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Towards Selective Ethylene Tetramerization**

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The metallacycle mechanism formulated to account for the excellent selectivity of catalytic ethylene-trimerization processes is today well-established.[1–3] Further ring expansion through the insertion of a fourth ethylene unit is believed to afford 1-octene.[4] However, selectivity becomes a major challenge in this event. If a fourth molecule of ethylene can be inserted readily into a seven-membered ring, it is clearly very difficult to prevent further expansion of the nine-membered ring (and thus the formation of heavier oligomers). In fact, in the entire patent and academic literature, only two homogeneous catalytic systems, discovered by researchers at Sasol[4a] and SK Energy,[4b] have been described that are capable of producing a substantial excess of 1-octene (about 70 %) over other α-olefins. The search for a catalytic system capable of producing 1-octene as the only product is still being pursued actively. One may even question whether *selective* tetramerization to produce *solely* 1-octene may ever be possible, unless an alternate mechanistic pathway is followed.

In our search for highly selective ethylene-tetramerization catalysts, we selected the 2,2′-dipyridylamine ligand with an alkylated central nitrogen atom. Alkylation of the central N atom to prevent anionization was deemed necessary to maintain the possibility of cationizing the monovalent metal center, as necessary for catalytic activity.[1p] Alkylation of the central nitrogen atom was also expected to diminish the established tendency of the ligand to form multiply bonded dimers or higher aggregates,[5] because of sterically induced deformation of the ligand backbone.[6]

A range of substituted $(2\text{-}C_5H_4N)_2NR$ derivatives and the corresponding trivalent chromium complexes $[\{(2\text{-}C_5H_4N)_2NR\}CrCl_3(thf)]$ (**1a**: R = Me; **1b**: $R = CH_2CMe_3$; **1c**: $R = CH_2SiMe_3$; **1d**: $R = C_{16}H_{33}$; **1e**: R = benzyl; **1f**: $R = C_3H_6Si(OEt)_3$; **1g**: $R = C_4H_8OEt$) were synthesized readily. The monomethyl Cr^{III} derivative $[\{(2\text{-}C_5H_4N)_2NCH_2SiMe_3\}CrMeCl_2(thf)]$ (**2c**) was prepared by treating **1c** with a stoichiometric amount of MeLi in THF or by the direct treatment of $[CrMeCl_2(thf)_3]$ with the ligand. The structures were all very similar (Figure 1).

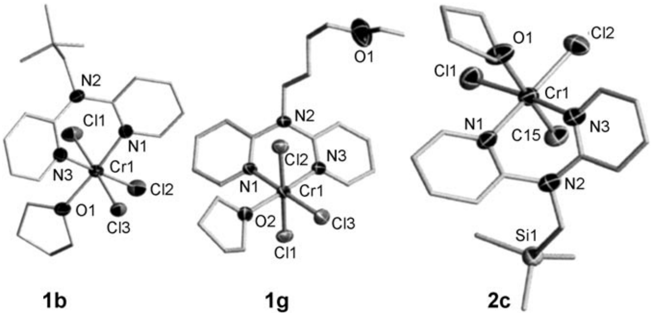

Figure 1. Thermal-ellipsoid (50 % probability) plots of **1b**, **1g**, and **2c**.[11]

When activated with methylaluminoxane (MAO) at 50 °C, all trivalent complexes underwent a vigorously exothermic reaction after an induction period of several minutes to form large amounts of a heavy α-olefin. In all cases, the ^{13}C NMR spectrum showed the presence of a vinylic residue and a complete lack of branching: features indicative of linear α-olefins. Under isoparabolic conditions, with temperatures rising to a maximum of 110 °C, we observed that, aside from polyethylene (PE) wax, a sizeable amount of highly pure 1-octene was formed, as shown by NMR spectroscopy and GC–MS (Figure 2). The thermal behavior of the reaction was remarkable. After an induction period of about 4 min, the temperature increased very rapidly to reach about 110 °C. When the reaction temperature was maintained constant at 80 °C with the aid of a cooling coil in the interior of the reactor, the waxy α-olefin appeared to be the sole product of the reaction (only traces of 1-octene were detected; Table 1, entry 7). A lower catalyst loading and variable pressure did not affect the activity significantly.[7] Attempts to diminish the amount of PE wax by carrying out the catalytic reaction in the presence of hydrogen gas did not affect the outcome. MAO appears to be the only usable activator, since no catalytic activity was observed with other common alkyl aluminum compounds, including trimethylaluminum (TMA), triisobutylaluminum, tetraisobutyldialuminoxane, triethylaluminum, and diethylaluminum chloride.[8] Interestingly, even the use of TMA-depleted MAO gave no reaction. Conversely, when a small amount of TMA (10 %) was added

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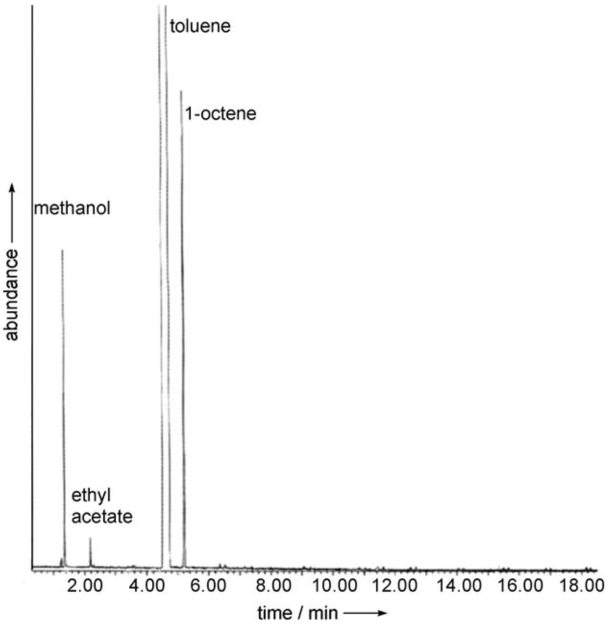


Figure 2. GC–MS chromatogram of the solution phase (Table 1, entry 10) showing the presence of MeOH (quenching agent), ethyl acetate (needle-rinsing agent), toluene (solvent), and 1-octene.

to the TMA-depleted system, the original catalytic behavior was restored, which indicates that both TMA and MAO are required to generate the active species. The necessity for the presence of TMA indicates its role as the alkylating agent, whereas MAO simply provides adequate Lewis acidity. However, attempts to activate the precursors with alkyl aluminum compounds and trityl borate[8a] resulted in no activity. The nature of the amine substituent significantly affected the catalytic behavior of the catalyst (Table 1), as also observed in the Sasol system.[9] In the present case, this behavior can be ascribed to differences in solubility of the catalyst precursors.

The formation of 1-octene only at elevated temperatures under isoparabolic conditions (and not under isothermal conditions at 80 °C) clearly indicated that one catalytically active species (responsible for the formation of the PE wax) is primarily generated at 50 °C, and a second catalytically active species responsible for the selective formation of 1-octene is generated exclusively at higher temperature (> 80 °C). However, experiments carried out at 100 °C as the initial temperature gave no 1-octene, thus indicating that the tetramerization catalyst is also rapidly deactivated at high temperature. This behavior is in agreement with the hypothesis that the thermolysis of organochromium(III) generates the catalytically active chromium(I) species.

To exclude the possible role of divalent chromium in this complex system, we prepared the divalent precursors **3b** and **3f** through the treatment of $[CrCl_2(thf)_2]$ with the appropriate ligand $(2\text{-}C_5H_4N)_2NR$ ($R = CH_2CMe_3$ and $C_3H_6Si(OEt)_3$, respectively) in THF. Suitable crystals could be grown only upon treatment with *N,N'*-dimethylformamide (DMF; Figure 3).

Catalytic testing of **3b** and **3f** under the usual reaction conditions showed that aside from the usual formation of large amounts of wax, only a small amount of α-olefins (Schulz–Flory distribution) was produced. The lack of selectivity for light oligomers not only excludes the possibility that divalent chromium might tetramerize ethylene, but also indicates that in this particular case, Cr^{II} is not even a precursor for the tetramerization catalyst. Therefore, thermolysis is most likely to occur directly at a trivalent organochromium center and bypass the divalent species through a double alkylation and consequent two-electron reduction to form the monovalent species. A divalent complex may have been generated from **1f** (which produced the most 1-octene) only when treatment with the activator was carried out at

Table 1: Results of the catalytic runs.[a]

Entry	Complex	T [°C]	Wax [g]	M_n [$g\,mol^{-1}$]	PDI	C_6 [mL]	C_6 [%]	C_8 [mL]	C_8 [wt %]	Other oligomers ($>C_{10}$) [mL]
1	**1a**	50–110	42	2233	2.1	traces	< 1	3.3	5.4	0.2
2	**1b**	50–110	60	2691	1.8	traces	< 1	5.8	6.4	–
3	**1c**	50–110	32	1954	2.2	–	–	2.6	5.6	–
4	**1d**	50-110	80	2283	1.9	traces	< 1	10.2	8.4	–
5	**1e**	50–110	55	3948	2.2	traces	< 1	4.2	5.2	–
6	**1f**	35–110	37	1974	2.0	0.8	1.2	4.1	6.8	2.2 ($\alpha = 0.92$)
7[b]	**1f**	80	80	4236	2.2	–	–	2.7	2.2	–
8	**1f**	50–110	60	2631	2.1	traces	< 1	13.1	13.5	–
9[c]	**1f**	50-110	–	–	–	–	–	–	–	–
10	**1g**	50-110	35	2566	2.2	–	–	6.9	12.3	traces
11	**2c**	50–110	62	1709	2.1	–	–	1.5	1.7	–
12	**3b**	50–110	25	2127	2.3	traces	< 1	traces	–	traces
13	**3f**	50–110	40	1411	2.3	0.4	< 1	2.1	3.5	1.2 ($\alpha = 0.97$)
14	**4f**	50–110	25	4848	2.6	9.0	19.6	traces	–	–
15	**4f**	35–110	12	1590	2.3	8.0	35.1	traces	–	–
16	**5f**	50–110	–	–	–	–	–	–	–	–
17	**6f**	60–110	57	1463	1.7	0.5	< 1	7.9	8.9	–

[a] Reaction conditions: catalyst (20 μmol), MAO (400 equiv), toluene (solvent, 150 mL), ethylene (40 bar), 1 h. Longer reaction times did not lead to a further increase in the amount of product formed. “Traces” means less than 1 %. [b] Catalyst loading: 10 μmol. [c] The complex was activated with TMA (40 equiv) and $[Ph_3C][B(C_6F_5)_4]$ (3 equiv). M_n = number-average molecular weight, PDI = polydispersity index.

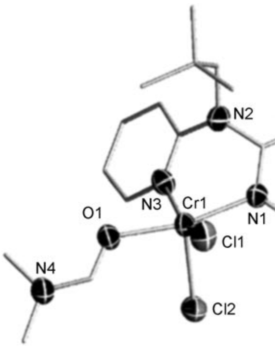
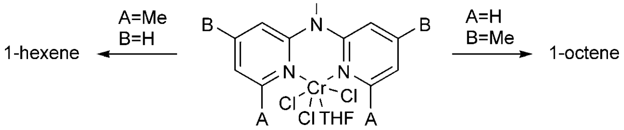


Figure 3. Thermal-ellipsoid (50% probability) plot of the DMF adduct of **3b**.

35 °C for about 20 min, before the temperature was increased to 50 °C, followed by the usual isoparabolic increase to 100 °C (Table 1, entry 6). In this case, instead of the selective formation of 1-octene, a small amount of a Schulz–Flory distribution of oligomers was obtained, as observed with the other divalent precursors.

Although a ring-expansion mechanism could effectively produce larger excesses of 1-octene, it is unlikely that it would enable *selective* tetramerization (e.g. > 99%), in the way it enables selective ethylene trimerization. Further expansion of the seven-membered ring (responsible for 1-hexene formation) to generate heavier oligomers could lead to the formation of a range of larger metallacycles, whose stability and activation energy of formation are not expected to be much different from those of the nine-membered ring. Therefore, we considered that the weakly binucleating nature of the ligand in the assembly of a non-Cr–Cr-ligated dinuclear Cr^I species might be a factor responsible for the selective formation of 1-octene (i.e. by the coupling of two neighboring chromacyclopentane units within a bimetallic structure and subsequent elimination of 1-octene). If this hypothesis is true, the introduction of substituents that prevent dinuclear aggregation could affect the selectivity of the present system. We therefore tested the effect of methyl substituents at the *ortho* positions of the pyridine rings (Scheme 1).

The corresponding complex $[\{2\text{-}(6\text{-Me-C}_5H_4N)_2NC_3H_6Si(OEt)_3\}CrCl_3(thf)]$ (**4f**) was synthesized and tested under the usual optimal reaction conditions (Table 1). Remarkably, complex **4f** behaved in a very similar manner to complexes **1**, but produced much less wax and a sizeable amount of pure 1-hexene (Table 1, entry 15). Interestingly, the divalent congener **5f** was catalytically inactive. We also prepared a similar ligand in which the methyl groups were placed in the *para* rather than *ortho* positions of the pyridine rings. The corresponding trivalent complex $[\{2\text{-}(4\text{-Me-C}_5H_4N)_2NC_3H_6Si(OEt)_3\}CrCl_3(thf)]$ (**6f**) showed the usual formation of 1-octene and a large amount of the waxy solid (Table 1, entry 17).



Scheme 1. Effect of methyl substituents at the *ortho* and *para* positions of the pyridine rings on the oligomerization.

This observation is particularly informative, since the repositioning of the methyl substituents from the *ortho* to the *para* positions of the aromatic rings is not expected to affect the electronic properties of the ligand. Thus, the switching of the selectivity from the selective formation of 1-octene to the selective formation of 1-hexene when the catalyst contains *ortho* Me groups can be ascribed exclusively to steric factors.

In conclusion, we have described the intriguing formation of pure 1-octene alongside low-molecular-weight polyethylene wax. This observation suggests that a truly selective ethylene-tetramerization catalyst may indeed exist. As a working hypothesis, we concur with the mechanistic concept recently proposed by Rosenthal and co-workers[10] that a dinuclear monovalent species, possibly without a Cr–Cr multiple bond, might be formed with the aid of a non-anionic bidentate ligand and promote the formation of 1-octene through a bimetallic reductive elimination.

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[11] CCDC 777160, 777161, 777162, 777163, 777164 (**1c**, **1e**, **1g**, **2c**, and **3b**) 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.