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Ethylene Tetramerization

A Highly Selective Ethylene Tetramerization Catalyst**

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The issue of selectivity has been the most challenging aspect of ethylene oligomerization since its discovery.[1] In the last three decades, trimerization systems with high selectivity have been discovered,[2] but tetramerization catalysts with high selectivity remain elusive.[3] Central to the future success of this endeavor is to understand the factors responsible for the selectivity of the catalytic cycle.[4]

Trivalent chromium complexes are the catalyst precursors that are most commonly used for these transformations. In the presence of alkyl aluminum activators, these species are reduced to the divalent state (responsible for nonselective oligomerization and/or polymerization) or the monovalent state (responsible for selectivity).[5] To complicate the scenario, there is also the possibility for these monovalent and divalent species to undergo disproportionative redox processes that give inactive zero-valent chromium together with higher-valent species that are readily available for further cycles of reduction/reoxidation.[6] Because of the presence of such a redox dynamism in the catalytic cycle, the ancillary ligand system determines the selectivity by preferentially stabilizing one particular oxidation state. For example, when highly reactive monovalent species are provided with a sufficiently long lifetime, selective oligomerization is initiated by the so-called redox reaction/ring-expansion mechanism.[2,5,7]

As mentioned above, selective ethylene tetramerization remains exceedingly rare. With a maximum of around 77% in the case of the process developed by SK Energy,[3d] the selectivity is definitely good, but still far from the levels obtained with the trimerization systems. In addition, the unavoidable formation of polymers poses serious reactor-fouling problems that complicate industrial application. The same redox reaction/ring expansion mechanism that accounts for the selectivity of the trimerization cycle has also been invoked for the rationalization of the tetramerization.[3b,8] Following this mechanism, it is conceivable that high selectivity cannot be reached. The selectivity in this mechanism is determined by the rate of the reduction/elimination step compared to the rate of further ring expansion. If the seven-membered ring is capable of expanding readily into the nine-membered ring, it is hard to imagine why additional expansion should not occur equally fast.[9] In the end, a distribution of oligomers is to be expected and 1-octene may be a dominant product.

Rosenthal and co-workers[10] first emphasized this problem and postulated an alternative mechanism for the highly selective formation of 1-octene. According to their hypothesis, a dimetallic system with two low-valent chromium centers that are not linked with each other may independently form two five-membered metallacycles. Cooperative dimetallic reductive elimination selectively affords 1-octene. It is by following this fascinating hypothesis that we have recently for the first time observed the formation of 1-octene that was uncontaminated by other olefins.[3e] Albeit a step forward, this particular system also produced large amounts of waxes, possibly as a result of incomplete reduction of the precatalyst to the monovalent state.

The combination of N and P donor atoms within an ancillary ligand system has resulted in selective oligomerization systems.[3,11] Recent studies in our research group on chromium complexes that are stabilized by a simple monoanionic $[Ph_2PN(R)]^-$ ligand system showed its versatility for assembling polymetallic structures and self-activating species, which occasionally show selective catalytic behavior.[12,13] To study how the nuclearity of the catalysts may affect the catalytic behavior, we have now linked two N/P-units with both ethylenic and propylenic bridges in order to stimulate the formation of dimetallic species. Herein, we describe the first catalytic system that has a good activity and is capable of producing pure 1-octene (up to 91% purity) with little or no polymer side products.

The ligands $Ph_2PN(R)(CH_2)_nN(R)PPh_2$ (**a**-Me: $n=2$, R = Me; **b**-Me: $n=3$, R = Me; **b**-Et: $n=3$, R = Et; **b**-*i*Pr: $n=3$, R = *i*Pr; Scheme 1) do not react with chromium salts in THF. Nonetheless, they readily ligate trivalent chromium salts in toluene as indicated by color change and dissolution upon mixing. The complexes were isolated as microcrystalline materials from toluene solutions after centrifugation and upon layering with hexane. Analytical and ESI-MS data were in agreement with simple ligand coordination. In the case of the reaction of $[CrCl_3(THF)_3]$ with **a**-Me, the precipitated complex was isolated, resuspended in toluene, and subsequently treated with alkyl aluminum reagents. When Et_2AlCl

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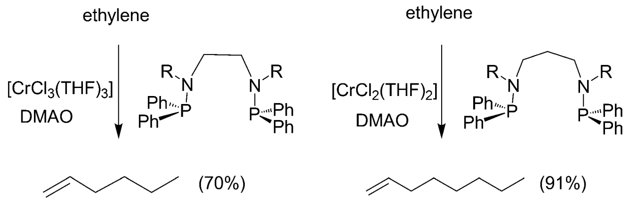


Scheme 1.

(DEAC) and Me_3Al (TMA) were used as alkyl aluminum reagents, two crystalline products could be obtained. The formulations ($\{[Ph_2PN(Me)(CH_2)_2N(Me)PPh_2]Cr(\mu\text{-}Cl)\}_2[(\mu\text{-}Cl)_2(AlEt_2)])^+(EtAlCl_3)^-\cdot(toluene)_{1.5}$ (**1a**-Me) and $[\{[Ph_2PN(Me)(CH_2)_2N(Me)PPh_2]Cr\}(\mu\text{-}Cl)_3]^+[AlMe_2Cl_2]^-$ (**2a**-Me) were obtained by X-ray crystal structure determinations (Figure 1 a and b, respectively).

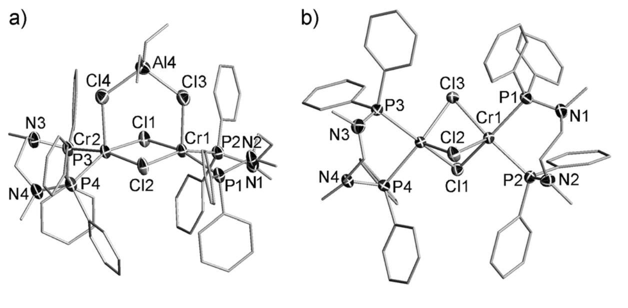


Figure 1. Partial thermal ellipsoid drawings for a) **1a**-Me and b) **2a**-Me cations. The $[EtAlCl_3]$ and $[Me_2AlCl_2]$ counteranions have been omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Both complexes showed similar dinuclear structures, in which each ligand chelates a single chromium atom with the two P donors. The Cr–N distances are well beyond bonding distance, and vary between 3.419 and 3.618 Å. The dimetallic structures are formed by either two bridging chlorine atoms and one bridging $[(\mu\text{-}Cl)_2AlEt_2]$ unit (**1a**-Me), or by three bridging chlorine atoms (**2a**-Me). In both cases, the counter anions ($[EtAlCl_3^-]$ and $[Me_2AlCl_2^-]$, respectively) are not connected with the dimetallic frame but part of the overall ionic structure. In both complexes the chromium centers are divalent. Reduction of the metal center is rather expected as it is often observed when trivalent chromium precursors are treated with alkyl aluminum reagents.[6,14]

The catalytic activity of complexes **1a**-Me and **2a**-Me was low because of their poor solubility in both methylcyclohexane (MeCy) and toluene. Test reactions that were carried out on the precipitated ligand–$CrCl_3$ adducts showed no difference in catalytic behavior to the in situ generated species. Therefore, extensive catalytic testing was carried out with in situ generated complexes, which were conveniently obtained by mixing either $[CrCl_3(THF)_3]$ or $[CrCl_2(THF)_2]$ with the appropriate ligand, activator, and solvent in the reactor which was pressurized with ethylene. The reactions were carried out in toluene by using methylaluminoxane (MAO) as co-catalyst and produced oligomers with Shulz–Flory (S-F) distributions, albeit with high catalytic activity. Interestingly, the product mixtures were polymer-free (Table 1). Conversely, when MeCy was used as solvent and TMA-depleted MAO (DMAO) as co-catalyst, a reasonably selective oligomerization catalyst was obtained. Although the catalytic activity is significantly lower than for the MAO-activated system in toluene, the product distributions were interesting because they consisted of mixtures of exclusively 1-hexene and 1-octene. Generally, 1-hexene was the dominant product, except when $[CrCl_2(THF)_2]$ was used or when a mixture of DMAO and Et_3Al was employed as a co-catalyst. The moderate predominance of ethylene tetramerization that we observed with the system **a**-Me/$[CrCl_3(THF)_3]$/DMAO prompted us to modify the ligand.

The simple introduction of an additional methylene group into the ethylene bridge that links the two N/P units (**b**-Me) had a remarkable impact on catalytic behavior (Table 2). Even in this case, the microcrystalline adducts with chromium salts showed the same catalytic behavior as the in situ generated species. Whereas use of MAO and DMAO in toluene resulted in an S-F distribution of oligomers (albeit with good catalytic activity and no polymer formation), the switch to MeCy as solvent resulted in a highly selective and reasonably active ethylene tetramerization system. Even more interesting, the product mixtures were polymer-free with the only by-product being 1-hexene. Increasing the temperature to 100 °C had a positive effect on the selectivity toward 1-octene while the activity remained the same. As it was observed for **a**-Me, use of $[CrCl_2(THF)_2]$ helps to increase the selectivity toward 1-octene to a record high of 91%. The addition of organoaluminum or organozinc activators to DMAO considerably improved the outcome of the catalytic runs in terms of both activity and selectivity. The addition of Et_3Al resulted in a peak activity toward to formation of 1-octene, while a good selectivity was maintained, although some polymer was also produced as a function of the amount of Et_3Al. Other additives such as iBu_3Al or Et_2Zn resulted in good selectivity for 1-octene, but also in a somewhat lower catalytic activity and the production of small amounts of

Table 1: Ethylene oligomerization with **a**-Me/$[CrCl_3(THF)_3]$ and **1a**-Me.[a]

Cat.	Co-cat.	Equiv	LAO [g]	PE [g]	Activity [$g\,g_{Cr}^{-1}\,h^{-1}$]	C_6	C_8 [mol %]	C_{10-18}
a-Me[b]	MAO	500	97	0	88917	28	26	46
a-Me[c]	DMAO	500	6	1.1	6910	70	31	0
a-Me[c,d]	DMAO	500	3	0	2750	40	60	0
a-Me[c]	DMAO/Me_3Al	500/100	3	0	2750	50	50	0
a-Me[c]	DMAO/Et_3Al	500/100	3	0	2750	37	61	2
a-Me[c]	DMAO/iBu_3Al	500/100	1	0	917	56	44	0
1a-Me[b]	MAO	500	50	0	45833	17	23	60
1a-Me[c]	DMAO	500	–	–	–	–	–	–

[a] Conditions: ligand (30 µmol), $[CrCl_3(THF)_3]$ (30 µmol), solvent (100 mL), 80 °C, ethylene (40 bar), 30 min. [b] Toluene as solvent. [c] MeCy as solvent. [d] $[CrCl_2(THF)_2]$. LAO = linear alpha olefin, PE = polyethylene.

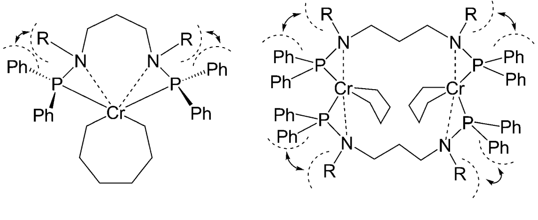
Table 2: Ethylene oligomerization with various ligands.[a]

Cat.	Co-cat.	Equiv	LAO [g]	PE [g]	Activity [g g_{Cr} h^{-1}]	C_6	C_8 [mol %]	C_{10-18}
b-Me[e]	MAO	500	18	0	16500	35	30	35
b-Me[e]	DMAO	500	22	0	11000	15	26	59
b-Me[f]	DMAO	500	8	0	7333	19	81	0
b-Me[f,h]	DMAO	500	6	1.0	6621	31	69	0
b-Me[f,i]	DMAO	500	3	3.0	6012	33	67	0
b-Me[b,f]	DMAO	500	8	0	7333	29	68	4
b-Me[c,f]	DMAO	500	8	0	7333	15	85	0
b-Me[d,f]	DMAO	500	2	0	1833	9	91	0
b-Me[f,j]	DMAO	500	1	0	555	35	65	0
b-Me[f,k]	DMAO	500	5	0.7	5480	28	72	0
b-Me[f,l]	DMAO	500	11	1.1	11494	27	67	6
b-Me[f,m]	DMAO	500	21	2.6	22186	59	15	24
b-Me[f,n]	DMAO	500	18	3.0	20346	27	17	56
b-Me[f]	DMAO/Me_3Al	500/100	12	0	11000	25	75	0
b-Me[f]	DMAO/Et_3Al	500/25	13	0.7	12814	18	77	5
b-Me[f]	DMAO/Et_3Al	500/100	22	4.1	25424	11	88	1
b-Me[f,g]	DMAO/Et_3Al	500/100	10	0.2	9424	23	77	0
b-Me[f]	DMAO/Et_3Al	500/250	5	0.4	5096	24	72	4
b-Me[f]	DMAO/$i$$Bu_3Al$	500/100	7	0.6	7186	10	89	1
b-Me[f]	DMAO/Et_2AlCl	500/100	1	1.1	2326	53	36	11
b-Me[f]	DMAO/Et_2Zn	500/100	2	0	1834	12	87	1
b-Et[f]	DMAO/Et_3Al	500/100	8	0.9	8488	33	67	0
b-*i*Pr[f]	DMAO	500	4	1.6	5718	59	41	0
b-*i*Pr[f]	DMAO/Et_3Al	500/100	6	0.4	6012	73	27	0
b-P*i*Pr[f]	DMAO	500	3	2.5	5956	41	59	0

[a] Conditions: ligand (30 μmol), $[CrCl_3(THF)_3]$ (30 μmol), solvent (100 mL), 80 °C, ethylene (40 bar), 30 min. [b] 60 °C. [c] 100 °C. [d] $[CrCl_2(THF)_2]$. [e] Toluene as solvent. [f] MeCy as solvent. [g] Ethylene (20 bar). [h] Ligand (60 μmol), $[CrCl_3(THF)_3]$ (30 μmol). [i] Ligand (30 μmol), $[CrCl_3(THF)_3]$ (60 μmol). [j] Catalyst (15 μmol). [k] Catalyst (22 μmol). [l] Catalyst (45 μmol). [m] Catalyst (60 μmol). [n] Catalyst (90 μmol).

polymer. The introduction of bulkier groups into the molecular scaffold at either the N (**b**-Et, **b**-*i*Pr) or P (**b**-P*i*Pr) atoms of the ligands decreased both activity and selectivity. Changing the Cr/ligand ratio negatively affected the activity and the selectivity. Variation of the overall catalyst loading dramatically affected the selectivity (Table 2, entries 2 and 9–13). The overall behavior has a non-straightforward interpretation and clearly showed the existences of two parallel trends. After the initial rise of the concentration of octene as a function of the loading, the selectivity switches toward 1-hexene to then decrease to an S-F distribution at the highest loadings. We take this as an indication for the existence of multiple equilibria in the catalytic mixture.

Given the similarity between **a**-Me and **b**-Me, the switch of selectivity from 1-hexene to 1-octene cannot be understood on the ground of differences in electronic features. Therefore, the longer $N(CH_2)_3N$ chain of **b**-Me remains the sole factor responsible for the unique selectivity toward ethylene tetramerization. Although we have no conclusive data, we speculate that such a remarkable sensitivity could be explained in terms of monomer versus dimer formation (Scheme 2). In fact, the formation of dichromium systems (both mono- and divalent) is indeed highly dependent on steric interactions within the ligand scaffold.[15] Thus, if we assume that monomeric and dimeric structures may coexist and that each of the two arrangements is responsible for the formation of either 1-hexene or 1-octene, it is natural that changes on the ligand scaffold may lead the catalytic cycle into either direction. Given that the ligand system is neutral, the formation of a dimeric structure might or might not require reversible dissociation of one ligand. The marked dependence on the nature of the activator may be difficult to rationalize and yet, it may fit with the same assumption, given that the aggregation with alkyl aluminum is also affecting the sterics of the catalytically active species (see for example the structure of **1a**-Me). However, even in the case that a dimetallic mechanism would be followed by the reaction, it would not necessarily imply bimetallic reductive elimination.



Scheme 2.

The selectivity is caused by monovalent chromium, the oxidation state of which is the only one known to date that is capable of performing the initial reductive coupling of the two ethylene molecules.[5] Unlike Sasol's PNP-based and SK Energy's PC_2P-based catalysts,[3a,b] the current system shows a strong solvent and co-catalyst dependence. Selective ethylene tetramerization has only been observed in MeCy. In toluene S-F distributions of α olefins were invariably obtained.

In conclusion, we have reported the first tetramerization catalyst with good activity that is capable of producing 1-octene with high purity and little or no polymer as a by-product. Both solvent and co-catalyst have a dramatic impact on the selectivity. Previously,[3e] we have observed a tetramerization system that produces 1-octene in more than 99% purity along with a large amount of wax. With the results reported herein, we have made a step forward by indicating that a potentially useful tetramerization system of high selectivity can indeed be obtained. Whether the present catalytic system may or may not be linked to Rosenthal and co-workers' hypothesis of a dimetallic system is not yet clear. The remarkable change in catalytic behavior upon such a minor modification on the ligand framework as going from **a**-Me to **b**-Me is puzzling, to say the least. Regrettably, these species have so far eluded crystallographic characterization that possibly could have conclusively supported the link between nuclearity and tetramerization behavior. Nonetheless, the fact that we are able to observe a tetramerization system of such high selectivity (up to 91 %) is encouraging and we are currently attempting to isolate self-activating catalytically active species as well as improving catalyst performance.

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