Catalyst Design

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A Chromium Ethylidene Complex as a Potent Catalyst for Selective Ethylene Trimerization**

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The factors transforming a statistical ethylene oligomerization process into selective tri- or tetramerization are being intensively scrutinized in both industrial and academic research.[1] Their identification also poses a genuine intellectual challenge, as the design of a selective catalytic system requires a complete understanding of the mechanistic features. The so-called ring-expansion mechanism for selective trimerization[2,3] is today unchallenged to the point that it is a paradigm among workers in the field.

Central to the understanding of the mechanism and to tailoring new catalysts is the question of the metal oxidation state.[1a] In the case of the chromium systems that are involved in the majority of these catalysts, the +I state has been conclusively linked to selective trimerization by both synthetic and spectroscopic work.[4–6] One of the characteristics of chromium, however, is the possibility of readily interconverting between +I, +II, and +III states as a part of a redox dynamism.[7] As each one of these oxidation states has its own distinctive catalytic behavior,[6a,b] stabilizing the desired state and slowing at the same time the dynamism is central to obtain selective behavior.

Mechanistic and synthetic work on the commercially used pyrrole-based Phillips trimerization system[6a,b] has allowed the structures of single-component self-activating precatalysts to be elucidated. All of these species consist of the pyrrolide ring being either σ- or π-bonded to the metal center and of an aluminate residue, which is invariably σ-coordinated to the pyrrolide nitrogen donor atom. There are two main features in this particular structural motif. First, the coordination of the aluminate introduces a zwitterionic type of electronic structure that in turn provides partial cationic character to the chromium center. Second, the alkyl group migrates from the aluminate to chromium during the dissociation of one of the pyrrolide rings in the form of an aluminum pyrrolide complex. The specific nature of the aluminum residue seems to play a very important role in the activation of the catalytic center for this system.[6a,b] However, the importance of its coordination to the pyrrolide nitrogen atom remains unclear. Is it the zwitterionic structure introduced by the coordination of aluminum? Or is it the alkyl transfer that makes the metal prone to further reduction to the +I state? In an attempt to address these and other questions that are important for tailoring the design of new catalysts, we have now probed the nature of the pyrrolide anion. The anion chosen bears two bulky *tert*-butyl groups in the two α positions, which could possibly prevent coordination of aluminum while maintaining an enhanced tendency for η^5-coordination.[8]

Deprotonation of 2,5-di-*tert*-butylpyrrole followed by reaction with $[\mathrm{CrCl_3(thf)_3}]$ afforded $[\{\eta^5\text{-}(t\mathrm{Bu})_2\mathrm{C_4H_2N}\}\mathrm{CrCl_2(thf)}]$ (**1**), which was isolated as dark violet-blue crystals.[13] The pseudo-tetrahedral piano-stool arrangement of **1** was elucidated by an X-ray crystal structure (Figure 1).[14] When activated with $\mathrm{AlEt_3}$ (5–15 equivalents), complex **1** is a highly active and selective trimerization catalyst (Table 1). The reaction time and also the temperature and quantity of alkyl aluminum activator affected both yield and purity of 1-hexene with respect to the side-product 2-hexene.

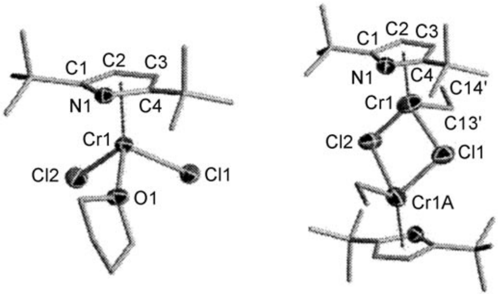

Figure 1. Structures of **1** (left) and **2** (right). Ellipsoids set at 50% probability; hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: **1**: Cr1–O1 2.045(2), Cr1–N1 2.199(3), Cr1–C4 2.213(3), Cr1–C1 2.249(3), Cr1–C3 2.257(3), Cr1–Cl2 2.2847(10), Cr1–Cl1 2.2873(10), Cr1–C2 2.286(4), N1–C1 1.377(4), N1–C4 1.387(4), C1–C2 1.434(5), C2–C3 1.401(5), C3–C4 1.414(5). **2**: Cr1–Cl2 2.188(3), Cr1–C13′ 2.202(15), Cr1–C3 2.226(6), Cr1–C2 2.225(5), Cr1–C1 2.281(5), Cr1–C4 2.289(5), Cr1–N1 2.312(3), Cr1–Cl1 2.3439(19), N1–C4 1.382(7), N1–C1 1.364(7), C1–C2 1.418(8), C2–C3 1.374(8), C3–C4 1.405(7), C13′–C14′ 1.496(14); Cr1-Cl1-Cr1A 89.39(10), Cl2-Cr1-Cl1 93.76(7), C13′-Cr1-Cl1 99.6(4).

In an attempt to isolate the catalytically active species, we reacted **1** with a stoichiometric amount of $\mathrm{AlEt_3}$. The violet-

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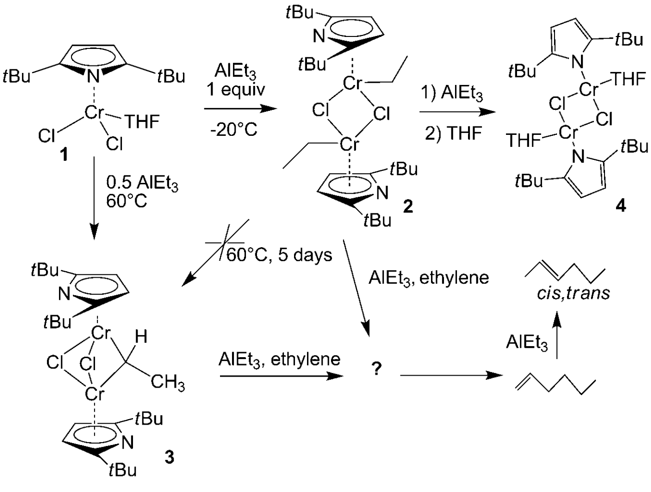
Table 1: Oligomerization studies.[a]

Entry	Catalyst	$AlEt_3$ [equiv]	*T* [°C]	Alkenes [mL]	PE [g]	1-hexene/ 2-hexene [mol %]	1-hexene [mol %]	Oligomerization activity [$g\,mol^{-1}\,Cr\,h^{-1}$]
1	**1**[b]	10	85	31	0	99	84	700600
2	**1**[b]	5	85	20	0	99	83	452000
3	**1**[b]	5	115	4	0.2	99	75	97100
4	**2**[c]	0	120	2	0.3	99	98	55200
5	**2**[d]	5	115	32	0.6	99	89	1486400
6	**2**[c]	10	85	35	0	99	95	791000
7	**2**[c]	10	100	39	0	99	93	881400
8	**2**[c]	10	110	40	0.4	99	89	917300
9	**2**[c]	10	150	4	0	95	73	90400
10	**2**[c]	15	85	25	0	99	91	565000
11	**2**[c]	50	85	15	0	99	92	339000
12	**3**[c]	0	120	0	0	0	0	0
13	**3**[d]	5	115	71	1.3	99	91	3295900
14	**4**[c]	10	0	0	0	0	0	0

[a] Conditions: Methylcyclohexane 100 mL, 30 min reaction time, 40 bar PE = poly(ethylene). [b] 60 μmol. [c] 30 μmol. [d] 15 μmol.

blue solution turned immediately dark red, affording deep-red crystals of the dinuclear species $[\{[\eta^5\text{-}(t\mathrm{Bu})_2C_4H_2N]CrEt\}_2(\mu\text{-}Cl)_2]$ (**2**; Scheme 1).[14] The dinuclear nature and the connectivity of this rare example of a chromium(III) ethyl derivative were clarified by an X-ray crystal structure (Figure 1). The structure consists of two edge-sharing tetrahedra with two identical piano-stool units connected by two bridging chlorides. The low magnetic moment is to be expected for the planar $\{Cr_2Cl_2\}$ core, with an intermetallic distance that is shorter than the sum of the Van der Waals radii. The complex is reasonably thermally robust, but slowly turned brown upon heating for about 30 minutes in toluene.



Scheme 1. Reactivity of complexes **1**–**4**.

During the preparation of **2**, it was discovered that if only 0.5 equivalent of $AlEt_3$ was added dropwise to solutions of **1** and the reaction was slowly carried out at room temperature, a distinctively different blue color developed, thus indicating the formation of a different species. The color did not change appreciably upon heating overnight. A new paramagnetic complex, formulated as $[\{[\eta^5\text{-}(t\mathrm{Bu})_2C_4H_2N]Cr\}_2(\mu\text{-}Cl)_2(\mu\text{-}CHCH_3)]$ (**3**), was isolated as deep-blue crystals from the aforementioned blue solutions.[14] The crystal structure revealed a dimeric chromium complex with a face-sharing bi-tetrahedral arrangement (Figure 2). The two distorted tetrahedra are bridged by two chlorine atoms and one carbon atom of a C_2 residue. The C–C distance of this particular unit (C13–C14 1.505(9)) is in the range of a C–C single bond. Chemical degradation experiments carried out with a D_2O/H_2O mixture in C_6D_6 followed by centrifugation and NMR spectroscopic characterization of the solution phase helped to partially simplify the spectrum. The ^{2}H NMR spectrum acquired with ^{1}H decoupling showed two peaks at $\delta = 0.748$ and 0.730 ppm, thus indicating the presence of the two isotopomers. ^{13}C NMR spectroscopy unequivocally showed the presence of a mixture of the isotopomers CD_2HCH_3, CDH_2CH_3, and CH_3CH_3. The ^{1}H NMR spectrum showed complete absence of olefinic residues. The resonances of a mixture of partly deuterated ethanes were present at $\delta = 0.778$ ppm as a complex signal resulting from both ^{1}H–^{1}H and ^{1}H–^{2}H coupling. Deuterium decoupling could not be properly carried out owing to dilution and line broadening. However, the ^{1}H^{13}C HMQC signal at $\delta = 0.778$ ppm in the proton section clearly showed coupling at $\delta = 6.78$ ppm of the ^{13}C NMR spectrum. The ^{13}C resonance was not clearly visible owing to low intensity and very possibly line broadening.

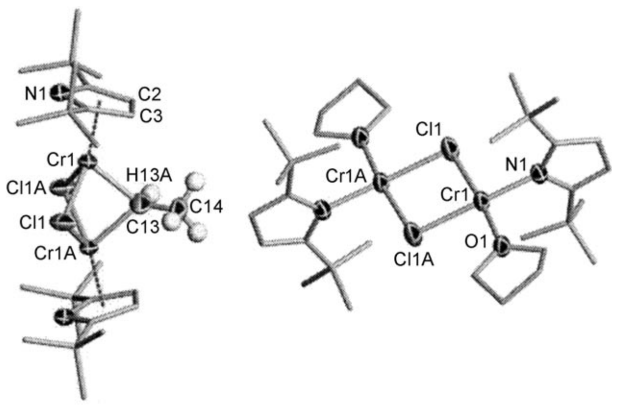


Figure 2. Structures of **3** (left) and **4** (right). Ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **3**: Cr1–C13 2.048(13), Cr1–C3 2.239(2), Cr1–C2 2.238(2), Cr1–C1 2.256(2), Cr1–C4 2.260(2), Cr1–N1 2.2791(18), Cr1–Cl1 2.359(3), Cr1–Cl1A 2.384(3), Cr1–Cr1A 2.6739(6), N1–C1 1.377(3), N1–C4 1.377(3), C1–C2 1.417(4), C2–C3 1.423(4), C3–C4 1.415(4), C13–C14 1.505(9); Cl1-Cr1-Cl1A 99.58(8), Cr1-Cl1-Cr1A 68.63(8), Cr1-C13-Cr1A 81.7(2). **4**: Cr1–N1 2.0121(19), Cr1–O1 2.0774(17), Cr1–Cl1A 2.3909(7), Cr1–Cl1 2.4048(7).

These findings compare reasonably well with literature data.[9] Finally, ESI-MS analysis provided the expected value for the molecular ion of the proposed formulation of **3**.

The formation of **3** is puzzling. In principle, the most direct way to form the bridging ethylidene could be a simple C–H σ-bond metathesis from the two ethyl groups present in **2**. This does not seem to be the case though, as thermolysis of **2** led to brown decomposition products with no evidence for the formation of the blue compound **3**, which could only be formed from **1** under the conditions previously discussed (Scheme 1). Therefore, its formation seems to be a reaction pathway alternative, and not subsequent to the formation of **2**, that is triggered at higher temperature by a lower Al:Cr ratio. Attempts to form **3** rationally by treating solutions of analytically pure **2** with either $AlEt_3$ or Et_2AlCl failed. The reactions afforded instead the dinuclear, square-planar complex $[\{[\sigma\text{-}(t\mathrm{Bu})_2C_4H_2N]Cr^{II}(thf)\}_2(\mu\text{-}Cl)_2]$ (**4**) that was isolated as blue crystals (Figure 2) after crystallization of the dried reaction residue from THF.[14] The retention of chlorine in the structure suggests that formation of **4** also proceeds by a non-straightforward mechanism. The σ-bonding of the pyrrolide anion in **4** is most likely due to the treatment with THF, which was required for triggering crystallization. Complex **4** is catalytically inactive.

Complex **2** is indeed a single-component, self-activating precatalyst that produces highly pure 1-hexene. The low activity is likely to be ascribed to both the robust dimeric structure, which is not easily dissociated in solution, and to partial catalyst poisoning owing to impurities (Figure 3). Furthermore, the formation of the chromium(I) catalytically active species from **2** will require a preliminary ethyl/chlorine exchange to generate a ligand–$CrEt_2$ function that is ready to undergo thermal reductive elimination. When treated with a few equivalents of $AlEt_3$, **2** became an excellent trimerization catalyst, producing a large amount of 1-hexene with a minor extent of isomerization. The reaction outcome was very sensitive to the temperature and catalyst and activator loadings: Higher loadings of $AlEt_3$ always resulted in an increase of 2-hexene in combination with higher temperatures.

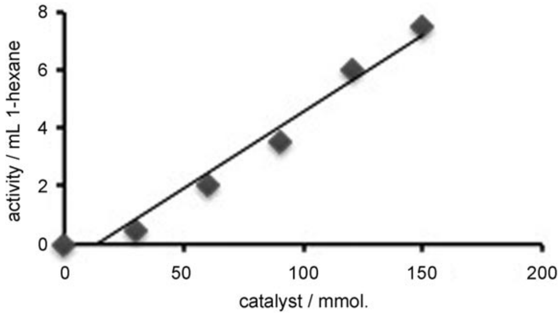


Figure 3. Plot of the single-component catalytic behavior of **2**.

The catalytic behavior of the ethylidene-bridged **3** is similar to **2**. Whereas no single-component catalytic behavior was observed even under harsh conditions, activation with a small amount of $AlEt_3$ and high temperatures gave record activity and good selectivity with the usual isomerization to *cis*/*trans* 2-hexene (30:70). The similarities in catalytic behavior between **2** and **3** when activated does not relate to the preliminary conversion of **2** to **3**, but rather to the fact that both species may possibly generate the same catalytically active chromium(I) intermediate.

Finally, the variable amount of isomerization of 1-hexene observed during this work (also observed with the commercial process using the Phillips catalytic system) is simply due to the alkyl aluminum activator. The degree of isomerization was found to increase with the temperature and the loading of $AlEt_3$ and did not depend on chromium. In a blank run with only $AlEt_3$, we found that at 110 °C, pure 1-hexene can be isomerized (93 %) in 1 hour to a thermodynamic mixture of *cis* and *trans* isomers (30:70 %) of 2-hexene. No 3-hexene was ever observed. It is therefore important to strike the right balance between reaction conditions and activator loading to maximize 1-hexene production.

In conclusion, we have presented a novel ethylene trimerization system related to the previously reported intermediates of the Phillips system.[6a,b] In contrast to those complexes, however, the bulky π-bonded pyrrolide ligand does not allow retention of AlR_3 at the pyrrole nitrogen atom without detracting from the trimerization performance. In this system, the role of organoaluminum seems to be exclusively confined to that of an alkylating agent. The serendipitous discovery of the first case of a Schrock-type chromium ethylidene is quite intriguing. We found it particularly stimulating regarding the recent mechanistic debate[10] regarding the possibility of a dinuclear Schrock type of alkylidene being a catalytically active intermediate in the oligomerization or even a polymerization process.[11] The isolation of such a species, which is closely reminiscent of the Takai olefination intermediate,[12] indicates that chromium Schrock carbenes may indeed exist. We are currently examining the reactivity of this unprecedented and catalytically active chromium ethylidene species.

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[13] For details of complex preparation and characterization, see the Supporting Information.

[14] CCDC 798697 (**1**), 798698 (**2**), 798699 (**3**), and 798700 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.