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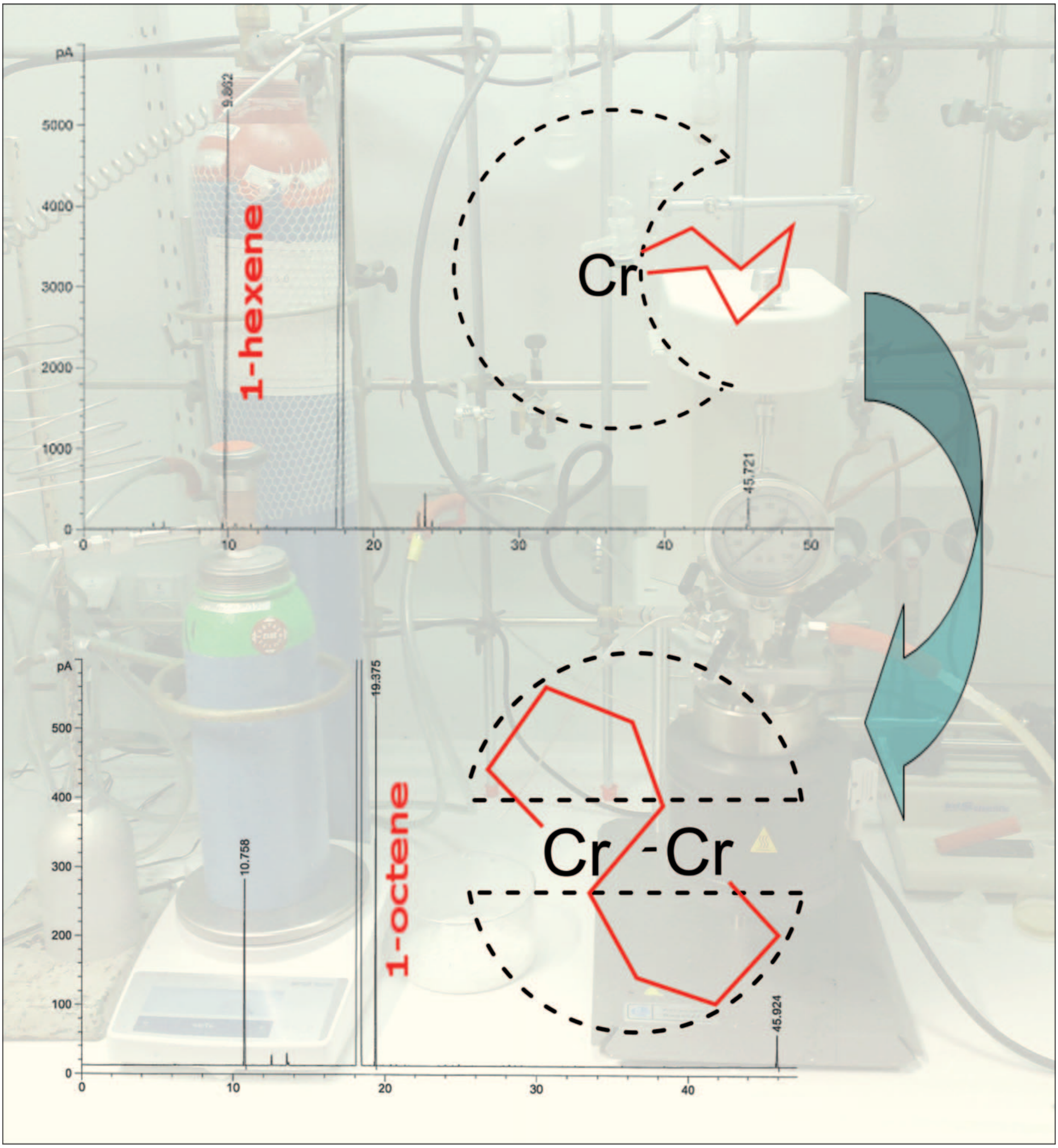
An Alternative Mechanistic Concept for Homogeneous Selective Ethylene Oligomerization of Chromium-Based Catalysts: Binuclear Metallacycles as a Reason for 1-Octene Selectivity?

Stephan Peitz,[a] Bhaskar R. Aluri,[a] Normen Peulecke,[a] Bernd H. Müller,[a]
Anina Wöhl,[b] Wolfgang Müller,*[b] Mohammed H. Al-Hazmi,[c] Fuad M. Mosa,[c] and
Uwe Rosenthal*[a]



Abstract: An alternative concept for the selective catalytic formation of 1-octene from ethylene via dimeric catalytic centers is proposed. The selectivity of the tetramerization systems depends on the capability of ligands to form binuclear complexes that subsequently build up and couple two separate metallacyclopentanes to form 1-octene selectively. Comparison of existing catalytic processes, the ability of the bis(diarylphosphino)amine (PNP) ligand to bridge two metal centers, and the experimental background support the proposed binuclear mechanism for ethylene tetramerization.

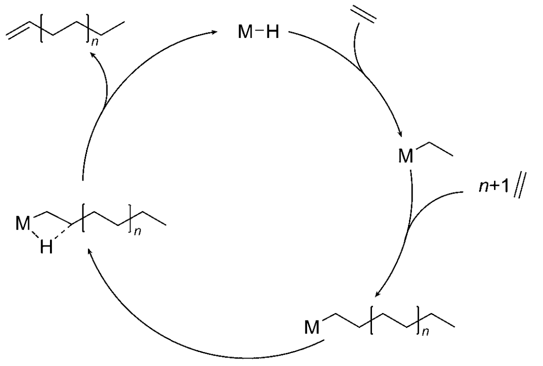
Keywords: chromium • dinuclear complexes • ethene • reaction mechanisms • selectivity

Introduction

Linear alpha olefins (LAOs) are useful and versatile intermediates for many industrially important substances, such as co-monomers for high-density polyethylene (HDPE) or linear low-density polyethylene (LLDPE) (C4 to C8), surfactants for detergents (C10 to C18), base stock and additives for synthetic lubricants (C10 to C18), or alcohols for plasticizers (C6 to C10).[1,2]

The existing technologies for producing LAOs are mostly based on ethylene oligomerization routes by an ethylene insertion/β-elimination mechanism (Scheme 1) resulting in a mathematical product distribution like Schulz–Flory or Poisson.[1,3] Thus, the conventional full range producers (e.g., Shell, Chevron Phillips, INEOS, UNITED) have to meet a formidable challenge to match the market demand.

Consequently, the deliberate production of the most economically viable LAOs, that is, co-monomer grade 1-hexene and/or 1-octene appears to be highly desirable.[2b] To achieve this, the traditional insertion/β-elimination mechanism has to be overcome. Manyik et al. at Union Carbide Corporation discovered, for the first time, the selective trimerization of ethylene to 1-hexene in the late 1960s.[4] They modified the heterogeneous Phillips chromium-based ethylene polymerization catalyst, leading to a polymer with C4 branches.[4] In a following publication, they explained the co-production of 1-hexene by the involvement of a metallacycle as a key intermediate.[5] This postulated mechanism was extended by Briggs[6] and is still accepted today.



Scheme 1. Ethylene oligomerization by a chain growth mechanism.

In 2004, a catalyst system for selective ethylene tetramerization was reported.[7] For this new system, the same metallacyclic mechanism as that used for 1-hexene generation is proposed, although structural proof is still missing. Thus, we herein report a new mechanistic approach for the selective tetramerization of ethylene to 1-octene based on binuclear metallacycles.

LAOs: Application and Demand

LAOs belong to the hydrocarbon group of olefins (alkenes), which are unsaturated and can be represented by the empirical formula C_nH_{2n}.[8] The reactive double bond, situated at the terminus of the molecule, makes LAOs interesting and versatile intermediates for many industrially important substances like co-monomers, alcohols, aldehydes, carboxylic acids, or sulfonates.[3] The global usage of LAOs was around 3.2 million tonnes in the year 2006.

However, the industrial application depends on the chain length, as shown in Table 1.[1,2] To serve different segments of the market, depending on the 1-olefin chain length, differences are observed in terms of market size and growth, geography, fragmentation, and so forth. While the co-monomer grade LAO market, which is closely linked to polyethylene production, has the highest growth rate of estimated 5.4–7.9% per year (2003–2010),[9] the demand for other LAOs, especially long chained ones, grows significantly slower. The market for 1-hexene will even expand more in the future, due to expiring patents concerning co-polymerization technologies. In particular, the market situation of 1-

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[a] S. Peitz, Dr. B. R. Aluri, Dr. N. Peulecke, Dr. B. H. Müller,
Prof. Dr. U. Rosenthal
Leibniz-Institut für Katalyse an der Universität Rostock e.V.
Albert-Einstein-Str. 29A
18059 Rostock (Germany)
E-mail: Uwe.rosenthal@catalysis.de

[b] Dr. A. Wöhl, Dr. W. Müller
Linde AG, Linde Engineering Division
Dr.-Carl-von-Linde-Str. 6-14
82049 Pullach (Germany)
E-mail: Wolfgang.mueller@linde-le.com

[c] Dr. M. H. Al-Hazmi, F. M. Mosa
Saudi Basic Industries Corporation
P.O. Box 42503
RIYADH 11551 (Saudi Arabia)

Table 1. Usage of LAOs (Global usage: 3.2 million tons) in 2006.[1,2]

Chain length	Final products	Market share [%]
C4–C8	co-monomer for LLDPE and HDPE	56
C6–C10	plasticizer	8[a]
C8–C18	base stock and additives for synthetic lubricants (PAO)	11
C10–C18	intermediates for detergents (linear alcohols, LAB, LAS)	12
others	amines, mercaptanes, and so forth	16

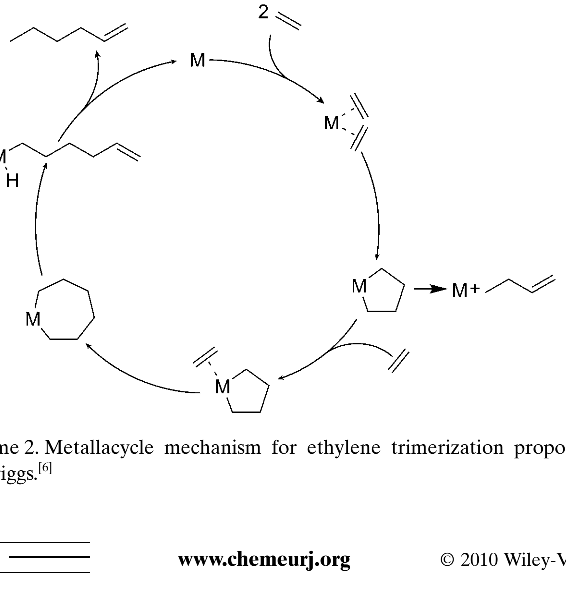
[a] Results from 1995.

hexene in the Middle East, Gulf States, and Asia is exceptionally tense as a result of the expanding polymer sector.

Metallacycles as Key Intermediates for Routes to α-Olefins

The various fields of application, market share, and the growth rate of each alpha-olefin segment, pose a big challenge to full range producers. Through the increasing demand for the high-value co-monomer fraction (C6 and C8), in recent years, many industrial and academic research groups have focused their interest on selective oligomerization, in particular the tri- and tetramerization of ethylene.[10]

The initial discovery of selective trimerization was made by Manyik, Walker, and Wilson of the Union Carbide Corporation, who filed the first patent in this field in 1967.[4] They observed the co-production of 1-hexene during the polymerization of ethylene with a modified heterogeneous Phillips catalyst, which led to a polymer with C4 branches. A few years later, they proposed, for the first time, metallacycles as key intermediates,[5] unlike the well-known insertion/β-elimination mechanism that led to a broad distribution (Schulz–Flory).[3,11] This mechanism was expanded by Briggs[6] in 1989 (Scheme 2) and is still accepted today and could be supported by several studies of the ethylene trimerization. Jolly and co-workers,[12] who published well-characterized chromacyclopentane and chromacycloheptane complexes, showed that the chromacycloheptane decomposes more readily under liberation of 1-hexene. More recently, Mashima et al.[13] succeeded to observe, by variable-temperature NMR spectroscopy, the metastable tantalacyclopentane during trimerization with a ligand-free, tantalum-based catalyst system, while Sita et al.[14] verified the existence of zirconacyclopentanes. Deuterium labeling studies conducted by Bercaw et al.[15,16] are consistent with the metallacyclic route, in which no H/D scrambling occurs in contrast to conventional oligomerization by an insertion/β-elimination mechanism.



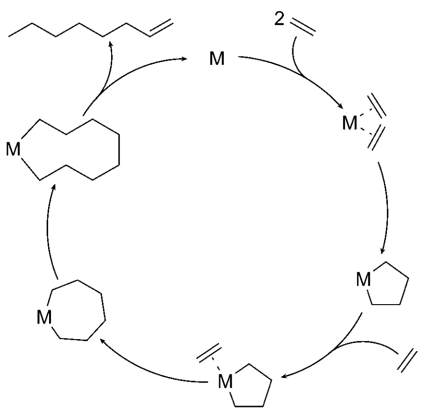
Scheme 2. Metallacycle mechanism for ethylene trimerization proposed by Briggs.[6]

In detail, the following elementary steps characterize the catalytic cycle for ethylene trimerization: First, two ethylene molecules coordinate at the catalyst complex, followed by an oxidative coupling reaction to form a metallacyclopentane. A third ethylene molecule coordinates and inserts into the ring to form a metallacycloheptane. This insertion must be faster than the elimination of 1-butene. Through β-H-elimination and a subsequent reductive C−H-elimination, 1-hexene is separated.[6] Herein, a stepwise mechanism involving a hexenyl-hydride or a 3,7-hydride shift in the metallacycloheptane is discussed.[17]

The main by-product, 1-butene, is presumably a result of early liberation of 1-butene from the metallacyclopentane. Through incorporation of 1-hexene or 1-butene molecules into the growing metallacycle, branched decenes can be formed as typical by-products.[17–19] According to these mechanistic suggestions, the difference in the relative stability of the formed five- and seven-membered rings with respect to elimination is the determining factor for the high selectivity to 1-hexene during ethylene trimerization. Various theoretical studies for Cr-,[20] Ta-,[21] and Ti-based[22–24] systems support the metallacyclic mechanism for the selective trimerization.

The most prominent, and one of the earliest, highly selective catalysts was developed by Chevron Phillips in the late 1980s,[25] yielding 1-hexene in an overall selectivity greater than 90%. After various improvements, the Chevron Phillips catalyst became the basis of the first commercialized trimerization technology, implemented in a 50000 tonnes per year plant in Qatar that went successfully on stream in 2003.

Following this concept, the selectivity towards 1-octene could be explained by further insertion of an ethylene molecule into the metallacycloheptane, leading to a metallacyclononane.[26,27] However, the required discrimination between seven- and nine-membered rings is currently discussed controversially and leads to some skepticism as to whether the selectivity to 1-octene can be reached by a mononuclear metallacyclic mechanism (Scheme 3).[21–23] If tetramerization is not explainable by the monometallic mechanism, alternatively a bimetallic mechanism based on two chromium centers, as discussed in the following section, appears conceivable.[28,29] Already Köhn stated in his highlight: “Although a monometallic mechanism is generally assumed, analogous bimetallic mechanisms based on two chromium(II) sites can also be formulated.”[28]



Scheme 3. Postulated metallacycle mechanism for ethylene tetramerization.[26,27]

Nevertheless, in 2004, a catalyst system for selective ethylene tetramerization was reported, using a modified bis(diarylphosphino)amine (PNP) chromium catalyst, which gives up to 68 wt % of 1-octene along with 1-hexene as the main by-product.[7]

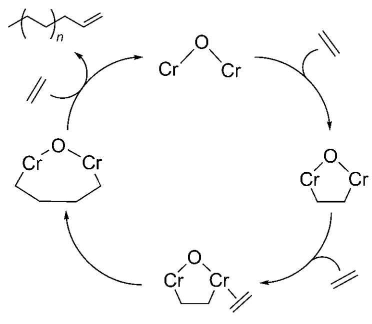
Other investigations also proposed a metallacyclic mechanism for the initiation step of the Phillips catalyst,[30] one of the most important heterogeneous catalysts for industrial polymerization. In some studies, the metallacyclic route is also suggested for unselective oligomerization reactions.[31–33] If that were true, clearly a very fine balance between the metallacyclic intermediates would be necessary to control selectivity in selective oligomerizations, which apparently has to be adjusted by proper tailoring of the ligand.

Binuclear Metallacycles as a Reason for Selectivity?

Whereas experimental evidence for a metallacycle at a mononuclear center already exists for the selective ethylene trimerization,[12,15] hints regarding selective tetramerization through a mononuclear ring mechanism are still missing and are highly controversial.[21,23]

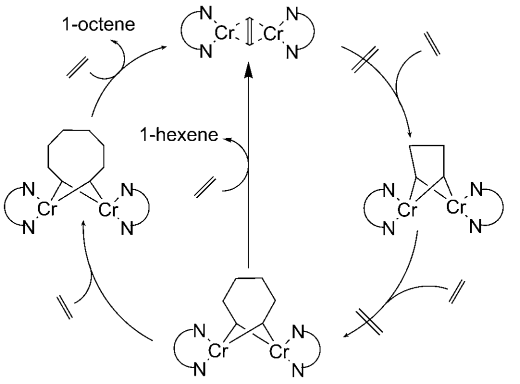
An alternative approach for the formation of 1-octene may be via a dimeric catalytic center, which means that between two chromium atoms, bridged by one or more ligands, a hydrocarbon cycle can be formed. However, up to now, no binuclear complexes were discussed seriously as essential requirements for the coupling reaction resulting in 1-octene, not to mention that no experimental results confirm this theory. It was only speculated that dimeric Cr^{II} species were responsible for cyclic C6 by-products formed during tetramerization by the Cr–PNP system.[26] Although bi- or multinuclear species for selective tetramerization were taken into account, no further detailed mechanistic concepts were proposed.[34]

This is somehow surprising because indications do exist for a binuclear mechanism in the Phillips and Union Carbide catalyst systems for ethylene polymerization, in which ethylene inserts between two bridged chromium atoms to form one metallacycle.[35] This postulated mechanism is supported by kinetic investigations[36] as well as density functional theory (DFT) studies (Scheme 4).[29]



Scheme 4. Binuclear mechanism in the Phillips and Union Carbide catalyst systems for ethylene polymerization.[36,37]

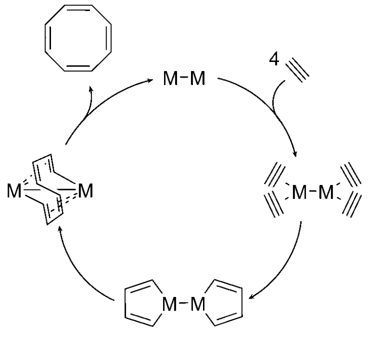
The conceivability of the concept of a binuclear center for selective ethylene oligomerization was supported by a synthesized complex consisting of two chromium centers bridged by a 1,4-butandiyl unit by Theopold et al.[37] Although the proposed catalytic cycle for selective oligomerization (Scheme 5) has not been realized so far, this example shows that two linked chromium atoms are able to build up a metallacycle.



Scheme 5. Unrealized catalytic cycle for selective tri- and tetramerization via a binuclear chromium complex proposed by Theopold and co-workers[37] (N∩N = 2,4-pentane-*N*,*N*′-bis(2,6-diisopropylphenylketiminate)).

Besides the possible parallelism to polymerization (Scheme 4), other structures in analogy to the metallacycloalkanes and related mechanisms should be discussed. For this purpose, metallacyclopentadienes, which are of high interest during alkyne oligomerization, seem to be most appropriate. Investigations into these interesting compounds led to highly efficient 1-alkyne tetramerization catalysts (TON: 1 000 000, selectivity: 96–97 %).[38]

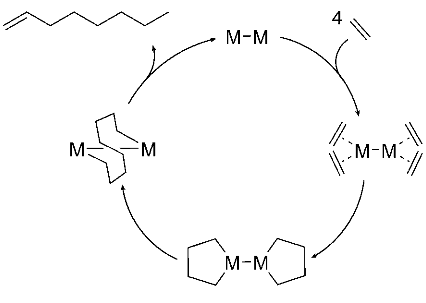
After an initial postulation of a mononuclear metallacycle mechanism for alkyne tetramerization,[39] Wilke et al. proposed that two metallacyclopentadienes can form a C8 cycle between the two metal centers, which can liberate cyclooctatetraene (Scheme 6).[40–42] Evidence for the proposed mechanism was found for nickel[40,42] and for chromium, in which even a binuclear intermediate was characterized by X-ray measurements.[41] Besides the alkyne tetramerization, cyclotrimerization of acetylene to benzene could also be realized by two bridged chromium centers.[43]



Scheme 6. Mechanism for the selective alkyne tetramerization to cyclooctatetraene proposed by Wilke and co-workers.[40–42]

After careful consideration, one comes to the conclusion that an analogous mechanism with coupling of two metallacyclopentanes at a binuclear center may unravel the mechanistic mystery of the selective ethylene tetramerization.[44]

This approach avoids the energetically improbable metallacyclononane,[21,23] which is postulated for the mononuclear mechanism.[26] Contrary to the catalytic cycle proposed by Theopold et al., which contains a binuclear center forming one ring (Scheme 5), this mechanism includes two C4 rings coupling with each other (Scheme 7). This has the advantage that the high selectivity towards 1-octene is explainable, because the discrimination between dimetallacyclodecene and larger rings is not required as it is for Theopold's one-ring mechanism. The latter can also lead to polyethylene as proposed for the Phillips and Union Carbide catalysts (Scheme 4). The mechanism for the reductive elimination of 1-octene from the C8-bridged dichromium species should not differ principally from that described for the mononuclear metallacycles.[16,28] The question regarding the oxidation state of chromium (Cr^0, Cr^I, Cr^{II}, etc.) during these conversions remains open.

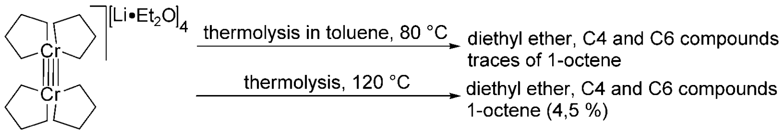


Scheme 7. Concept for a binuclear mechanism for the selective ethylene tetramerization.[44]

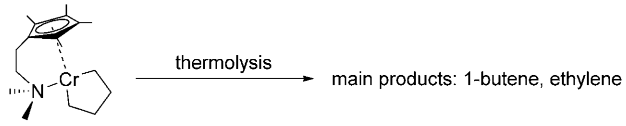
Experimental Background

An indication for the postulated approach is delivered by the thermolysis of defined binuclear chromium complexes with one or more metallacycles. For example, Kurras' tetralithiumtetrabutanediyldichromate[45] liberated 1-octene during thermolysis[46] (Scheme 8).

In contrast to this result, for a mononuclear chromacylopentane only the formation of 1-butene and ethylene instead of C8 was published (Scheme 9).[12] This suggests that a coupling of two C4 units to form one C8 ring is possible (Scheme 7).



Scheme 8. Thermolysis of the dinuclear model compound tetralithium tetrabutanediyldichromate results in 1-octene liberation.[46]



Scheme 9. Thermolysis of a mononuclear chromacylopentane results in 1-butene and ethylene liberation.[12]

For the systematic development of highly selective tetramerization catalysts, it is important to know how to encourage the chromium to form dimeric structures. For a multitude of chromium complexes, Cotton documented that the choice of the coordinated ligand influences strongly the chromium–chromium interaction.[47] Accordingly, with the number of bridge atoms, the equilibrium changes between mono- and binuclear complexes. This means that chromium, in the presence of a ligand of the type L = ABC, is more likely to form a dimeric chromium structure than in the presence of L = ABCD[47] (Scheme 10). In this context L = ABC represents a three-atom and L = ABCD a four-atom multidentate ligand.

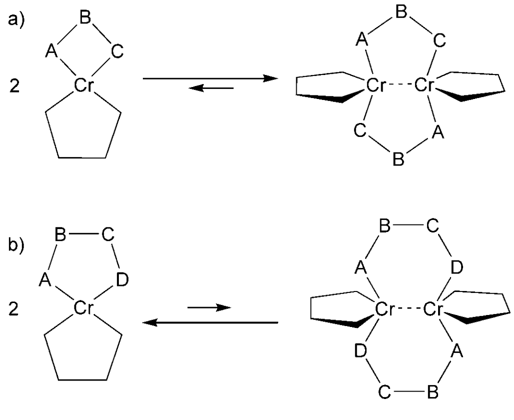
Examples for the formation of a mononuclear complex with ligands similar to L = ABCD, which are active as trimerization catalysts, are numerous. A possible recipe, for ex-

Scheme 10. Formation of a binuclear versus a mononuclear chromium complex as a function of the coordinated ligand.

ample, would be to coordinate the ^{MeO}PNP ligand[48] threefold to one chromium atom and to shape it like a pocket.[49] Also, the recently published isolated single-component trimerization catalyst based on a NPN ligand, with a multiatomic backbone, shows a mononuclear structure.[50] Even our newly discovered novel homogeneous catalyst for selective ethylene trimerization with its four-atomic aminophosphine ligand (PNPN$^-$ backbone) fits very well into this scheme of ligand characteristics for the selective trimerization.[51] This leads to the strong assumption that ligands of the type L = ABCD, which are able to form a mononuclear chromium complex, are required for selective trimerization.

In contrast, Sasol's PNP ligand,[7] resembling L = ABC, may afford a binuclear structure through its bridging nature.[52–54] In this context, the change in selectivity with the Cr–^{MeO}PNP system from C6 towards C8, using the Cr–PNP system may be explainable by the change from a mono- to a binuclear center.[55] Following this concept, the proposed binuclear mechanism for the selective tetramerization is conceivable, although strong experimental evidence is still missing.

Depending on the number of atoms in the ligands, the equilibrium changes between mono- and binuclear complexes (L = ABC represents three-atom and L = ABCD four-atom ligands). This means that chromium, in the presence of a ligand of the type L = ABC, is more likely to form dimeric chromium structures with bridging L = ABC (Scheme 11a) than in the presence of chelating L = ABCD (Scheme 11b). Generally, this is well documented by Cotton and Walter for many dinuclear chromium compounds.[47] The existence of a metal–metal bond between the two chromium atoms is not essential to this concept, but will help to form dinuclear complexes.



Scheme 11. Equilibrium changes between mono- and binuclear chromium complexes.

This is reflected by additional examples for complexes with a quadruple bond between the chromium atoms from our own group,[55] for example, the above-mentioned tetralithium tetrabutanediyldichromate[45] with tetrabutanediyl units $-CH_2-CH_2-CH_2-CH_2-$ (as L = ABCD chelating) and a dichromium tetrakis(dimethylphosphoniumbismethylide), $[Cr_2\{(CH_2)_2PMe_2\}_4]$,[56] with dimethylphosphoniumbismethylide units $[(CH_2)_2PMe_2]^-$ (as L = ABC bridging) ligands.[57,58] This quite general rule has some exceptions, as shown for tetraallyldichromium $[Cr_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-}\eta^3\text{-}C_3H_5)_2]$[59] with allyl groups (as L = ABC bridging as well as chelating).[60,61] Even most of the recently described dinuclear chromium complexes with a quintuple bond follow, in principle, this concept of the stabilization of dinuclear complexes by L = ABC.[62–64]

Sasol's PNP ligands,[7] as typical L = ABC ligands, are the best for selective tetramerization but not totally exclusive. A very small number of exceptions exist with L = ABCD, giving some 1-octene selectivity like PNNP[7] and PCCP.[7,65]

For the highly selective oligomerization catalysts, it is important to know, in detail, how the ligands influence the chromium either to form dimeric structures (with or without chromium–chromium interactions) or alternatively monomeric structures.

Summary and Outlook

We attribute the differences of selectivity between ethylene tri- and tetramerization systems to the capability of the tetramerization ligands to form binuclear complexes that subsequently build up two metallacyclopentanes in one moiety. These two C4 units are then coupled to form 1-octene selectively. This approach avoids the energetically improbable metallacyclononane, which is postulated for the mononuclear mechanism. In general, for trimerization, a ligand capable of enclosing the mononuclear active center is necessary. In turn, the ability of the PNP ligand to bridge two metal centers supports the herein proposed binuclear mechanism for ethylene tetramerization.

It is evident that without further detailed characterization of catalytically active tetramerization species and their kinetics, a basal proof of this theory is not possible. Moreover, the influence of chromium oxidation state, aluminum activator, and solvent on the selectivity of the oligomerization reaction has to be investigated in more detail. Therefore, further effort must be made to achieve this.[66]

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[66] Note added in proof (June 9, 2010): We thankfully became aware that Professor Sandro Gambarotta et al. have found experimental indications for 1-octene selectivity induced by dinuclear Cr complexes. Sandro Gambarotta, private communication, June 2010.