichiometry of the reaction, interestingly, the GC–MS of the reaction mixture indicated the presence of a small amount of 1-hexene instead of the expected ethylene. It is tempting to speculate that an in situ generated Cr(I) byproduct is responsible for the transformation the ethylene byproduct into 1-hexene.

Complex **2** is a reduced species formally containing one Cr(I) ion per trimeric structure. Although DFT clearly indicated that three metals are all divalent, yet the complex acts as a self-activating catalyst for ethylene selective trimerization (Table 1). In turn, this indicates that it is capable of supplying a genuine monovalent chromium unit as a result of the self-activation. This behavior is closely reminiscent of the family of low-valent synthons of the bis-pyridine iminato ligand.[15] When solutions of **2** in methylcyclohexane were exposed to 35 bar of ethylene gas

at 80 °C, a moderate amount of highly pure 1-hexene was formed. The moderate activity may be easily understood in terms of low concentration of the catalytically active species. Thermal conditions are also required for the initial dissociation of the trimer producing only one catalytically active monovalent moiety. In situ generation of **2** by activating **1** with 2 equiv of vinyl Grignard basically produced the same outcome at high temperature with a slight increase of activity. Remarkably, an identical run at room temperature doubled the activity.

In conclusion, we have herein reported the first case of activation of a selective ethylene trimerization catalyst precursor by stoichiometric amount of a Grignard reagent. The surprising vinyl reductive coupling affording the butadiene-diyl residue allowed the stabilization of a reduced species capable of feeding Cr(I) into the catalytic cycle. Also, the fact that a moderate amount of 1-hexene accompanies the formation of **2** indicates that a catalytically active species of high potency might in fact be generated and well supported by this versatile ligand system. Further work to clarify this potentially important issue is underway.

■ EXPERIMENTAL SECTION

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. Ligands $(t\text{-Bu})NH-PBr(Ph)_2-NH(t\text{-Bu})$ and **1** were prepared according to the literature procedure.[11,16] Vinylmagnesium chloride (1.6 M in THF) was purchased from Aldrich and used as received. Liquid mixtures from catalytic runs were analyzed by using a CP 9000 gas chromatograph (GC) equipped with a 30 mL × 0.32 mm i.d., capillary CP volamine column and a FID detector. All single-point experiments were performed in duplicate. The yield was determined by ^1H NMR spectroscopy (Varian Mercury 400 MHz spectrometer). Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer.

Preparation of $\{\pi\text{-}[(t\text{-Bu})N-P(Ph)_2-N(t\text{-Bu})]Cr\}_2(\mu,\mu',\eta^4,\eta^{4'}\text{-}C_4H_4)\{\sigma\text{-}[(t\text{-Bu})N-P(Ph)_2-N(t\text{-Bu})]Cr\}$ **(2).** A solution of $[(t\text{-Bu})NP(Ph)_2N(t\text{-Bu})]CrCl_2Li(THF)_2$ (**1**) (0.601 g, 1.0 mmol) in THF (10 mL) was treated with vinylmagnesium chloride (1.1 mmol, 0.7 mL) and followed by the addition of 1,4-dioxane (1.1 mmol, 0.97 mL). The reaction was stirred for 18 h, and then solvent was removed in vacuo and hexane (10 mL) was added. The suspension was centrifuged, and the resulting solution was reduced to 4 mL and stored at −40 °C in the freezer for 4 days. The resulting brown crystals were filtered and washed with cold hexanes (10 mL) and dried in vacuo to give 0.154 g, 0.129 mmol, 39%. Anal. Calcd for $C_{64}H_{88}Cr_3N_6P_3$ (desolvated): C, 64.58; H, 7.45; N, 7.06. Found: C, 64.54; H, 7.46; N, 7.07. ESI-MS (rel. int.) $m/z =$ 1190.722 ($[M + H]^+$, 0.10), 1145.777 ($[M − 3Me]^+$, 0.16), 1101.825 ($[M + H − 6Me]^+$, 0.12), 739.509 ($[M + H − C25H40CrN2P]^+$, 76.85), 693.541 ($[M + H − C28H48CrN2P]^+$, 100).

Polymerization and Oligomerization Results. Catalytic runs were carried out in a 200−300 mL high pressure Büchi reactor 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 were cooled to 0 °C prior to releasing the overpressure and quenching with MeOH and HCl.

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° (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 F2. 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. Details and tables of crystal structure refinement and solution are given in the Supporting Information.

The initial solution suggested the presence of two cocrystallized, disordered, and partially occupied toluene solvent molecules in the lattice. To maintain an acceptable data to parameter ratio and because of the difficulties of modeling the disorder with moderate quality data set, the data were treated with the Squeeze routine of PLATON.[17] Such treatment resulted in removal of solvent generated reflections and appearance of void space per cell equal to 1383.1 Å^3 with an electron count per cell equal to 84 electrons. The electron count was consistent with one and two/third toluene molecules per cell. On the basis of this calculation, appropriate changes were made to the formula of the asymmetric unit.

Computational Details. DFT calculations were performed using the Gaussian 03 package[18] using the PBE[19] and B3LYP[20] exchange-correlation functionals and the TZVP[21] basis set. Tight SCF convergence criteria were used for all calculations. The converged wave functions were tested to confirm that they correspond to the ground-state surface. All calculations for the analysis of the electronic structure, including the generation of initial wave functions, Mulliken population analysis,[22] and the calculation of Mayer bond order indices,[23] atomic valences,[24] and populations of fragment orbitals,[24] were performed using the AOMix software package.[25]

Magnetic Measurements. The 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. The dc analyses were performed on polycrystalline samples, wrapped in a polyethylene membrane and under a field ranging from 0 to 7 T between 1.8 and 300 K. The magnetization data were collected at 100 K to probe the possible presence of ferromagnetic impurities. A diamagnetic correction was applied for the sample holder.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Full ref 18 and details of magnetic measurements and crystallographic data for this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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