

Ethylene Tetramerization: A New Route to Produce 1-Octene in Exceptionally High Selectivities

Annette Bollmann,^{*,†} Kevin Blann,[†] John T. Dixon,[†] Fiona M. Hess,[†] Esna Killian,[†] Hulisani Maumela,[†] David S. McGuinness,[‡] David H. Morgan,[†] Arno Neveling,[†] Stefanus Otto,[†] Matthew Overett,[†] Alexandra M. Z. Slawin,[§] Peter Wasserscheid,[#] and Sven Kuhlmann[#]

R & D Division, Sasol Technology (Pty) Ltd., 1 Klasie Havenga Road, Sasolburg 1947, South Africa, Sasol Technology U.K. Ltd., Purdie Building, North Haugh, St. Andrews, KY16 9ST, U.K., School of Chemistry, University of St. Andrews, Purdie Building, St. Andrews, Fife, KY16 9ST, U.K., and Lehrstuhl fuer Chemische Reaktionstechnik der Universitaet Erlangen-Nuernberg, Egerlandstrasse 3, D-91058 Erlangen, Germany

Received July 22, 2004; E-mail: Annette.bollmann@sasol.com

Linear α -olefins, such as 1-hexene and 1-octene, are used, among other applications, as comonomers in the production of linear low-density polyethylene (LLDPE). The conventional method of producing 1-hexene and 1-octene is by oligomerization of ethylene, which yields a wide spectrum of linear α -olefins (LAOs).¹ A more-selective route to 1-hexene is via trimerization of ethylene. In this regard, a number of trimerization catalyst systems have been developed,² most of them based on chromium catalysts, including the Phillips pyrrolide system,³ the Sasol mixed heteroatomic systems,^{4,5} and the BP diphosphine system.⁶ However, from a market perspective, an analogous ethylene tetramerization route to 1-octene is highly desirable but has been unknown to date.

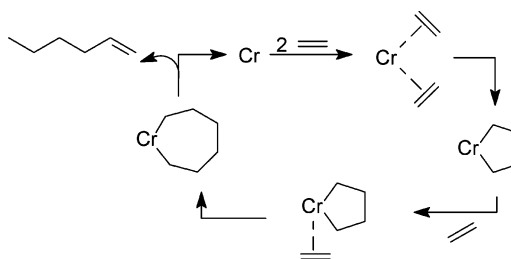
The common belief is that ethylene tetramerization is improbable. This is because if ethylene tetramerization were to proceed via a similar mechanism to that proposed for ethylene trimerization (Scheme 1),⁷ it would imply expansion of a seven-membered to a nine-membered metallacycle intermediate. It has been argued that this is unlikely to occur^{8,9} since the nine-membered ring is the least-favored medium-sized ring and should thus be disfavored relative to the seven-membered ring.⁹

We now, for the first time, report such an ethylene tetramerization reaction that produces 1-octene in good selectivity. The catalyst system for this transformation is an aluminoxane-activated chromium/((R²)₂P)₂NR¹ system, yielding 1-octene in selectivities up to 70%. A number of the diphosphinoamine (PNP) ligands with various substituents on both the N and P atoms were evaluated at two different sets of reaction conditions. All of these gave active catalysts for the production of 1-octene in good selectivity, while concurrently producing varying quantities of 1-hexene, methylcyclopentane, and methylene cyclopentane as the major side products. Selected examples are provided in Table 1.

While the substituent on the N atom had little effect on the 1-octene selectivity, it profoundly affected both catalyst productivity and 1-hexene selectivity (Table 1, entries 1–5). The highest α -selectivity for C₆ was obtained with isopropyl and cyclohexyl substituents, indicating that α -branching appears to be crucial.

Variations of the substituents on the P atoms also yielded active catalysts for the production of 1-octene in good selectivity (Table 1, entries 6, 7, 9, and 10). Ligands with bulkier aromatic substituents, such as biphenyl and naphthyl groups, gave between 54 and 56% C₈ products at 65 °C and 30 bar. Surprisingly, ligands containing heteroaromatic substituents, such as thiophenyl groups, yielded in excess of 60% C₈ products at 45 °C and 45 bar. Even

Scheme 1. Proposed Catalytic Cycle for Ethylene Trimerization



Scheme 2. Ligands for Ethylene Tetramerization

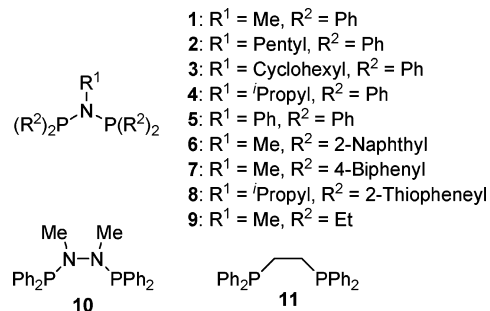


Table 1. Ethylene Tetramerization with Ligands 1–11

entry (ligand)	P (bar)	T (°C)	productivity (g/g Cr/h)	PE (%)	C ₆ (%)	1-C ₆ (%)	C ₈ (%)	1-C ₈ (%)
1 (1)	30	65	26500	1.4	24.8	39.4	59.0	94.1
2 (2)	30	65	43600	0.3	24.9	54.7	58.1	96.8
3 (3)	30	65	8050	0.5	32.1	86.1	59.4	99.3
4 (4)	30	65	11700	0.3	32.7	86.5	60.6	99.2
5 (5)	30	65	8570	0.4	27.3	67.8	61.6	97.8
6 (6)	30	65	52600	1.3	26.0	38.7	54.2	93.4
7 (7)	30	65	30800	1.8	22.9	38.6	56.1	95.3
8 (4)	45	45	272400	1.1	16.9	70.3	68.3	98.8
9 (8)	45	45	17200	2.4	16.6	42.5	60.3	96.6
10 (9)	45	45	4400	13.6	16.8	64.6	45.2	97.4
11 (10)	45	45	26200	8.0	25.2	69.6	58.8	98.4
12 (11)	45	45	24800	35.1	19.7	38.2	39.2	96.6
13 (12) ^b	45	45	8800	6.7	18	46.0	61.6	96.5

^a All reactions were conducted in a 300 mL Parr reactor; % = weight %. Standard reaction conditions: 0.033 mmol Cr(THF)₃Cl₃ (entries 7–11; Cr(acac)₃), 2 equiv of ligand, 300 equiv of MAO, 100 mL of toluene, 30 min. ^b The preformed complex **12** containing ligand **5** was used.

the use of ligands with alkyl substituents, such as ethyl groups, furnished more than 45% C₈ products at 45 °C and 45 bar.

Finally, the scope of the ligands was extended to systems outside the PNP configuration. It was found that a PNNP ligand (**10**) and a

[†] Sasol Technology.

[‡] Sasol Technology, U.K.

[§] University of St. Andrews.

[#] Universitaet Erlangen-Nuernberg.

Table 2. Ethylene Tetramerization with Ligand **4**^a

entry	[Cr] (mmol)	activator	equiv	solvent	productivity (g/g Cr/h)	PE (%)	C ₆ (%)	1-C ₆ (%)	C ₈ (%)	1-C ₈ (%)
1	0.033	MAO	300	toluene	272400	1.05	16.9	70.3	68.3	98.8
2 ^b	0.033	MAO	300	toluene	285200	0.07	16.6	65.6	68.9	98.5
3	0.033	EAO/TMA	1000/250	toluene	27400	0.10	17.8	68.3	71.6	98.5
4	0.033	MAO/SiO ₂ /TMA	340/100	toluene	102000	1.20	19.5	69.8	68.6	98.7
5	0.02	MMAO-3A	300	toluene	285100	0.1	16.0	66.4	70.7	97.9
6	0.01	MAO	200	cyclohexane	591000	1.0	14.1	63.0	67.4	98.7

^a Standard reaction conditions: Cr(acac)₃ as Cr precursor, 1.35 equiv of ligand ((Ph₂P)₂NⁱPr), 45 °C, 45 bar, 30 min. ^b When 2.5 bar of H₂ was added.

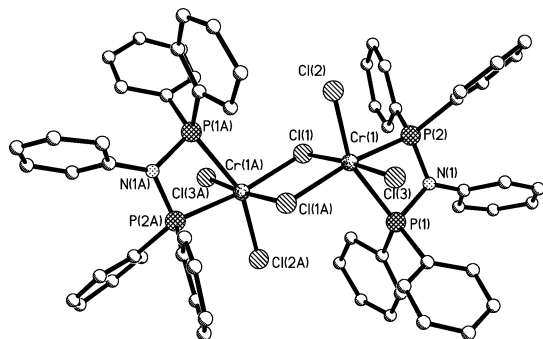


Figure 1. Molecular structure of [Cr(PNP)Cl₂(μ-Cl)]₂. Selected bond distances and angles: Cr(1)–P(1) 2.578(2) Å; Cr(1)–P(2) 2.419(2) Å; P(1)–Cr(1)–P(2) 66.62(7)°; P(1)–N(1)–P(2) 106.5(3)°.

simple carbon-bridged diphosphine system, such as diphenylphosphinoethane (dppe) (**11**), were also active for tetramerization.

It is also noteworthy that the use of the chromium/(Ph₂P)₂NⁱPr system and methylaluminoxane (MAO) as an activator led to substantially higher productivities at 45 bar and 45 °C (Table 1, entries 4 and 8). This may be attributed to greater catalyst stability and higher ethylene solubility under these conditions. This system was thus chosen for further investigations at these reaction conditions (Table 2). The addition of 2.5 bar of hydrogen to the system resulted in a remarkable decrease in solids formation, with little effect on selectivities and productivity (Table 2, entries 1 and 2). Other activators, such as modified methylaluminoxane (MMAO-3A), ethylaluminoxane (EAO), and silica-supported MAO in combination with TMA, also proved to be suitable co-catalysts for this system. Further extensive optimization showed that catalyst productivities in excess of 500 000 g/g Cr/h could be achieved in paraffinic solvents, such as cyclohexane.

While catalyst preparations were typically conducted in situ (i.e., the ligand, Cr(III) precursor, and activator were added separately to the reactor), it was also possible to conduct catalytic reactions using preformed PNP–Cr(III) complexes. For example, a (Ph₂P)₂N(Ph)–Cr(III) chloride complex was synthesized. An X-ray structure determination¹⁰ of this complex revealed the chloride-bridged dimer [Cr(PNP)Cl₂(μ-Cl)]₂ (**12**). The chromium centers of the binuclear

complex display a distorted octahedral geometry. The Cr–Cr bond distance of 3.611(2) Å is indicative of little or no metal–metal bonding. Compound **12**, when activated with MAO in toluene, gave good C₈ selectivities at a reasonable catalyst productivity (Table 1, entry 13).

In conclusion, we have now reported an unprecedented ethylene tetramerization reaction that produces 1-octene in selectivities exceeding 70%. A variety of PNP and related diphosphine ligands, in combination with Cr(III) compounds activated by aluminoxanes, were found to be very active and efficient catalysts for this purpose. Productivities in excess of 500 000 g/g Cr/h could be achieved. Further research on kinetic and fundamental aspects of this reaction is ongoing.

Acknowledgment. The authors thank Sasol Technology (Pty) Ltd. for permission to publish this work.

Supporting Information Available: Preparation of **1–9** and **12**. Experimental details for tetramerization experiments. Full product distribution for entry 1, Table 1. Crystallographic data for **12**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Alpha Olefins (02/03–4). *PERP Report*; Nexant Chem Systems. (b) Vogt, D. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996; Vol. 1, p 245.
- (2) For a recent review, see: Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, in press.
- (3) Freeman, J. W.; Buster, J. L.; Knudsen, R. D. U.S. Patent 5,856,257 (Phillips Petroleum Company), January 5, 1999.
- (4) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Dixon, J. T.; Grove, J. J. C.; Hu, C.; Englert, U. *Chem. Commun.* **2003**, 334.
- (5) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D. H.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F. M.; Englert, U. *J. Am. Chem. Soc.* **2003**, *125*, 5272.
- (6) (a) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858. (b) Agapie, T.; Schofer, S. L.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 1304.
- (7) (a) Briggs, J. R. *J. Chem. Soc., Chem. Commun.* **1989**, 674. (b) Emrich, R.; Heinemann, O.; Jolly, P. W.; Kruger, C.; Verhovnik, G. P. *J. Organometallics* **1997**, *16*, 1511. (c) Meijboom, N.; Schaverien, C.; Orpen, A. G. *Organometallics* **1990**, *9*, 774.
- (8) Yu, Z.-X.; Houk, K. N. *Angew. Chem., Int. Ed.* **2003**, *42*, 808.
- (9) Blok, A. N. J.; Budzelaar, P. H. M.; Gal, A. W. *Organometallics* **2003**, *22*, 2564.
- (10) See Supporting Information for crystallographic data.

JA045602N