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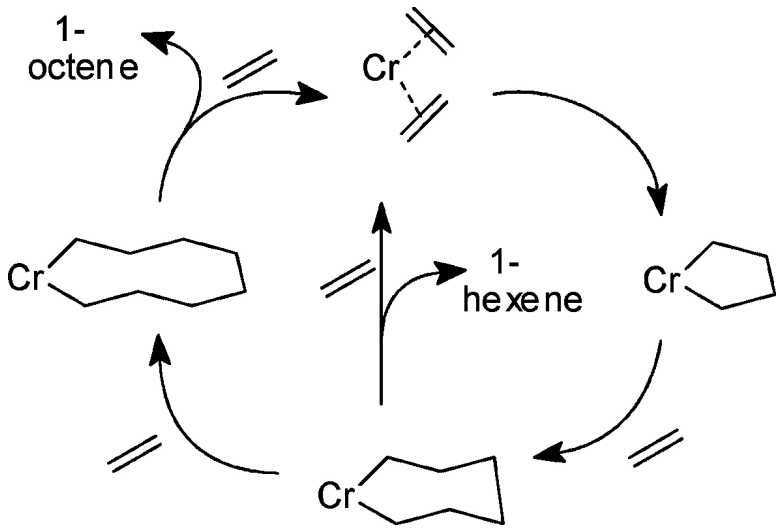

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Mechanistic Investigations of the Ethylene Tetramerisation Reaction

Matthew J. Overett,*,† Kevin Blann,† Annette Bollmann,† John T. Dixon,† Daleen Haasbroek,† Esna Killian,† Hulisani Maumela,† David S. McGuinness,‡ and David H. Morgan†

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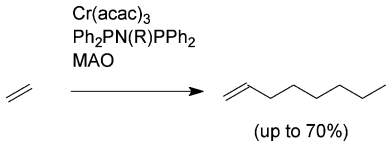
Abstract: The unprecedented selective tetramerisation of ethylene to 1-octene was recently reported. In the present study various mechanistic aspects of this novel transformation were investigated. The unusually high 1-octene selectivity in chromium-catalyzed ethylene tetramerisation reactions is caused by the unique extended metallacyclic mechanism in operation. Both 1-octene and higher 1-alkenes are formed by further ethylene insertion into a metallacycloheptane intermediate, whereas 1-hexene is formed by elimination from this species as in other reported trimerisation reactions. This is supported by deuterium labeling studies, analysis of the molar distribution of 1-alkene products, and identification of secondary co-oligomerization reaction products. In addition, the formation of two C_6 cyclic products, methylenecyclopentane and methylcyclopentane, is discussed, and a bimetallic disproportionation mechanism to account for the available data is proposed.

Background

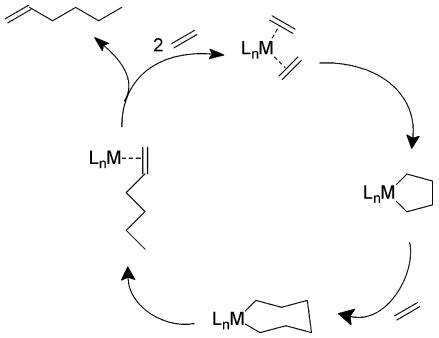
Commercial processes for the production of linear alpha-olefins (LAOs) typically rely on nonselective ethylene oligomerization reactions.[1] More selective processes for the production of the higher-value LAOs are highly desirable from an industrial viewpoint. The selective trimerisation of ethylene to 1-hexene is a well-known technology.[2] However, until recently, a corresponding selective tetramerisation reaction of ethylene to give 1-octene was unknown. We recently reported the first catalyst capable of this transformation with selectivities of up to 70% 1-octene.[3] The active catalyst is typically generated in situ by the addition of an aluminoxane (e.g., methylaluminoxane) to a mixture of a Cr(III) source and a bidentate diphosphinoamine ligand (Scheme 1).

The observed selectivity in ethylene trimerisation reactions is a consequence of the unusual metallacyclic mechanism in operation (Scheme 2).[4] Oxidative coupling of two ethylene molecules with the active catalytic metal gives a metallacyclopentane intermediate. The geometrical constraints of this species limit interaction of the β-hydrogens with the metal, thus preventing the elimination of 1-butene. Coordination and subsequent insertion of another ethylene is thus facilitated, and the resultant metallacycloheptane is sufficiently flexible for β-hydride transfer and reductive elimination of 1-hexene. Until recently, it was thought unlikely that further ethylene insertion to give a metallacyclononane could compete with 1-hexene elimination or that selective elimination of 1-octene from such a species would take place.[5]

Scheme 1. First Selective Ethylene Tetramerisation Reaction



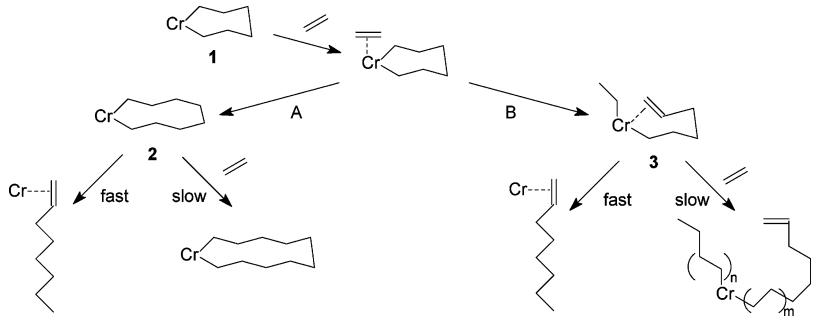
Scheme 2. Catalytic Cycle for the Trimerisation of Ethylene



† Sasol Technology.
‡ Sasol Technology, U.K.

(1) Alpha Olefins (02/03-4), PERP report, Nextant Chem Systems.
(2) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, *689*, 3641.
(3) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712.
(4) (a) Briggs, J. R. *J. Chem. Soc., Chem. Commun*. **1989**, 674. (b) Emrich, R.; Heinemann, O.; Jolly, P. W.; Kruger, C.; G. P. J. Verhovnik, G. P. J. *Organometallics* **1997**, *16*, 1511. (c) Meijboom, N.; Schaveien, C.; Orpen, A. G., *Organometallics* **1990**, *9*, 774. (d) Agapie, T.; Schofer, S. J.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc*, **2004**, *125*, 1304.
(5) (a) Yu, Z.-X.; Houk, K. N. *Angew. Chem., Int. Ed.* **2003**, *42*, 808. (b) Blok, A. N. J.; Budzelaar, P. H. M.; Gal, A. W. *Organometallics* **2003**, *22*, 2564.

Scheme 3. Postulated Mechanisms for the Formation of 1-Octene



Scheme 4. Postulated Mechanisms for the Formation of Methylcyclopentane and Methylenecyclopentane

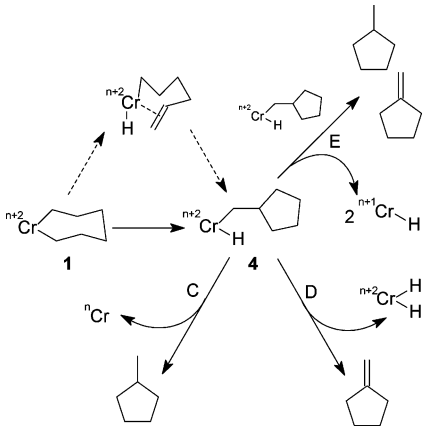


Table 1. Rate and Selectivity for an Ethylene Tetramerisation Reaction

Cr (μmol)	Al:Cr	temp (°C)	press (bar)	time (min)	activity (g/g Cr)	C_4 (%)	1-hexene (%)	C_6 cyclics (%)	1-octene (%)	C_{10}–C_{14} (%)	PE (%)
5	500	60	45	45	1.2×10^6	0.8	13.8	4.1	66.3	10.4	0.3

The discovery of the selective ethylene tetramerisation reaction is thus of profound interest from a mechanistic point of view. An understanding of its mechanism may lead to the improvement of 1-octene selectivity and to the design of new tetramerisation catalysts. We report here the results of a study that confirms the intermediacy of metallacyclic species in the formation of 1-octene and allows us to propose a mechanism that accounts for the primary and secondary products formed in a typical tetramerisation reaction.

Analysis of an Ethylene Tetramerisation Product Mixture

An ethylene tetramerisation reaction was performed using a catalyst generated in situ from $Cr(acac)_3$, $Ph_2PN(^iPr)PPh_2$, and MMAO.[3] The product mixture was then analyzed by gas chromatography flame-ionization detection (GC-FID) and GC mass spectrometry (GC-MS) (Table 1). Although selectivities to 1-octene of close to 70 mass % can be achieved, significant quantities of other products are also formed, including 1-butene, 1-hexene, methylcyclopentane, methylenecyclopentane, 2-propenylcyclopentane, *n*-propylcyclopentane, $C_{10}-C_{36}+$ 1-alkenes, $C_4-C_{20}+$ *n*-alkanes, and a complex mixture of C_{10}, C_{12}, and C_{14} secondary oligomerization products. Detailed product identification is given in the Supporting Information. A complete mechanism for the ethylene tetramerisation reaction must thus account for the formation of all these products.

Mechanistic Proposals

We have previously shown that ethylene tetramerisation and trimerisation reactions with Cr/diphosphine/aluminoxane catalysts are closely related and that the selectivity to 1-hexene or 1-octene may be controlled by subtle ligand modifications through both steric and coordinative effects.[6] It thus seems reasonable that a common metallacycloheptane intermediate[4] (**1**, Scheme 3), proven for related Cr/diphosphine-catalyzed trimerisation reactions,[4d] is involved in the pathways to both 1-hexene and 1-octene. Two proposed mechanisms for the formation of 1-octene may thus be considered (Scheme 3). In the first possibility, a further coordination and insertion of ethylene into the metallacycloheptane intermediate **1** (pathway A) is followed by 1-octene elimination from the resultant metallacyclononane species (**2**). This elimination, either via formal β-hydride transfer to the metal[4a] or a concerted metal assisted hydride transfer,[5a,7] is facile relative to further insertion of ethylene to give higher metallacycles. In the second possibility, β-hydride transfer from the metallacycloheptane to a coordinated ethylene[8] (or to the metal with subsequent ethylene insertion into Cr−H) gives a hexenyl ethyl Cr species (**3**), and reductive elimination to give 1-octene is facile relative to linear chain growth of this species (pathway B).

Methylcyclopentane and methylenecyclopentane are typically formed in a ratio of 1:1 and are the third most abundant products formed after 1-octene and 1-hexene. The mechanism of formation of these cyclic products is thus of interest, particularly as methylenecyclopentane is not a stoichiometric oligomer of ethylene. We propose that rearrangement of **1** to the Cr cyclopentylmethyl hydride species **4** competes with 1-hexene elimination and ethylene insertion (Scheme 4). This may take place via a formal β-hydride transfer to metal, with a subsequent cyclization of the 5-hexenyl moiety analogous to that in the cyclopolymerization of 1,5-hexadiene to form poly(methylene-1,3-cyclopentane).[9] Alternatively, the rearrangement may take place in a single concerted step. A cyclopentylmethyl intermediate species has also been invoked to account for the zirconium-catalyzed oligomerization of ethylene to methylenecyclo-

(6) (a) Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J. *Chem. Commun.* **2005**, 620. (b) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S. *Chem. Commun.* **2005**, 622.
(7) (a) Janse van Rensberg, W. J.; Grové, C.; Steynberg, J. P.; Stark, K. B.; Huyser, J. J.; Steynberg, P. J. *Organometallics* **2004**, *23*, 1207. (b) Tobisch S., Ziegler, T. *Organometallics* **2003**, *22*, 5392.
(8) Manyik, R. M.; Walker, W. E.; Wilson, T. P. *J. Catal.* **1977**, *47*, 197.
(9) (a) Marvel, C. S.; Stille J. K. *J. Am. Chem. Soc.* **1958**, *80*, 1740. (b) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953. (c) Cavallo, L.; Guerra, G.; Corradini, P.; Resconi, L.; Waymouth, R. M. *Macromolecules* **1993**, *26*, 260.

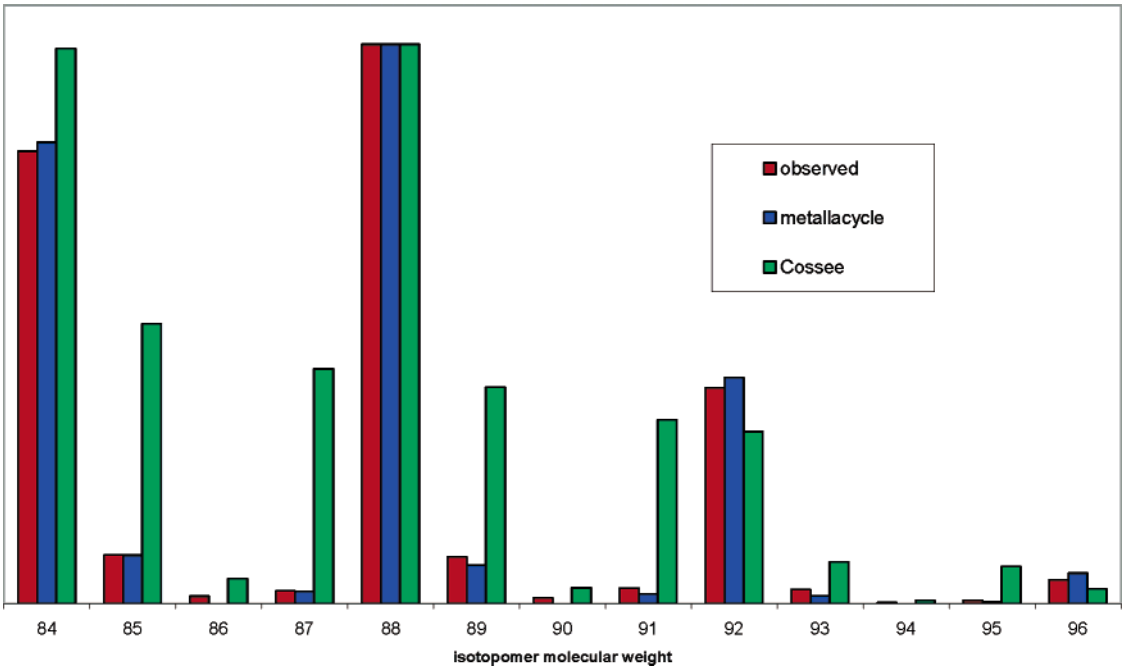


Figure 1. Observed 1-hexene isotopomer distribution against predicted distributions for the metallacycle and Cossee−Arlman mechanisms.

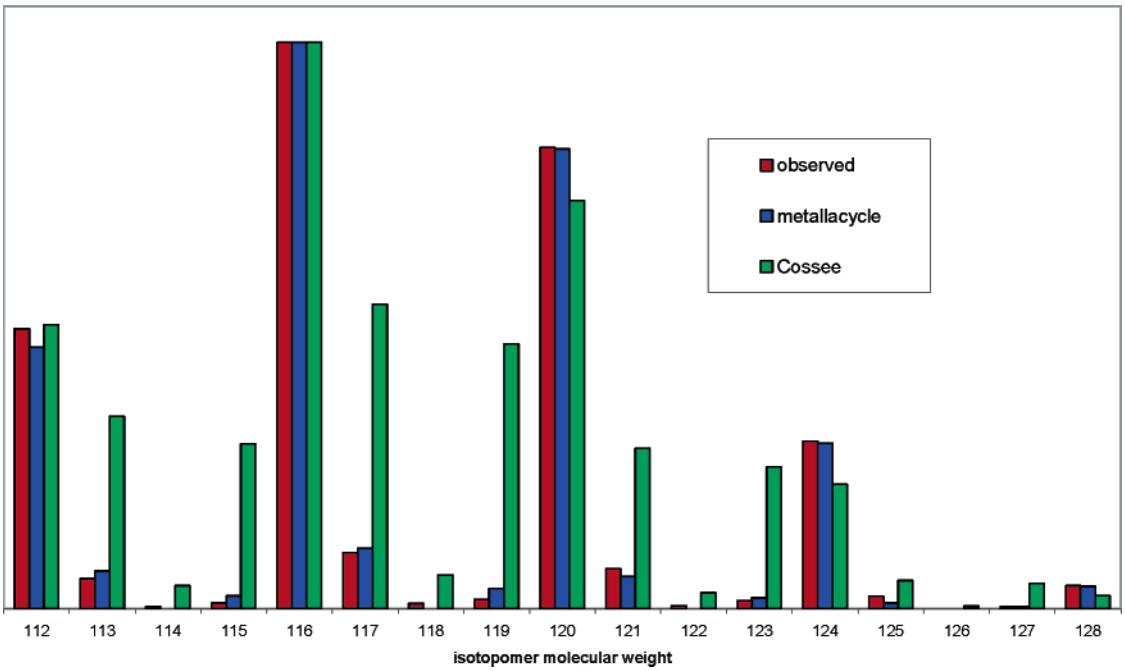


Figure 2. Observed 1-octene isotopomer distribution against predicted distributions for the metallacycle and Cossee−Arlman mechanisms.

pentane.[10] From this intermediate, two alternatives may be considered (Scheme 4). First, the Cr cyclopentylmethyl hydride species undergoes two competitive reactions with similar rates, namely, reductive elimination to give methylcyclopentane and β-hydride elimination to give methylenecyclopentane (pathways C and D). Second, however, the equimolar formation of methylcyclopentane and methylenecyclopentane under a variety of reaction conditions is suggestive of a disproportionation process (pathway E). For example, it is known that disproportionation of cyclopentylmethyl free radicals yields these two cyclic products.[11]

(10) Wang, M.; Shen, Y.; Qian, M.; Li, R.; He, R. *J. Organomet. Chem.* **2000**, *599*, 143.

Deuterium-Labeling Studies

The metallacycle mechanism for ethylene trimerisation was for the first time conclusively demonstrated by Bercaw and co-workers using a series of experiments with deuterated and partially deuterated ethylene.[4d] For example, a 1:1 mixture of C_2H_4 and C_2D_4 was trimerised using the Cr/(*o*-MeOPh)$_2$PN(Me)P(*o*-MeOPh)$_2$/MAO catalyst system first described by Wass and co-workers.[12] The resultant 1-hexene isotopomer distribution

(11) (a) Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 4395. (b) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843. (c) Foster, D. F.; Glidewell, C.; Cole-Hamilton, D. J.; Povey, I. M.; Hoare, R. D.; Pemble, M. E. *J. Cryst. Growth* **1994**, *145*, 104. (d) Foster, D. F.; Bell, W.; Stevenson, J.; Cole-Hamilton, D. J.; Hails, J. E. *J. Cryst. Growth* **1994**, *145*, 520.

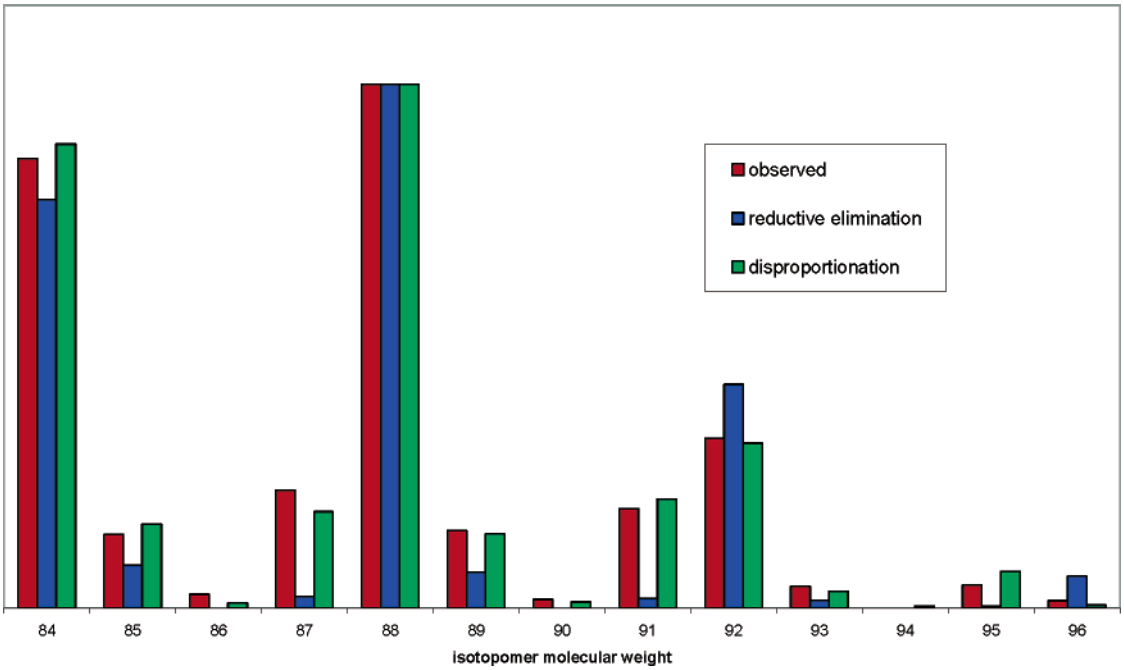


Figure 3. Observed methylcyclopentane isotopomer distribution against predicted distributions for the metal-mediated reductive elimination and dispropotionation mechanisms

of a 1:3:3:1 ratio of C_6H_{12}, $C_6H_8D_4$, $C_6H_4D_8$, and C_6D_{12} was consistent with a metallacyclic mechanism involving no H/D scrambling.

Similarly, in the present study, a mixture of C_2H_4 and C_2D_4 was exposed to a tetramerisation catalyst generated in situ by the combination of $Cr(acac)_3$, $Ph_2PN(^iPr)PPh_2$, and an aluminoxane cocatalyst. The products of this reaction were then analyzed by GC-FID and GC-MS. 1-Octene, 1-hexene, and methylcyclopentane were obtained in sufficient amounts to obtain quantitative isotopomer distributions in the GC-MS analysis. The ratio of C_2H_4 to C_2D_4 incorporated in each product may be calculated, independent of mechanism, from the isotopomer distribution. By use of this value, and a first order correction for the natural abundance of deuterium in hydrogen (0.79% D) and the imperfect labeling of the deuterated ethylene (0.5% H), theoretical isotopomer distributions for 1-octene and 1-hexene produced by both the proposed metallacyclic mechanism and the Cossee−Arlman linear chain growth mechanism[13] may be calculated.[14] The correlation of the observed isotopomer distribution with the predicted distribution for the metallacyclic mechanism is excellent for both these products (Figures 1 and 2). For 1-octene formation, however, this experiment does not distinguish between the two mechanisms in Scheme 3, as neither mechanism involves H/D scrambling. The formation of 1-hexene and 1-octene via the Cossee−Arlman mechanism, as expected, is however excluded.

It is worth noting that the ratio of standard ethylene to deuterated ethylene incorporated (x) differs for the C_6 and C_8 products. Whereas x was determined to be the same within experimental error for 1-hexene and methylcyclopentane (2.5 and 2.4, respectively), the value of x for 1-octene was significantly lower (1.9). This implies that secondary kinetic isotope effects (higher reactivity of standard ethylene vs deuterated ethylene) are in operation. These kinetic isotope effects are expected to be higher for the rate-determining step in the reaction. Thus the greater preference for standard ethylene incorporation in the C_6 products suggests that the rate-determining step is the oxidative coupling of the first two ethylenes to form the metallacyclopentane intermediate and not the subsequent ethylene insertions to give metallacycloheptane and metallacyclononane species. This agrees with other studies that have used the second order dependence of rate on ethylene concentration in trimerisation reactions to deduce that formation of the metallacyclopentane is rate determining.[8]

The formation of methylcyclopentane by reductive elimination of the Cr cyclopentylmethyl hydride species **4** (pathway C, Scheme 4) involves no H/D scrambling, and thus the isotopomer distribution should follow the same pattern as for 1-hexene. On the other hand, a disproportionation mechanism of cyclic formation does involve H/D scrambling in the disproportionation step, and this should allow distinction between the two mechanisms by analysis of the isotopomer distributions of this C_6 cyclic product. It can clearly be seen that the observed distribution does not correlate well with the predicted distribution for a mechanism, such as reductive elimination, where no scrambling is involved (Figure 3).

The calculation of a theoretical distribution for the disproportionation mechanism is complicated by two kinetic isotope effects involved, namely, for the β-hydride transfer to the metal (k_1) and for the hydrogen transfer of the disproportionation step itself (k_2).[14] The values of k_1 (equivalent to k_H/k_D if irreversibility is assumed) and k_2 are unknown. However, by application of a least-squares optimization of the theoretical distribution against the observed distribution, with k_1 and k_2 as variables, a good fit between the theoretical and observed distributions is obtained

(12) Carter, C.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858.
(13) (a) Cossee, P. *J. Catal.* **1964**, *3*, 80. (b) Arlman, E. J.; Cossee, P. *J. Catal.* **1964**, *3*, 99.
(14) Details of the mathematical derivations are given in the Supporting Information.

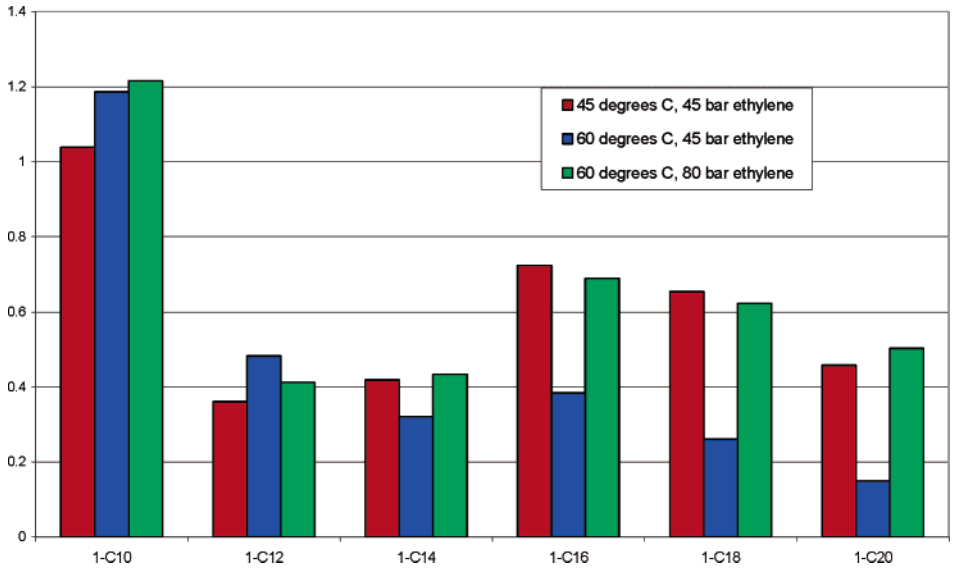


Figure 4. Molar amounts of higher 1-alkenes as a percentage of 1-octene formed.

(Figure 3) and reasonable values of k_1 and k_2 are deduced ($k_1 = 3.0$; $k_2 = 4.9$). By comparison, k_H/k_D (also assuming irreversibility) was determined as 2.4 for the β-hydride transfer from metallacycloheptane at room temperature in a closely related trimerisation system.[4d]

Analysis of C_{10}+ 1-Alkenes

Tetramerisation reactions typically produce a full range of higher 1-alkenes, albeit as minor products. These oligomers may be formed by extension of a metallacyclononane through further insertions of ethylene or by a different, linear chain growth, catalytic species. In the former case, the distribution of 1-alkenes will depend on the relative lability of each extended metallacycle vs the probability of further insertion. In the latter case, a Schulz−Flory distribution, typical of linear chain growth mechanisms, should be apparent.

A series of ethylene tetramerisation reactions were performed under three different temperature and pressure conditions (45 bar ethylene, 45 °C; 45 bar, 60 °C; 80 bar, 60 °C). The relative molar amounts of all linear 1-alkenes above C_8 were carefully determined by GC-FID and scaled as a percentage of the molar amount of 1-octene produced (Figure 4). The resulting distribution is inconsistent with a linear chain growth mechanism, where the molar amount of C_{n+2} 1-alkene cannot exceed that of C_n 1-alkene. This is especially clear under conditions of high ethylene solubility (45 bar ethylene, 45 °C; 80 bar, 60 °C reactions), where 1-hexadecene exceeds 1-tetradecene, which in turn equals or exceeds 1-dodecene.

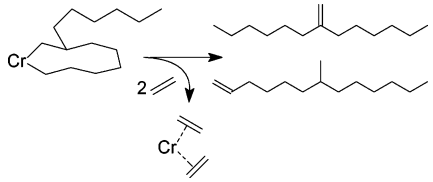
The observed distribution is consistent with an extended metallacycle mechanism, where subtle variations in conformation confer greater stability against 1-alkene elimination on some metallacycles than others. By assuming no difference in the rate of ethylene insertion, the relative stabilities of a $Cr-C_n$ metallacycle may be approximated by the 1-alkene molar ratio of $\sum C_x$: C_n (for all $x > n$). By this measure, the $Cr-C_{12}$ and $Cr-C_{14}$ metallacycles are the most stable of the metallacycles $Cr-C_n$ ($n \geq 8$) Similarly, the metallacyclononane($Cr-C_8$) is the least stable of the large metallacycles, which is the reason for the high selectivity to 1-octene.

These results provide evidence in support of an extended metallacycle mechanism for the formation of all 1-alkenes in the tetramerisation reaction. The observed selectivities are governed by the relative rates of 1-alkene elimination vs further ethylene insertion. Clearly, a key role of the ligand in tetramerisation is to stabilize the metallacycloheptane but not the metallacyclononane intermediate against 1-alkene elimination.

Analysis of Secondary (C_{10}, C_{12}, and C_{14}) Products

Tetramerisation reactions produce a complex mixture of oligomers from co-trimerisation and co-tetramerisation of ethylene with 1-hexene and 1-octene. The amount of these products formed is proportional to the productivity of the reaction, i.e., the ratio of 1-hexene and 1-octene to available ethylene. Further proof that these products are not formed directly from ethylene is obtained by spiking a tetramerisation reaction with 1-pentene. In this case, C_9 co-trimerisation and C_{11} co-tetramerisation products are also formed. However, only trace quantities of 1-nonene and 1-undecene are formed, which further demonstrates that the substantially more abundant 1-decene, 1-dodecene, and 1-tetradecene are not formed as secondary products.

Scheme 5. Proposed Formation of 7-Methylenetridecane and 7-Methyl-1-tridecene



Analysis of the structures of these co-oligomerization products gives further insight into the mechanism of tetramerisation. Of particular interest are the branched C_{14} products, as these can only be formed by co-tetramerisation reactions. Of the two most abundant C_{14} oligomers (ca. 70% of the secondary C_{14} products), one was positively identified as 7-methylenetridecane. Upon hydrogenation, these two oligomers were converted to a single product, 7-methyltridecane, thereby demonstrating that they are

isomers with the same skeletal structure.[15] It may thus reasonably be postulated that the second isomer is 7-methyl-1-tridecene. Formation of these co-tetramers is readily rationalized from a substituted metallacyclononane intermediate as shown in Scheme 5. The preference for this mode of co-oligomerization (1,2-insertion of alkene adjacent to metal) has previously been reported for trimerisation reactions, where 5-methyl-1-nonene was found to be the most abundant co-trimer.[16] The hydrogenated C_{14} region contains only two peaks apart from 7-methyltridecane and tetradecane. While these were not identified, hydrogenation of the four C_{14} oligomers deriving from the other two possible modes of 1-octene incorporation into a metallacyclononane (4- and 5-hexylmetallacyclononane) would be expected to give two branched alkanes (6-ethyldodecane and 5-propylundecane).

The predominance of 7-methylene-tridecane and 7-methyl-1-tridecene as secondary C_{14} products cannot plausibly be explained by the mechanism involving a β-hydride transfer from metallacycloheptane to a coordinated alkene (pathway B, Scheme 3). While in principle these products are accessible via such a pathway, they would be derived from very different modes of incorporation, and 5-propyl-1-undecene and 1-tetradecene (as a secondary product) would be expected to be more abundant than 7-methylene-tridecane and 7-methyl-1-tridecene, respectively.[15]

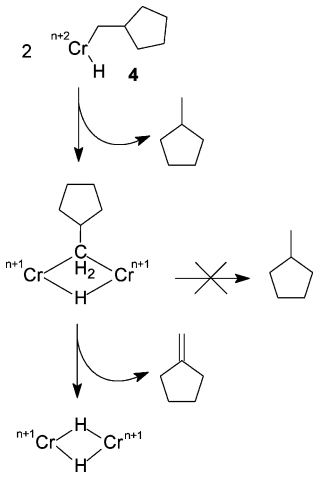
As with the C_{14} oligomers, the C_{10} and C_{12} secondary products that could be identified are expected co-oligomerization products deriving from metallacyclic catalytic intermediates with hexene or octene incorporation.[15]

Formation of the Cyclic Products

The 1:1 ratio of methylcyclopentane and methylenecyclopentane formed under a variety of reaction conditions is plausibly explained by a disproportionation process but not easily rationalized by competitive reductive elimination and β-hydride elimination reactions from a common intermediate. In addition, the deuterium labeling results are more consistent with a disproportionation mechanism.

The formation of methylcyclopentane and methylenecyclopentane from cyclopentylmethyl or 5-hexen-1-yl free radicals is well established.[11] With this in mind, homolytic Cr-alkyl cleavage of **4** (Scheme 4) may be envisioned as the origin of cyclopentylmethyl radicals. Of relevance in this regard is chemistry reported by Theopold and co-workers in which reaction of the Cr(III) compound [Cp*Cr(THF)$(bz)_2$] with 2,2′-bipyridyl gave the unexpected Cr(II) product [Cp*Cr(bipy)(bz)].[17] A homolytic reduction yielding a benzyl radical byproduct was hypothesized. However, in addition to disproportionation, free cyclopentylmethyl radicals also couple to give 1,2-dicyclopentylethane and abstract H• from other available sources, such as the solvent.[11a] To test for the intermediacy of free radicals, comparison of tetramerisation product mixtures with an authentic sample of 1,2-dicyclopentylethane[18] by GC-MS analysis was made. This indicated the absence of the coupled product. Furthermore, tetramerisation reactions conducted in the presence of an excellent H• donor such as triphenylmethane still produce 1:1 ratios of the C_6 cyclic products, where more methylcyclopentane may have been expected. These results strongly suggest that free radicals are not involved.

Scheme 6. Postulated Binuclear Mechanism for the Formation of the C_6 Cyclics



The mechanism of cyclic formation thus remains unproven; however, a recent report by Theopold and co-workers suggests a plausible answer. Reaction of the Cr(III) compound [nacnacCr$(CH_2SiMe_3)_2$] (nacnac = *N*,*N*′-bis(2,6-dimethylphenyl)-2,4-pentanediiminato) with H_2 gives the Cr(II) alkyl hydride species [(nacnacCr)$_2$(μ-CH_2SiMe_3)(μ-H)].[19] This transformation proceeds by hydrogenolysis of one alkyl group followed by a binuclear reductive elimination to give $SiMe_4$ and the above binuclear Cr(II) complex, which is remarkably stable against alkane elimination. A similar reaction occurred in attempts to prepare [nacnacCrEt_2]. The isolated species was found to be [(nacnacCr)$_2$(μ-H)$_2$]. This was reportedly formed by successive β-hydride elimination of the diethyl complex, binuclear reductive elimination of ethane, presumably yielding [(nacnacCr)$_2$(μ-Et)(μ-H)], and a second β-hydride elimination to give the Cr(II) hydride dimer. The analogy of this chemistry to the proposed Cr cyclopentylmethyl hydride species **4** (Scheme 4) is direct and allows the proposal of a bimetallic disproportionation mechanism (Scheme 6) to account for the equimolar formation of the C_6 cyclic products, the results of the deuterium labeling studies, and the absence of free radical byproducts in tetramerisation product mixtures.

It should be noted that this proposed pathway leaves the catalytic chromium in a formal Cr^{n+1} oxidation state, assuming a Cr^n/Cr^{n+2} catalytic cycle for the formation of 1-hexene and 1-octene. The active catalyst thus needs to be "regenerated" in some process which restores the Cr^n/Cr^{n+2} oxidation state and the overall hydrogen balance of the catalytic reaction. One possibility is the ethylene mediated disproportionation of the Cr^{n+1} hydride dimer into Cr^{n+2} dihydride and Cr^n bis(ethylene) mononuclear species; however this remains just one of several possibilities.

(15) See Supporting Information for chromatograms of the C14 region (unhydrogenated and hydrogenated) and further mechanistic analysis of the observed secondary products.
(16) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Organometallics* **2002**, *21*, 5122.
(17) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738.
(18) Zelinsky, N. D.; Michlina, S. E.; Eventowa, M. S. *Chem. Ber.* **1933**, *66*, 1422.
(19) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Golen, J. A.; Rheingold, A. L.; Theopold, K. H. *Chem. Commun.* **2003**, 1164.

Table 2. Effect of Temperature and Pressure on Formation of Higher 1-Alkenes

temp (°C)	press (bar)	1-hexene (mass %)	1-octene (mass %)	1-decene (molar % of 1-octene)	1-C_{12} (molar % of 1-octene)	1-C_{14} (molar % of 1-octene)	1-C_{16} (molar % of 1-octene)	1-C_{18} (molar % of 1-octene)	1-C_{20} (molar % of 1-octene)
45	45	11.5	68.8	1.04	0.36	0.42	0.72	0.65	0.46
60	45	13.7	66.4	1.19	0.48	0.32	0.48	0.26	0.15
60	80	10.7	69.9	1.22	0.41	0.43	0.69	0.62	0.50

Table 3. Ethylene Tetramerisation in the Presence of 1-Pentene

activity (g/g Cr)	1-hexene (%)	C_6 cyclics (%)	1-octene (%)	C_9 (%)	C_{10} (%)	C_{11} (%)	C_{12} (%)	C_{14} (%)	P.E. (%)
1.2×10^5	15.8	4.3	67.3	1.4	1.7	1.9	3.1	2.1	0.2

A complete correspondence of the mechanism of cyclic formation with the chemistry reported by Theopold and coworkers would imply that the active tetramerisation catalyst adopts a Cr^{I}/Cr^{III} catalytic cycle with Cr^{II} intermediates involved in the formation of the cyclics. However, elucidation of the exact structures and oxidation states of the active catalytic species is not in the ambit of this study.

Conclusions

A variety of evidence has been obtained which supports an extended metallacyclic mechanism for the formation of all the 1-alkenes in ethylene tetramerisation reactions. The unique feature of the tetramerisation catalyst is the enhanced stability (relative to trimerisation catalysts) against 1-hexene elimination from the metallacycloheptane intermediate. This stability allows competitive reactions leading to the formation of 1-octene (ethylene insertion) and cyclic products (rearrangement and disproportionation). The high selectivity to 1-octene is thus a consequence of both the relative stability of the metallacycloheptane intermediate and the instability of the metallacyclononane species. Clearly, these differences with respect to ethylene trimerisation systems must be caused by subtle ligand-mediated electronic and steric effects. Molecular modeling studies into the fundamental origins of the observed selectivities in tetramerisation reactions are underway.

Experimental Section

General Considerations. Methylcyclohexane, 1,3-diisopropylbenzene, and 1-pentene were purified by passage through a column of activated alumina. 1,2-Dicyclopentylethane and $Ph_2PN(^iPr)PPh_2$ were prepared by literature procedures.[18,20] MMAO-3A (in heptanes, methylaluminoxane with ca. 30% replacement of methyl groups by isobutyl groups) and MMAO-12 (in toluene, c.a. 5% replacement of methyl groups by *n*-octyl groups) were obtained from Akzo-Nobel. Ethylene-d_4 was obtained from Sigma Aldrich. GC analyses were conducted on instruments equipped with a PONA 50 m × 0.5 μm × 0.2 mm inside diameter (i.d.) column and either electron impact ionization mass spectrometry (GC-MS) or FID. Identification of the components was done with a combination of the Wiley275 library, boiling point information, interpretation of the mass spectra with first principles, and elution order.

Ethylene Tetramerisation Reaction with $Cr(acac)_3/Ph_2PN(^iPr)PPh_2$/MMAO-3A. MMAO-3A (2.5 mmol Al) was added to a stirred mixture of $Cr(acac)_3$ (1.75 mg, 5.0 μmol) and $Ph_2PN(^iPr)PPh_2$ (3.2 mg, 7.5 μmol) in methylcyclohexane (5 mL). This solution was immediately added to an autoclave containing methylcyclohexane (195 mL) at 60 °C and pressurized to 45 bar with ethylene. A gas-entraining stirrer at 1000 rpm was used to obtain thorough mixing. The reaction mixture was maintained at 60 °C, and ethylene was fed on demand. After 45 min, the ethylene supply was terminated and the reaction mixture was cooled to 10 °C and depressurized. The liquid products were analyzed by GC-FID to determine selectivities and the solids were recovered by filtration. The mass of the product formed was 312 g. After filtration through a plug of silica, the light products and solvent were removed in vacuo into a trap at −196 °C. The two fractions thus obtained (concentrated in light products and heavy products respectively) were analyzed by GC-MS. Full-product identification is given in the Supporting Information. The heavy fraction was hydrogenated (10% Pd on C, 50 bar H_2) and again analyzed by GC-MS.

Deuterium-Labeling Study. A U-shaped $^1/_2$ in. metal pipe containing a few glass beads was fitted with ball valves at each end, dried in the oven, and cooled under vacuum. Deuterated ethylene was condensed from a lecture bottle into the tube at −196 °C. The tube was sealed and warmed to room temperature, and the pressure (∼15 bar) was measured using a gauge fitted to the one end. Standard ethylene was then added up to 35 bar. The catalyst mixture [$Cr(acac)_3$ (7.0 mg, 20 μmol), $Ph_2PN(^iPr)PPh_2$ (10.7 mg, 25 μmol), and MMAO-12 (9.0 mmol Al) in 1,3-diisopropylbenzene (15 mL)] was forced in with high-pressure N_2. The temperature of the reaction was maintained at 40 °C by immersing the tube in warm water, and mass transfer of ethylene into the reaction mixture was ensured by shaking the tube regularly. After 1 h, the mixture was cooled to 0 °C and slowly depressurized. Ethanol (0.5 mL) was added, and the volatile products were distilled at 70 °C under vacuum into a trap at −196 °C. The clear liquid product was analyzed by GC-FID and GC-MS. Details of the resulting isotopomer distributions are given in the Supporting Information.

Analysis of Higher 1-Alkenes. Runs were conducted under three different temperature and pressure conditions. A stirred mixture of $Cr(acac)_3$ (3.49 mg, 10 μmol) and $Ph_2PN(^iPr)PPh_2$ (6.4 mg, 15 μmol) in methylcyclohexane (10 mL) was added to an autoclave containing methylcyclohexane (90 mL) and MMAO-3A (5.0 mmol Al). The reactor was pressurized with ethylene and maintained at the required temperature and pressure throughout the reaction. A gas-entraining stirrer at 1000 rpm was used to obtain thorough mixing. When the reactor was full, the ethylene supply was terminated and the reaction mixture was cooled to 10 °C and depressurized. The liquid products were analyzed by GC-FID, and the solids were recovered by filtration. The selectivities are shown in Table 2.

Ethylene Tetramerisation in the Presence of 1-Pentene. MMAO-3A (5.0 mmol Al) was added to a stirred mixture of $Cr(acac)_3$ (3.50 mg, 10.0 μmol) and $Ph_2PN(^iPr)PPh_2$ (6.4 mg, 15.0 μmol) in methylcyclohexane (5 mL). This solution was immediately added to an autoclave containing methylcyclohexane (115 mL) and 1-pentene (80 mL) at 60 °C and pressurized to 45 bar with ethylene. A gas-entraining stirrer at 1000 rpm was used to obtain thorough mixing. The reaction mixture was maintained at 60 °C, and ethylene was fed on demand. After 45 min, the ethylene supply was terminated and the reaction mixture was cooled to 10 °C and depressurized. The liquid products were analyzed by GC-FID and GC-MS, and the solids were recovered by filtration. The mass of the product formed was 150 g, and the selectivities are shown in Table 3.

(20) Balakrishna, M. S.; Prakasha, T. K.; Krishnamurthy, S. S. *J. Organomet. Chem.* **1990**, *390*, 203.

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Supporting Information Available: Full product analysis of a typical ethylene tetramerisation reaction, including secondary products and mathematical derivations of predicted isotopomer distributions in the deuterium labeling studies for various mechanisms. This material is available free of charge via the Internet at http://pubs.acs.org.

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