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Switchable Chromium(II) Ethylene Oligomerization/ Polymerization Catalyst

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*Summary: The tri- and divalent chromium derivatives of [N-Me,tripyrr] ([N-Me,tripyrr] = 2,5-bis(diphenyl(pyrrol-2-yl)methyl)-1-methylpyrrole) [N-Me,tripyrr]CrCl (**1**), and [N-Me,tripyrr]Cr(L)$_2$·(THF)$_{0.5}$ (**2**) [L = THF (**2a**), pyridine (**2b**)] were obtained in good yield from the reaction of the dipotassium salt of the ligand with CrCl$_3$(THF)$_3$ and CrCl$_2$(THF)$_2$, respectively. Reaction of the dilithium salt of the ligand with CrCl$_2$(THF)$_2$ led to the divalent analogue [N-Me,tripyrr]Cr(μ-Cl)Li(THF)$_3$ (**3**), wherein a Li−Cl unit was retained by the metal center. The compounds were tested for ethylene oligomerization activity upon activation with two different alumoxanes. In the case of MAO, the Cr(II) catalyst precursors **2b** and **3** showed a marked increase in activity with respect to the trivalent **1**. The product distributions from compounds **1** and **2b** were nearly identical, indicating that the Cr(II) oxidation state provides better catalyst precursors. Use of the i-BuAlO activator instead of MAO afforded exclusively polymerization with high activity and produced linear, low molecular weight polyethylene.*

Since the original discovery by Manyik of the ability of a mixture of CrCl$_3$, pyrrole, and MAO to transform ethylene into 1-hexene with high yield and good selectivity,[1] this fascinating process has received a steady increase in attention.[2] Today, encouraging progress has been made in the direction of making the reaction more selective.[3,4] There is a rather general consensus that the oligomerization proceeds with a preliminary reductive coupling of ethylene and formation of a chromocyclopentane intermediate,[5,6] followed by further insertions before reductive elimination completes the catalytic cycle. While the reductive coupling of ethylene is a two-electron process, the oxidation state of chromium in the catalytically active intermediate remains uncertain[5] despite the fact that all the known chromium catalyst precursors are based on the trivalent state as a rule with very few exceptions.[2a,4a,7]

The ability of the [PNP]CrCl$_3$ [PNP = Ar$_2$PN(R)PAr$_2$; R = Cy, Me; Ar = Ph, Ar] catalyst to exceed the Flory−Schultz distribution,[8] effectively producing the highly desirable 1-octene, has recently marked a milestone in this field.[4] A subsequent investigation aimed at isolating intermediates of this remarkable system[9] has pointed out that the catalyst precursor (1) is more active if it is

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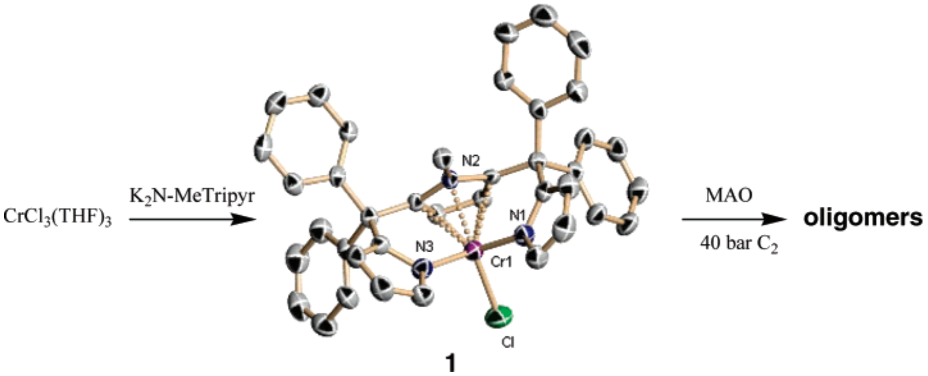
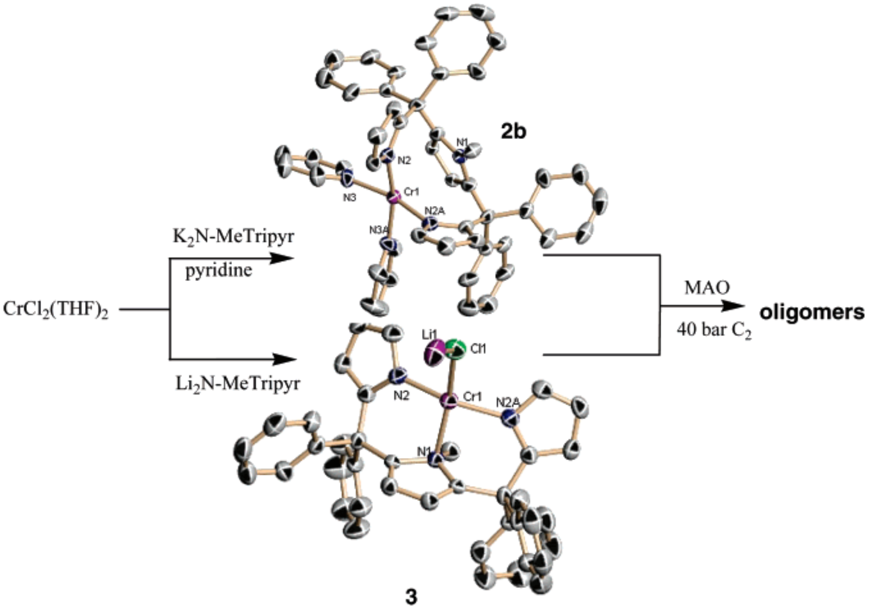
Scheme 1



Scheme 2



based on divalent chromium; (2) may possess a cationic nature; and (3) may retain a Cl−$AlMe_3$ in the coordination sphere of the metal center. These findings, which gave some insight into this catalytic system, prompted us to try to probe their generality. Given the well-known ability of the pyrrolide anion to promote very high catalytic activity,[7] we have selected the dianion of 2,5-bis(diphenyl(1H-pyrrol-2-yl)methyl)-1-methylpyrrole [N-Me,tripyrr] as a ligand. The rationale for this selection was twofold. The presence of two anionic pyrrolide rings and consequent chelating effect were regarded as beneficial for preventing ligand dissociation. Second, the presence of a third pyrrole ring in the ligand framework, with the N atom alkylated and held by the chelating geometry at a close proximity to the metal center in a sort of "forced π-bonding", could provide electron density on demand to the metal center via slippage of the π-bonded ring. This idea was suggested by the fact that ligand hemilability may be a winning card for good activity and selectivity, as in the case of a Ti-based catalytic system.[10]

The reaction of the dipotassium salt of the tripyrrole ligand with either $CrCl_3(THF)_3$ or $CrCl_2(THF)_2$ afforded the corresponding tri- and divalent complexes [N-Me,tripyrr]CrCl (**1**) (Scheme 1) and [N-Me,tripyrr]-Cr$(THF)_2$ (**2a**) (Scheme 2).[11] Complex **2a** could not be separated from the KCl byproduct and recrystallized due to its very poor solubility. Nevertheless, its in situ treatment with pyridine conveniently transformed this species into the corresponding bis-pyridine adduct [N-Me,tripyrr]Cr$(pyridine)_2\cdot(THF)_{0.5}$ (**2b**), which was isolated in crystalline, analytically pure form and high yield (94%).[11] The crystal structures of both **1** and **2b**[11] showed the expected arrangement. The only substantial difference arises from the π-oriented alkylated pyrrole ring, which shows a regular π-bonding in the first case but gives instead a nonbonding contact in the second [Cr−centroid = 2.00 and 2.70, respectively]. This is probably the result of the diminished Lewis acidity of the divalent chromium atom, in turn confirming that the ligand may provide π-coordination on demand.

When the reaction of $CrCl_2(THF)_2$ was carried out with the di*lithium* salt of the ligand, another divalent complex, [N-Me, tripyrr]Cr(μ-Cl)Li$(THF)_3$ (**3**), was obtained in crystalline form and moderate yield.[11] The crystal structure (Scheme 2) of this species[10] differs from **1** in two main points. First, the chlorine atom is bridging a Li$(THF)_3$ unit, and second, there is only one bonding

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(11) See Supporting Information.

Table 1. Catalytic Activity Results with 2000 equiv of MAO, 40 bar, 50 °C, 30 μmol of Catalyst, 150 mL Total Toluene Volume[a]

catalyst	olefin activity (g/g Cr h)	olig. (g)	PE (g)	product distribution 1-olefins (mol %)					
				C4	C6	C8	C10	C12	C14
1	3813	8.25	1.75	14.74	40.09	22.50	11.61	5.98	3.36
2b	23 296	54.0	2.30	12.35	36.77	22.68	13.16	7.77	2.70
3	20 708	48.0	16.2	0	13.87	32.74	23.29	15.41	9.18
blank	n/a	0	0.42	0	0	0	0	0	0

[a] Blank reaction was carried out with $CrCl_2(THF)_2$.

contact with the former π-oriented ring with the N atom [Cr−N(1) = 2.239(13) Å], which in turn assumes a rather obvious sp^3 character.

The catalytic activity of these species in terms of ethylene oligomerization (Table 1) was very high while in combination with a large amount of MAO. The product distribution (Table 1) clearly indicates that complexes **1** and **2b** are related given the very similar distribution of oligomers and the small amount of PE formed. In the presence of a reducing medium, such as provided by the MAO activator, it is hard to imagine a reaction pathway where the divalent **2b** is oxidized to a higher oxidation state. Vice versa, it is quite reasonable to expect that the trivalent **1** may instead be reduced to the divalent state.[12] Therefore, we propose that the trivalent **1** is simply a precursor to a *divalent* species. Accordingly, the activity of the divalent **2b** was found to be *6 times* greater than the trivalent **1**. This is remarkable while considering that **2b** has two molecules of pyridine coordinated to the metal center. On the other hand, complex **2b** displays reversible color change from purple to emerald green in warm toluene, most likely as a result of pyridine dissociation equilibrium. Interesting questions arise about the role of MAO in the activation process of **2b**. Obviously, further reduction to the monovalent state cannot be ruled out at this stage.

The divalent **3** displays a somewhat different type of selectivity in the sense that 1-octene is the major component of the reaction mixture. Also no significant amount of C_4 was detected in this case despite identical workup and the quantity of PE was substantially larger. It should be reiterated that the retention of LiCl through the bridging chloride, instead of the presence of the two pyridines, is the only difference between the two divalent compounds **3** and **2b**. As indicated by the different interaction of the metal center with the alkylated pyrrole ring, this has a direct impact on the metal Lewis acidity. On the other hand, the coordination of a chlorine atom attached to other metallic residues such as Me_3Al has indeed been indicated by both experimental[5h] and theoretical work[5d] as an important point for both high catalytic activity and preferential formation of 1-octene. Therefore, it is tempting to suggest that this structural motif may be somehow preserved during the activation of **3** by MAO.

Finally, activation of **2b** with 400 equiv of IBAO (tetraisobutyldialuminumoxane) afforded an even more unexpected change of reactivity. First, no oligomerization products could be detected in the reaction mixture. Second, the reaction produced only highly linear, low molecular weight polyethylene (MW = 11 000, PD = 2.3) with a rather respectable activity (884 kg PE/mmol/h) when compared to other existing chromium polymerization catalysts.[13] This unprecedented switch from oligomerization toward polymerization, as an exclusive function of the nature of the Al activator, is a fact with no straightforward explanation. Its understanding will provide a further step toward clarifying the factors that control the reactivity and performance of divalent chromium catalysts.

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Supporting Information Available: Complete crystallographic data (CIF) for the complexes and full details on preparation, characterization, and oligomerization experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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