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New Self-Activating Organochromium Catalyst Precursor for Selective Ethylene Trimerization.

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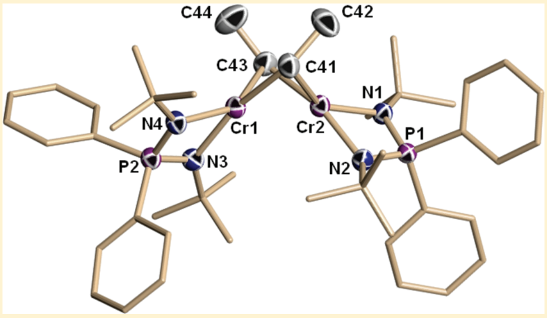

ABSTRACT: Two catalytic systems based on anionic ligands with the NPN structural motif, bearing tri- and pentavalent phosphorus, respectively, have been compared vis-à-vis their ability to selectively trimerize ethylene. In the case of the trivalent phosphorus ligands, reaction of the Cr(II) catalyst precursor [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr (**1**) with 2 equiv of MeLi afforded the Cr(III) species [(*t*-Bu)NP(Me)N(*t*-Bu)]$_2$CrLi(OEt$_2$) (**2**). The same reaction with 3 equiv of MeLi yielded instead the Cr(II) species {[(*t*-Bu)NP(Me)N(*t*-Bu)]Cr(μ-Me)}$_2${Li(THF)}$_2$ (**3**). The P atoms of both **2** and **3** have been methylated. Activation of **2** and **3** with MAO produced an S-F distribution of oligomers. Conversely, activation of **3** with EtAlCl$_2$ exclusively afforded 1-hexene together with a small amount of polymer as a byproduct. Treatment of **2** with EtAlCl$_2$ did not yield an active catalyst. The reaction of CrCl$_2$(THF)$_2$ with [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]$^-$Li$^+$, containing pentavalent phosphorus, afforded the Cr(II) derivative [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ-Cl)$_2$Li(THF)$_2$ (**4**). Its alkylation with EtLi gave the ethyl-bridged dimer {[(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ-Et)}$_2$ (**5**), which, upon thermolysis, afforded [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]$_2$Cr (**6**). The structures of **5** and **3** are closely related, having in common two bridging alkyls and the same metal oxidation state but differing with respect to the P atom oxidation state and the presence/absence of alkali-metal cations. The catalytic behavior instead is remarkably different. Complex **5** is active as a self-activating selective ethylene trimerization catalyst, while complex **3** requires activation.

INTRODUCTION

Linear α-olefins (LAOs) are important commodity chemicals central to the industrial preparation of many diversified products essential to our modern lifestyle.[1] These compounds are typically produced as a statistical distribution, which has to be fractionated through an energy-intensive separation process to afford the individual LAOs for specific applications.[2] The problem is particularly acute for the light LAOs, given the steadily increasing demand of 1-hexene and 1-octene as comonomers for LLDPE production. For these reasons, introducing selectivity into the catalytic oligomerization cycle is particularly being pursued.[3]

In addition to the keen industrial relevance for discovering selective tri- and tetramerization catalysts, developing such systems poses genuine intellectual challenges. In fact, specific mechanistic pathways must be engineered in order for the desired selectivity to be introduced in the catalytic cycle. For example, it is commonly accepted that selective trimerization is achieved with the so-called ring expansion redox mechanism.[4,5] The same mechanism has also been proposed for rationalizing the behavior of the very few existing quasi-selective tetramerization catalysts (70%).[5] However, it becomes increasingly apparent that a tetramerization with selectivity higher than that currently provided by the few existing trimerization systems cannot be achieved via the same ring expansion mechanism and would require an alternative pathway.[6]

In any event, controlling the metal oxidation state is central to obtain a selective catalytic system. Recent synthetic,[7] spectroscopic,[8] and theoretical[9] work has established that Cr(I) is responsible for the selective ethylene oligomerization, while Cr(II) yields nonselective oligomerization catalysts. It remains unclear if polyethylene is produced only by Cr(III) or also by Cr(II) species.[10] Thus, clearly defined reductions and availability of ligands that can adequately stabilize Cr(I) may open the way to new and better performing selective ethylene oligomerization catalysts. There are formidable challenges, however. The +I state of chromium is characterized by an exceptionally high reactivity, as clearly indicated by the occurrence of dinitrogen fixation,[11] arene coordination,[12] metal−metal quintuple bond formation,[13] etc. In addition, all the *isolated* Cr(I) species are, with only two

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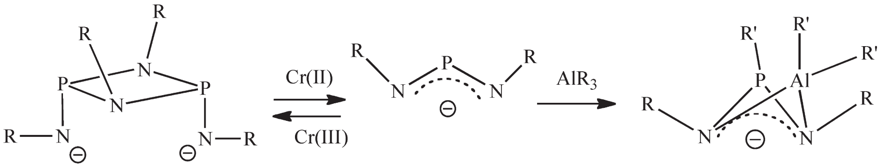
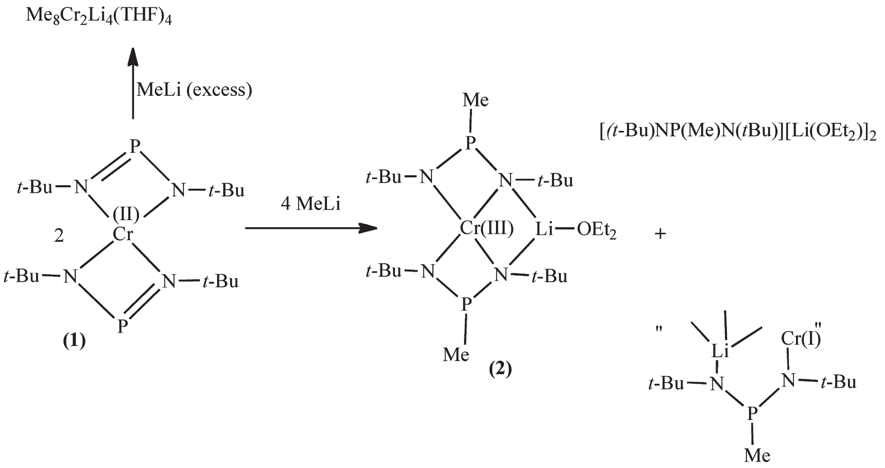
Scheme 1



Scheme 2



exceptions,[7a,c] catalytically inert. An ingenious alternative to the problems posed by selective reduction to the +I state (disproportionations, ligand fragmentations, etc.) consists of the recently developed abstraction of CO from some representatives of the large family of highly stable Cr(I) carbonyl derivatives.[5m,7a−7c] A pragmatic solution to the instability of the highly reactive Cr(I) species remains designing catalyst precursors with the metal in the stable +III state to be *directly* reduced to Cr(I) under the conditions required by the oligomerization reaction. However, even the in situ reduction of Cr(III) precursors poses a problem, since the +II state must be necessarily bypassed. Due to its intrinsic stability, the +II state often prevents further reduction and furnishes only nonselective ethylene oligomerization catalysts, albeit occasionally highly active.[4w,14] A possibility of bypassing Cr(II) consists of an initial double alkylation of Cr(III) precursors followed by a thermal two-electron reductive elimination.[15]

We have recently found that the NPN ligand may afford chromium complexes of switchable catalytic behavior (from polymerization to statistical oligomerization or trimerization) depending on the activation conditions.[14h,16] In turn, this indicates that this family of ligands has the ability of stabilizing each of the three critical chromium oxidation states and impedes or even prevents their interconversion after activation. To this end, we have observed that, first, the original P_2N_4 structure can be both cleaved and re-formed, depending on the countercation coordination requirements (Scheme 1).[15,16] Second, the activators consistently alkylate the ligand P atom with its aluminum residues remaining connected to the molecular frame. Third, given the occasional appearance of selective behavior, it is clear that the ligand, given the appropriate alkylating agent, has sufficient capability to stabilize catalytically selective Cr(I) intermediates.[17]

In this paper, we have analyzed the effect of the alkylation and oxidation of the P atom on the relative stability of the +II versus +III state and their effect on organochromium species that in turn may act as catalyst precursors in the absence of aluminate activators.

RESULTS AND DISCUSSION

To deliberately alkylate the P(III)-containing NPN framework, MeLi was the most obvious choice. The preparation and characterization of the Cr(II) catalyst precursor [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr (**1**) was previously described.[14h] Its reaction with MeLi proceeded in a remarkably different manner, depending on the stoichiometric ratio. While large amounts of MeLi (4−5 equiv) afforded the Cr(II) derivative $Me_8Cr_2Li_4(Et_2O)_4$,[18] the reaction with 2 equiv afforded the Cr(III) species [(*t*-Bu)NP(Me)N(*t*-Bu)]$_2$CrLi(OEt$_2$) (**2**). In this complex both P atoms have been methylated and one partially solvated lithium atom was retained to provide electroneutrality to the Cr(III) metal center (Scheme 2).

The oxidation of chromium from the +II to the +III state upon treatment with MeLi (certainly a reducing rather than an oxidizing agent) is explained by assuming a disproportionation between two Cr(II) intermediates (Scheme 2). In turn, this requires that a low-valent complex, probably Cr(I), must have been generated as a partner of the formation of **2** along with the alkylated form of the ligand dilithium salt. Unfortunately, all attempts to isolate or even trap the low-valent chromium byproduct via reoxidation reactions did not afford any identifiable compound.

The crystal structure of **2** (Figure 1) shows the Cr(III) atom in a distorted-tetrahedral coordination environment (N(2)−Cr(1)−N(1) = 77.67(8)°, N(1)−Cr(1)−N(1A) = 102.89°, N(2)−Cr(1)−N(1A) = 130.72(9)°, and N(2A)−Cr(1)−N(1) = 130.71(9)°) defined by the four nitrogen donor atoms of two separate NPN anions. This distortion is likely to be attributed to the presence of the two lithium atoms, each bridging two nitrogens of two ligands (N(1)−Li(2) = 2.097(5) Å).

Instead, the reaction of **1** with 3 equiv of MeLi afforded an interesting dinuclear and almost diamagnetic Cr(II) complex, formulated as {[(*t*-Bu)NP(Me)N(*t*-Bu)]Cr(μ-Me)}$_2${Li(THF)}$_2$ (**3**) (Scheme 3). The ^{1}H NMR spectrum of **3** shows a minor line broadening, but all the expected resonances with correct intensity were clearly identified. This reaction is, from a formal point of view, rather straightforward, implying the usual ligand alkylation, dissociation of alkylated ligand dilithium salt, and coordination of the third 1 equiv of MeLi prior to dimeric aggregation. However, it is also conceivable that the reaction may instead proceed via preliminary disproportionation and formation of **2** (Scheme 4), since treatment of **2** with MeLi also affords **3**. In this event the additional MeLi is required for the reduction of the metal center.

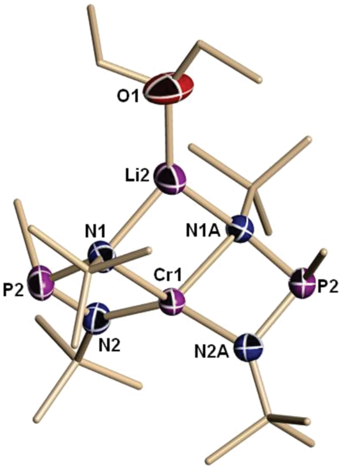
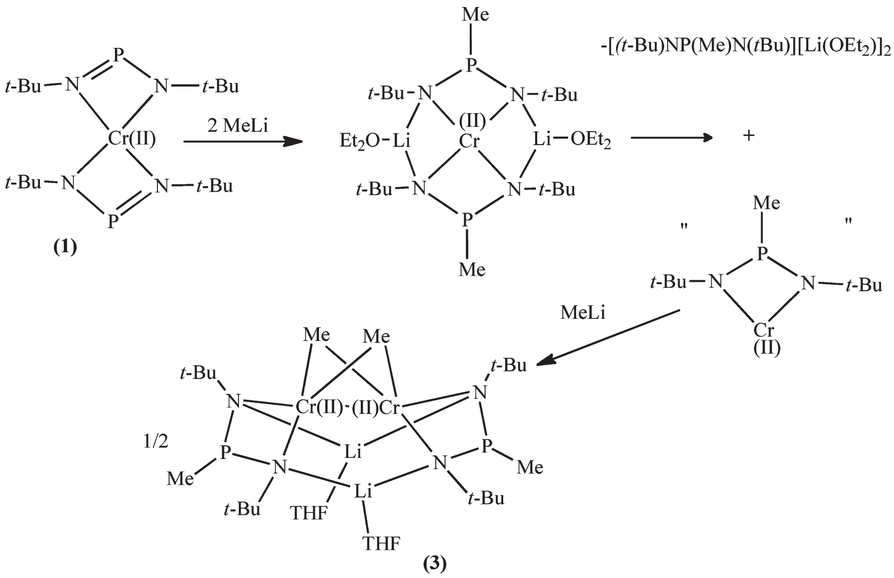


Figure 1. Plot of **2** with ellipsoids set at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr(1)−N(2) = 1.902(2), Cr(1)−N(2A) = 1.902(2), Cr(1)−N(1) = 2.022(2), Cr(1)−N(1A) = 2.022(2), N(1)−Li(2) = 2.097(5), Li(2)−O(1) = 1.926(7); N(2)−Cr(1)−N(1) = 77.67(8), N(1)−Cr(1)−N(1A) = 102.89(12), N(2)−Cr(1)−N(1A) = 130.72(9), N(2A)−Cr(1)−N(1) = 130.71(9), N(2)−P(2)−N(1) = 91.16(10), N(1A)−Li(2)−N(1) = 97.9(3).

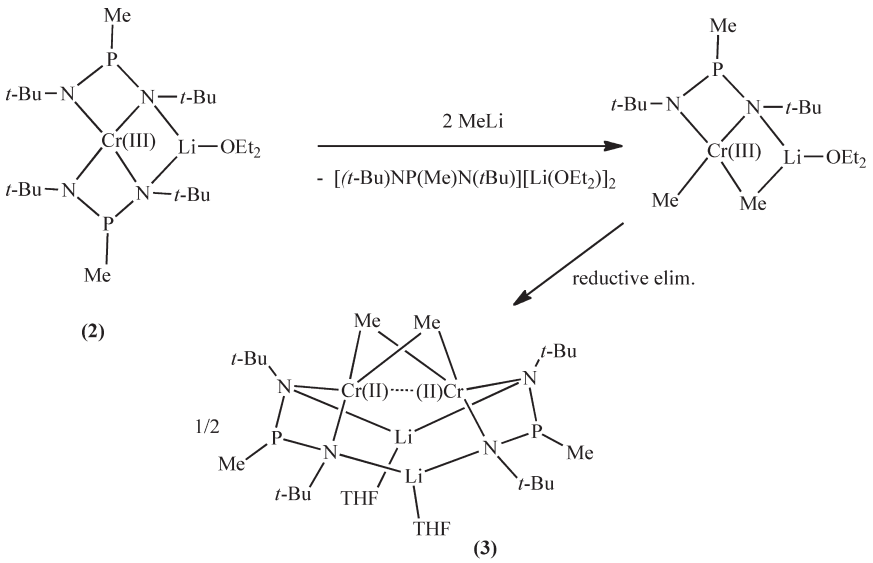
The crystal structure of **3** (Figure 2) consists of two chromium atoms, each chelated by one methylated ligand and bridged by two methyl groups. The Cr$_2$(μ-Me)$_2$ core is severely folded with a very short Cr−Cr contact (Cr(1)−Cr(2) = 2.0148(15) Å). The coordination environment around each chromium atom is slightly distorted square planar (N(1)−Cr(1)−C(19) = 176.71(17)°, N(1)−Cr(1)−N(2) = 76.92(15)°, N(1)−Cr(1)−C(20) = 102.85(18)°) and is defined by the two N donor atoms of the chelating ligand (C(1)−N(1) = 2.061(4) Å, Cr(1)−N(2) = 2.073(4) Å) as well as by the two bridging methyl groups (Cr(1)−C(19) = 2.199(5) Å and Cr(1)−C(20) = 2.296(5) Å). Two lithium atoms, each solvated by one THF, bridge one nitrogen atom of each ligand (N(1)−Li(2) = 2.122(9) Å).

Both **2** and **3** display a rather disappointing catalytic behavior. Activation with MAO in toluene yielded strictly nonselective behavior, albeit with high activity (Table 1). Complex **3** was also tested as a single-component catalyst and was thermolyzed (100 °C) under an ethylene atmosphere (35 bar). No activity or degradation of the complex was observed. In turn, this emphasizes the high stability of organochromium(II) complexes and reiterates the need for bypassing this oxidation state in order to obtain selective ethylene oligomerization catalysts. Interestingly, though, activation of **3** with RAlCl$_2$ (R = Me, Et) in MeCy selectively produced 1-hexene, along with a small amount of polymer as a byproduct. This behavior was also observed in toluene, the only difference being a substantially lower activity. This is in agreement with the often

Scheme 3



Scheme 4



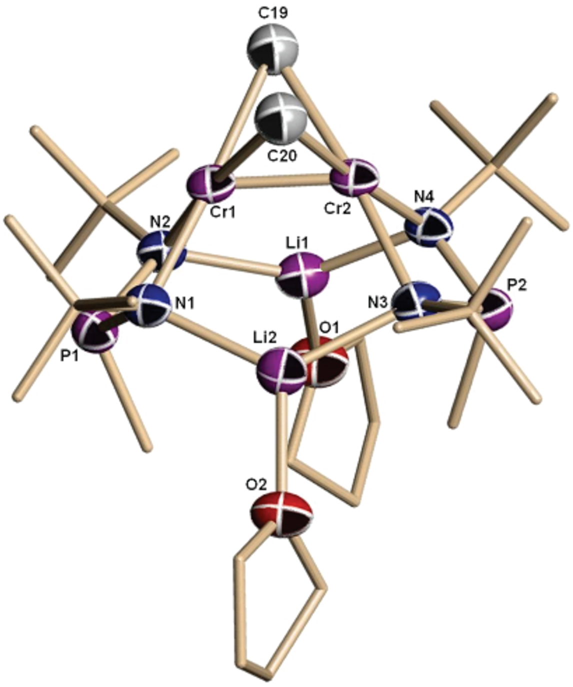


Figure 2. Plot of **3** with ellipsoids set at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr(1)–Cr(2) = 2.0148(15), Cr(1)–C(19) = 2.199(5), Cr(1)–C(20) = 2.296(5), Cr(2)–C(20) = 2.187(5), Cr(2)–C(19) = 2.295(5), Cr(1)–N(1) = 2.061(4), Cr(1)–N(2) = 2.073(4), N(1)–Li(2) = 2.122(9); Cr(1)–C(19)–Cr(2) = 53.22(11), Cr(2)–C(20)–Cr(1) = 53.35(11), N(1)–Cr(1)–N(2) = 76.92(15), N(1)–Cr(1)–C(19) = 176.71(17), N(1)–Cr(1)–C(20) = 102.85(18), Cr(2)–Cr(1)–C(19) = 65.85(15), Cr(2)–Cr(1)–C(20) = 60.55(13), N(1)–Li(2)–N(3) = 125.2(4).

observed poisoning effect of aromatic solvents, possibly responsible for an excessive stabilization of intermediate Cr(I) species.[6a,b]

The selective behavior observed upon activation with $EtAlCl_2$ suggests the necessity for the presence in the catalyst precursor of both chlorine and a more reducing alkyl. The "chlorine effect" is a primary characteristic of the commercially used pyrrolato-based catalytic system,[17] and the characterization of its catalytically active intermediates has fully elucidated its role.[7c] For example, in the case of the Cr(II) dimeric tetramethylpyrrolato catalyst precursor $[\{\eta^5\text{-}2,3,4,5\text{-}Me_4C_4N(AlClMe_2)Cr\}(\mu\text{-}Me)_2]$, also a Me-bridged dimer,[7d] the very strong chlorine effect is mainly due to its ability to trigger the disproportionation to the +III and —-I states. Although in the present case we lack direct proof, we reasoned that the effect might be very similar (Scheme 5).

In order to probe the viability of this mechanistic hypothesis, DFT calculations were carried out to evaluate the free energy variation associated with each step of the proposed mechanism (Figure 3). Geometry optimization calculations at the spin-unrestricted PBE level on the full structure of **3** yielded geometrical parameters in agreement with the experimental crystallographic values. Complex **3** contains a short Cr–Cr distance and is almost diamagnetic with small residual paramagnetism. In perfect agreement, calculations indicated that the ground-state configuration of the complex is the open-shell singlet where two Cr(II) ions are antiferromagnetically coupled with a Mayer bond order for the Cr–Cr interaction of only 1.22. Calculations carried out on the closed-shell singlet with the quadruple Cr–Cr bond predicted a structure with a much shorter Cr···Cr distance (1.796 Å) and also a higher energy (ΔG = 16.5 kcal mol^{-1} relative to the open-shell singlet).

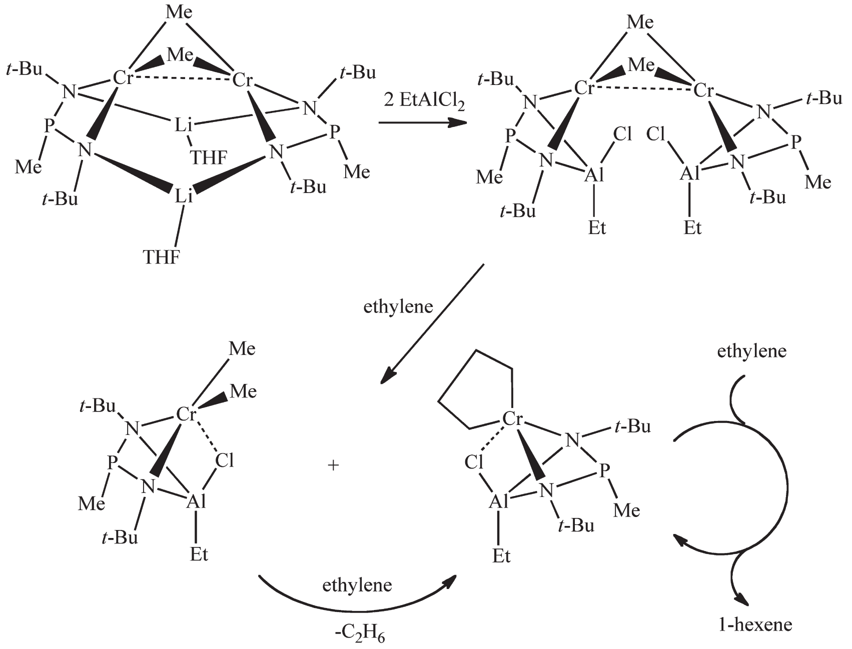
The reaction of **3** with $[RAlCl_2]_2$ removes two Li(THF) units as $[LiCl(THF)]_2$ and replace them with two AlRCl moieties. Calculations on the intermediate species **a** were carried out and, similar to the case for complex **3**, gave the open-shell singlet as the ground state (two Cr(II) ions are antiferromagnetically coupled). Interestingly, the anticipated formation of chlorine bridges between chromium and aluminum is responsible for the beginning of the disruption of the dimetallic structure, eventually leading to heterolytic cleavage in the following step. The situation is strikingly similar to that of the aforementioned aluminum pyrrolyl Cr(II)

Table 1. Oligomerization of Ethylene[a]

						amt (mol %)		
cat.	Al:Cr	cocat.	amt of alkene (mL)	amt of PE (g)	activity (g/((mmol of Cr)/h))	C6	C8	C10–20
2^b	1000	MAO	90	0.8	2130	24	23	53
2^b	500	MAO	63	2.6	1560	33	27	40
2^c	5	Et_3Al	0	traces	0	0	0	0
2^c	5	Et_2AlCl	0	0	0	0	0	0
2^c	5	$EtAlCl_2$	0	traces	0	0	0	0
3^{c,d}			0	0	0	0	0	0
3^b	1000	MAO	59	1.1	1420	28	25	47
3^b	500	MAO	42	2.9	1080	29	25	46
3^c	5	Et_3Al	0	traces	0	0	0	0
3^c	5	Et_2AlCl	0	0	0	0	0	0
3^c	5	$EtAlCl_2$	2	0.2	52	99.9	0	0
3^c	2	$EtAlCl_2$	5	0.9	143	99.9	0	0
3^b	2	$EtAlCl_2$	1	0.4	36	99.9	0	0
3^c	2	$MeAlCl_2$	9	1.15	287	99.9	0	0

[a] Conditions: loading 30 μmol of chromium complex, 35 bar of ethylene, reaction temperature 60 °C, reaction time 60 min. [b] 100 mL of toluene. [c] 100 mL of methylcyclohexane. [d] Reaction temperature 100 °C.

Scheme 5



system, a highly active and selective trimerization catalyst.[7d] In the present case, the process appears to be thermodynamically highly favored. The value of ΔG becomes even more negative if other forms of LiCl(THF) (e.g., tetrameric) are being considered. Interestingly, the calculation predicts that the replacement of Li ions by aluminate cations resolves into a lengthening of the Cr–Cr distance to 2.44 Å that compares well to that of the ethyl-bridged **5** (see below) with very similar arrangement and no countercations.

The disproportionative splitting of the dinuclear structure by ethylene with formation of the two Cr(III) metallacyclic and dimethyl intermediates is thermodynamically uphill (ΔG_r = +9.8 kcal mol^{-1}). However, the reductive elimination of ethane from the dimethyl intermediate **b** is thermodynamically favorable (ΔG_r = −3.8 kcal mol^{-1}). If C_2H_4 is added to intermediate **b** and methane and propylene are released as products, the ΔG_r value of this reaction step is also negative (−11.4 kcal mol^{-1}).[7d] The metallacyclic system is, of course, the key intermediate capable of expanding the cycle and therefore starting the selective oligomerization.

The data above clearly indicate that the Cr(II) **3** may in fact be used as precursor for selective trimerization but only in the presence of halogenated aluminum alkyl activators capable of triggering disproportionation and consequent reduction to the +I state responsible for the formation of the metallacycle. Activators such as MAO do not possess such ability in this catalytic system and gave only Schulz−Flory (S-F) distributions of oligomers or no activity at all. In turn, this indicates that neither reduction of the +II state nor disproportionation to the +III and +I states occurred.

Given the critical role of the aluminate species in determining the catalytic behavior of NPN complexes and the noninnocent behavior of this particular ligand system, we have now oxidized the trivalent P atom to its pentavalent state. This modification was aimed at verifying that an increased electron-withdrawing effect, resulting from the higher oxidation state of phosphorus, could possibly better stabilize Cr(I) intermediates via charge transfer. We have recently described the synthesis of the Cr(II) species [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ-Cl)$_2$Li(THF)$_2$ (**4**), which showed a near-record catalytic activity in producing polymer-free S-F distributions of oligomers upon activation with MAO.[19] We were anticipating that in this case the role of the activator would be solely that of alkylating the metal center. Therefore, we have reacted the Cr(II) species **4** with EtLi, in the hope that ethyl groups bonded to chromium could make the metal more inclined toward reduction to the +I state.

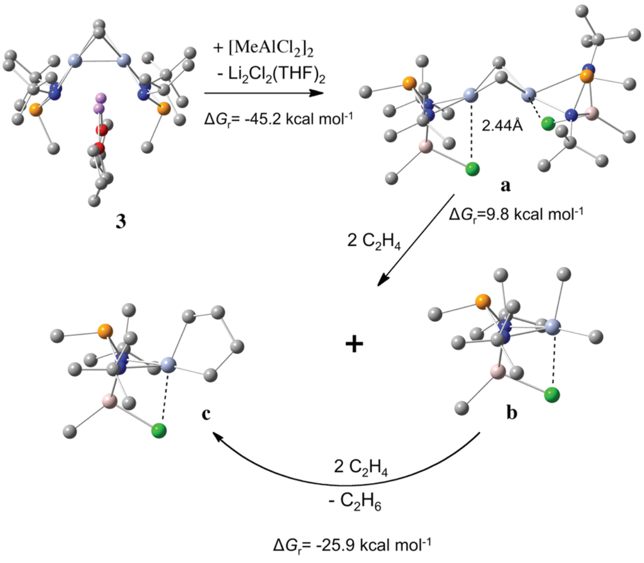


Figure 3

The reaction proceeded smoothly at room temperature, affording the corresponding dinuclear and paramagnetic {[(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ-Et)}$_2$ (**5**) (Scheme 6). The structure of **5** is the result of a straightforward chlorine replacement by an ethyl group with additional dissociation of the LiCl unit. In addition to the absence of the lithium counterions, the dimeric arrangement with the two bridging ethyl groups in **5** is closely reminiscent of the case for **3**. Clearly, the expected reduction did not occur.

The dimeric structure of **5** (Figure 4) consists of two [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr units bridged by two ethyl groups (Cr(1)−C(41) = 2.143(2) Å, Cr(2)−C(43) = 2.145(2) Å) forming a folded Cr$_2$Et$_2$ core. The coordination geometry around each metal center is distorted square planar (N(2)−Cr(1)−N(1) = 72.07(6)°, N(2)−Cr(1)−C(41) = 107.29(8)°, N(1)−Cr(1)−C(41) = 144.04(7)°, N(2)−Cr(1)−Cr(2) = 120.45(5)°, N(1)−Cr(1)−Cr(2) = 150.78(5)°, C(41)−Cr(1)−Cr(2) = 61.72(6)°) and is defined by the two bridging carbon atoms and each ligand's nitrogen donors (Cr(1)−N(2) = 2.0542(16) Å, Cr(1)−N(1) = 2.0970(16) Å). The deviation from square planarity is probably due to the long-range steric interaction between the *t*-Bu groups of two units. This is in striking contrast to the perfect planarity of the metal centers in **3** as a possible result of the rigidity introduced by the two alkali-metal cations.

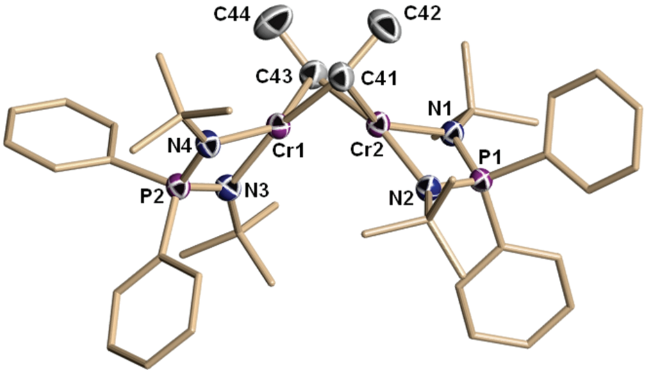
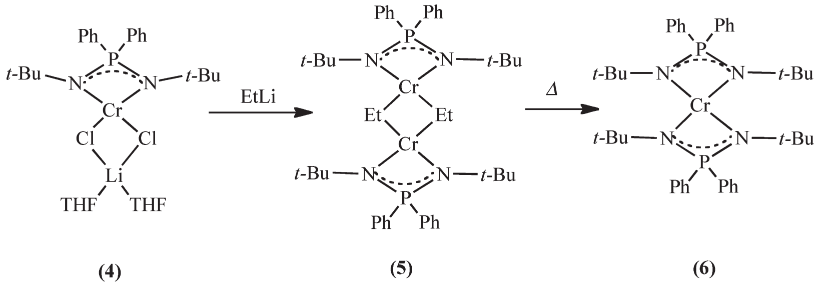


Figure 4. Plot of **5** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Cr(1)−N(2) = 2.0542(16), Cr(1)−N(1) = 2.0970(16), Cr(1)−C(41) = 2.143(2), Cr(1)−Cr(2) = 2.3282(5), Cr(2)−C(43) = 2.145(2); N(2)−Cr(1)−N(1) = 72.07(6), N(2)−Cr(1)−C(41) = 107.29(8), N(1)−Cr(1)−C(41) = 144.04(7), N(2)−Cr(1)−Cr(2) = 120.45(5), N(1)−Cr(1)−Cr(2) = 150.78(5), C(41)−Cr(1)−Cr(2) = 61.72(6).

Scheme 6



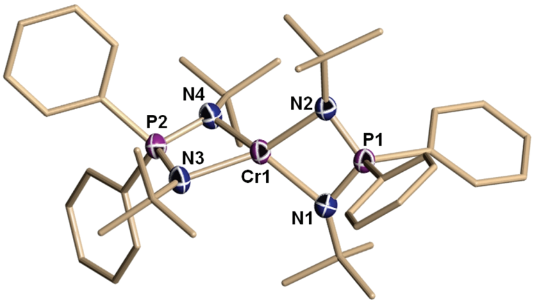


Figure 5. Plot of **6** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Cr(1)−N(1) = 2.100(3), Cr(1)−N(4) = 2.104(3), Cr(1)−N(3) = 2.112(3), Cr(1)−N(2) = 2.111(3); N(1)−Cr(1)−N(4) = 144.06(13), N(1)−Cr(1)−N(3) = 119.53(14), N(4)−Cr(1)−N(3) = 71.47(13), N(1)−Cr(1)−N(2) = 71.30(12), N(4)−Cr(1)−N(2) = 120.69(13), N(3)−Cr(1)−N(2) = 145.59(13).

There is an interesting comparison that can be made between the structures of **3** and **5**. In complex **3**, the ligand frame is dianionic due to the alkylation of the P atoms. In turn, this requires the Cr_2R_2 core to retain two lithium counterions between the two ligands, thus providing additional bridging interactions. In complex **5**, the ligand bears instead the formal charge of −1, for which there is no necessity for retention of the alkali-metal cation. This has a profound effect on the Cr−Cr distance (Cr(1)−Cr(2) = 2.3282(5) Å), being remarkably elongated in comparison to that in **3** (Cr(1)−Cr(2) = 2.0148(15) Å), as well as on the magnetism of the complex (paramagnetic versus almost diamagnetic). In our opinion, this provides once again a good illustration of the intriguing and yet elusive nature of the Cr−Cr interaction.[20] In the present case, the Cr−Cr distance is affected by the ligand's formal charge and the presence of the alkali-metal cations. Only these two factors appear to be responsible for the occurrence of the short Cr−Cr contact of the diamagnetic **3** and long distance of the paramagnetic **5**.

The presence of the two Et groups in the dinuclear structure of **5**, the absence of alkali-metal cations, and the monoanionic nature of the ligand altogether make this species better suited, in comparison to **3,** to form a Cr(I), catalytically active intermediate. Upon having observed that solutions of **5** have the tendency to slowly decompose at room temperature, a deliberate attempt to flash-thermolyze the complex was carried out by heating its solution to 110 °C for few seconds (Scheme 6). As anticipated, the thermolysis of **5** afforded a new Cr(II) complex, where one of the metal centers has basically extracted the other's ligand to form the square-planar and paramagnetic $[(t\text{-Bu})NP(Ph)_2N(t\text{-Bu})]_2Cr$ (**6**). The reaction was accompanied by separation of some colloidal metallic chromium.

The crystal structure of **6** (Figure 5) shows a severely flattened tetrahedral chromium atom (N(1)−Cr(1)−N(4) = 144.06(13)°, N(1)−Cr(1)−N(3) = 119.53(14)°, N(4)−Cr(1)−N(3) = 71.47(13)°, N(1)−Cr(1)−N(2) = 71.30(12)°, N(4)−Cr(1)−N(2) = 120.69(13)°, N(3)−Cr(1)−N(2) = 145.59(13)°) surrounded by the four nitrogen donor atoms of the two ligands (Cr(1)−N(1) = 2.100(3) Å, Cr(1)−N(4) = 2.104(3) Å, Cr(1)−N(3) = 2.112(3) Å, Cr(1)−N(2) = 2.111(3) Å).

The formation of **6**, as a result of the thermolysis of **5**, is rather indicative of the inclination toward disproportionative decomposition pathways. The reaction may simply be envisioned with the initial elimination of a ethylene/ethane/butane mixture (observed when the thermolysis was carried out in sealed and centrifuged NMR tubes) and intermediate formation of the Cr(I) putative intermediate "$[(t\text{-Bu})NP(Ph)_2N(t\text{-Bu})]Cr$", most likely dinuclear. In the absence of ethylene, this species may rapidly regain stability only via ligand scrambling, forming **6** and colloidal chromium. In agreement with this proposal implying the transient formation of Cr(I) by heterolytic splitting of the dimer, complex **5** indeed acts, in toluene and under ethylene pressure, as a self-activating, single-component trimerization catalyst (Table 2). This is in striking contrast with the behavior of **3**, which required instead activation by at least a stoichiometric amount of $RAlCl_2$. In what seems to be now a distinctive feature of the (NPN)Cr catalytic systems, the solvent has a marked effect on the catalytic behavior. An identical self-activating experiment carried out on a solution of **5** in MeCy doubled the activity but replaced the highly selective formation of 1-hexene with an S-F distribution.

Although in the pyrrolato selective trimerization catalyst toluene has a poisoning effect, in this case it obviously lends a minimum stability for the formation of the Cr(I) species responsible for selectivity. Lack of such a stabilizing effect, as in the case of MeCy, clearly makes the formation of Cr(I) more problematic with consequent retention of the +II state. As in the case of **3**, activation of **5** with MAO in toluene gave the usual nonselective oligomerization with surprisingly high activity. Thus, it seems that in toluene **3** and **5**, when activated with MAO, give similar catalytically active species or at least species with metal centers in the same +II state. Complex **6** is instead a mediocre nonselective catalyst, as expected from the fact that the activator cannot easily extract one of the two ligands.

In conclusion, we have herein reported the synthesis and characterization of the two closely related organochromium(II) complexes **3** and **5**. The only differences are (1) the oxidation state of the P atom and (2) the ligand's anionic charge (+I versus +II). These differences affect not only the Cr−Cr interaction of dimetallic species but also the catalytic behavior. In turn, this speaks for the different support provided by the two ligands to the catalytically selective Cr(I). The comparison between the two species is not as rigorous as may be desired, given the different nature of the alkyl functions bonded to chromium in both complexes (Me versus Et). Unfortunately, it was not possible to prepare and characterize the ethyl **3** and methyl **5** analogues. Nonetheless, the fact that **3** may be activated into a selective trimerization catalyst with only 2 equiv of $RAlCl_2$ suggests that both ligands can indeed sufficiently stabilize a Cr(I) intermediate during the catalytic cycle.

■ EXPERIMENTAL SECTION

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. The liquid product mixtures 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 an FID detector. The yield was determined by ^1H NMR spectroscopy (Varian Mercury 400 MHz spectrometer). Samples for magnetic susceptibility were preweighed inside a drybox equipped with an analytical balance and measured on a Johnson Matthey Magnetic Susceptibility balance. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination were obtained with a Bruker diffractometer equipped with a 1K Smart CCD area detector. The complexes $[(t\text{-Bu})NPN(t\text{-Bu})]_2Cr$ (**1**) and $[(t\text{-Bu})NP(Ph)_2N(t\text{-Bu})]Cr(\mu\text{-Cl})_2Li(THF)_2$ (**4**) were prepared according to a

Table 2. Ethylene Oligomerization Results[a]

cat.	Al:Cr	solvent	cocat.	amt of alkenes (mL)	temp (°C)	PE (g)	activity (g/((mmol of Cr) h))	C6 (mol %)	C8 (mol %)	C10−C16 (mol %)
5		toluene		4	100	0	93	99	traces	traces
5[b]	1000	toluene	MAO	106	100	0	4947	37	26	37
5		MeCy		8	60	0.3	197	39	32	29
6	1000	MeCy	MAO	9	60	0	210	24	22	54

[a] Conditions: loading 30 μmol of complex, 35 bar of ethylene, reaction time 60 min, 100 mL of solvent. [b] catalyst loading 15 μmol.

published procedure.[15a,16] Et_3Al (93%, Strem), Et_2AlCl (97%, Strem), $EtAlCl_2$ (1 M in hexane, Aldrich), Me_2AlCl (Aldrich), and MAO (10 wt %, Aldrich) were used as received.

Preparation of [(*t*-Bu)NP(Me)N(*t*-Bu)]$_2$CrLi(OEt$_2$) (2). A solution of [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr (**1**; 0.398 g, 1.0 mmol) in THF (10 mL) was treated with MeLi (1.31 mL, 2.1 mmol, 1.6 M in diethyl ether) at −20 °C. The mixture was stirred at room temperature for 20 h. Then the solvent was removed in vacuo and replaced with diethyl ether (5.0 mL). The resulting green suspension was centrifuged, and the supernatant was then stored at −30 °C for 3 days, forming deep green crystals of **2**. The crystals were washed with cold hexanes (10 mL) and dried in vacuo to give analytically pure **2** (0.209 g, 0.41 mmol, 41%). μ_{eff} = 3.93 μ_B. Anal. Calcd (found) for $C_{22}H_{52}CrLiN_4OP_2$: C, 51.86 (51.87); H, 10.29 (10.25); N, 11.00 (10.96).

Preparation of {[(*t*-Bu)NP(Me)N(*t*-Bu)]$_2$Cr(μ-Me)}$_2${Li(THF)}$_2$ (3). A solution of [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr (**1**; 0.398 g, 1.0 mmol) in THF (20 mL) was treated with MeLi (2.06 mL, 3.3 mmol, 1.6 M in diethyl ether) at −20 °C. The solution was stirred at 40 °C for 1 day and then cooled to room temperature. Then the solvent was removed in vacuo and replaced with hexane (5 mL). The resulting brown solution was centrifuged; storing the resulting solution at −30 °C for 6 days afforded brown crystals of **3**, which were filtered and washed with cold hexanes and dried in vacuo (0.140 g, 0.21 mmol, 42%). ^{1}H NMR (C_6D_6, 300 MHz, 300 K): δ −0.01 (br, 6H, Cr-CH_3), 1.45 (br, 36H, C(CH_3)$_3$), 1.58 (br, 8H, THF), 2.1 (br, 6H, P-CH_3), 3.59 (br, 8H, THF). ^{31}P{^{1}H} NMR (C_6D_6, 300 MHz, 300 K): δ 87.05 (s). MS (ESI) *m*/*z* (M + H)$^+$ 669.41. Anal. Calcd (found) for $C_{28}H_{64}Cr_2Li_2N_4O_2P_2$: C 50.29 (50.25), H 9.65 (9.62), N 8.38 (8.39).

Preparation of {[(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ-Et)}$_2$ (5). A green-blue solution of [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]CrCl$_2$Li(THF)$_2$ (**4**; 0.601 g, 1.0 mmol) in THF (5 mL) was treated with slow addition of EtLi (2.2 mL, 1.1 mmol, 0.5 M in hexanes) at −35 °C, and the resulting brown solution was stirred for 2 h at room temperature. The solvent was removed in vacuo and the residue redissolved in diethyl ether (10 mL). The suspension was centrifuged and the supernatant concentrated to 4 mL and stored at −35 °C for 3 days. Brown crystals of **5** were filtered and washed with cold hexanes (10 mL) and dried in vacuo (0.26 g, 0.32 mmol, 64%). μ_{eff} = 2.79 μ_B. Anal. Calcd (found) for $C_{44}H_{66}Cr_2N_4P_2$: C, 64.69 (64.64); H, 8.14 (8.13); N, 6.86 (6.83).

Preparation of [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]$_2$Cr (6). In a 50 mL round-bottom Schlenk flask, 0.816 g (1.0 mmol) of complex **5** was dissolved in toluene (20 mL). The solution was refluxed at 110 °C for 3 h, producing some insoluble black material while retaining the original solution's brown color. The suspension was centrifuged, the supernatant was dried in vacuo, and the brown powder was then dissolved in diethyl ether (5 mL) and stored at −35 °C for 3 days. Brown crystals of **6** were filtered, washed with cold hexanes (10 mL), and dried in vacuo (0.33 g, 0.47 mmol, 47%). μ_{eff} = 4.92 μ_B. Anal. Calcd (found) for $C_{40}H_{56}CrN_4P_2$: C, 67.97 (67.89); H, 7.99 (8.03); N, 7.93 (7.96).

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 or MeCy 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 MeOH and HCl. The activity was measured by NMR by integrating the resonances of the vinyl protons against those of the toluene solvent methyl group. Individual olefins were qusantified by GC. Results of catalytic runs are given in Table 1.

Computational Details. DFT calculations were performed using the Gaussian 09 package[21] using the PBE[22] functional and the TZVP[23] basis set. The spin-unrestricted formalism was used for all open-shell species. Tight SCF convergence criteria were used for all calculations. Harmonic frequency calculations were performed on the optimized structures to establish the nature of stationary points and to calculate Gibbs free energies at 298 K and 1 atm. 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,[24] the calculation of Mayer bond order indices,[25] natural population analysis (NPA)[26]-derived spin densities, and populations of fragment orbitals,[27] were performed using the AOMix software package.[28]

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 φ = 0.00° (600 frames), at φ = 120.00° (600 frames), and φ = 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 extensive listings of bond distances and angles are given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. CIF files and tables giving crystallographic data for the complexes reported in this paper and extensive listings of geometrical parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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