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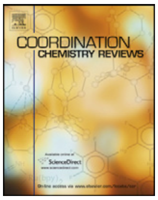

Review

New processes for the selective production of 1-octene

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ABSTRACT

Linear α-olefins, especially 1-hexene and 1-octene, are key components for the production of LLDPE and the demand for 1-hexene and 1-octene increased enormously in recent years. To meet this demand several processes were developed in the last decade to produce 1-hexene and 1-octene selectively. Here we review the new processes for 1-octene production based on homogeneous catalysts.

Sasol's coal-based high temperature Fischer–Tropsch technology produces an Anderson–Schulz–Flory distribution of hydrocarbons with high α-olefin content and the desired alkenes, including 1-heptene and 1-octene, are separated by distillation. In this case, as in the SHOP process, 1-octene constitutes only a minor part of the total yield.

Abbreviations: 1-C6, 1-hexene; 1-C8, 1-octene; 1-MOD, 1-methoxy-2,7-octadiene; 3-MOD, 3-methoxy-1,7-octadiene; Bd, 1,3-butadiene; BINAP, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; CO, carbon monoxide; Cr(acac)$_3$, chromium tris(acetylacetonate); dcype, 1,2-bis(dicyclohexylphosphino)ethane; depe, 1,2-bis(diethylphosphino)ethane; DPEphos, Bis[(2-diphenylphosphino)phenyl] ether; dppb, 1,4-bis(diphenylphosphino)butane; dppe, 1,2-bis(diphenylphosphino)ethane; dppm, 1,1-bis(diphenylphosphino)methane; dppp, 1,3-bis(diphenylphosphino)propane; FT, Fischer–Tropsch; HDPE, High Density Polyethylene; IR, infrared; LDPE, Low Density Polyethylene; LLDPE, Linear Low Density Polyethylene; MAO, methyl aluminoxane; MMAO, modified methyl aluminoxane; NHC, N-heterocyclic carbene; OCT, 1,3,7-octatriene; PE, polyethylene; PP, Polypropylene; SHOP, Shell Higher Olefin Process; SPhos, 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl; TOF, Turn Over Frequency; TON, Turn Over Number; tppts, tris(3-sulfophenyl)phosphine trisodium salt; VCH, 4-vinylcyclohexene; Xanphos, 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene.

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Nowadays other technologies are being applied or considered for on-purpose 1-octene production: hydroformylation of 1-heptene, the telomerization of 1,3-butadiene, and ethene tetramerization.

1-Heptene can be converted in three steps to 1-octene: (1) hydroformylation of 1-heptene to octanal, (2) hydrogenation of octanal to 1-octanol, and (3) dehydration of 1-octanol to 1-octene. This process was commercialized by Sasol.

Dow commercialized a process based on butadiene. Telomerization of butadiene with methanol in the presence of a palladium catalyst yields 1-methoxy-2,7-octadiene, which is fully hydrogenated to 1-methoxyoctane in the next step. Subsequent cracking of 1-methoxyoctane gives 1-octene and methanol for recycle. Recently highly active and stable phosphine based systems were reported that show particularly good performance for the industrially attractive feedstock, the C_4 cut of the paraffin cracker.

1-Hexene can be obtained by ethene trimerization by a family of catalysts based mainly on Cr. High selectivity to 1-hexene can be achieved thanks the propensity of the chromium based catalyst to form 7-membered ring metallacycles. Sasol has found catalyst systems that allow the formation of a 9-membered metallacycle in large proportion relative to 7-membered ring formation, yielding 1-octene.

1. Introduction: background

Linear Alpha Olefins, or 1-alkenes as we should say, are an important feedstock for chemical industry ever since petrochemicals took off around 50 years ago. Initially they were produced from paraffinic wax via thermal cracking, which gives a large proportion of 1-alkenes as the primary products, together with alkanes. The mixtures of internal alkenes and 1-alkenes could be hydroformylated by the first generation of catalysts, based on Co, and in this way detergent alcohols could be prepared. Dehydration of 1-alkanols was also used as a route to produce 1-alkenes, but both routes were abandoned. Dehydration though has come in focus again with the introduction of the new processes to be outlined in this review.

Steam cracking of lighter alkanes and catalytic cracking of higher paraffins to ethene, propene, butene, dienes, and alkynes paved the route to a C_{2-4} alkene based petrochemical industry. Since the mid 1970s C_{4-18} alkenes have been produced via oligomerization of ethene, with the Shell Higher Olefins Process [1]. Together with similar processes (Chevron) the world production is in the order of magnitude of that of polymers, i.e. 10 s of Mt/a. Today's main uses of these 1-alkenes, together with the primary lower alkenes, have been summarized in Table 1.

As a result of the ethene oligomerization as the source of 1-alkenes the market is dominated by the even homologues and apart from propene, the odd ones are non-existent. SHOP, which came on stream in 1977, was developed to fulfill the need for detergent range alkenes (C_{10-11}, before hydroformylation), but as can be seen from Table 1 the range from C_4 up to C_{20} was desired. As the reaction is an oligomerization reaction employing chain transfer, the product distribution is very broad, a Schulz–Flory distribution, or geometric distribution. This means that the maximum yield of 1-alkenes by weight in this range is only 50–60% [2]. The remaining higher 1-alkene fraction is isomerized, and metathesized with C_{2-4} alkenes to give broad mixtures of products from which by distillation is separated the desired fraction of internal alkenes (C_{10-11}), used in the cobalt hydroformylation process for detergent alcohols. The SHOP process has been reviewed extensively and would not be discussed here [3]. A block scheme of the process is shown in Scheme 1.

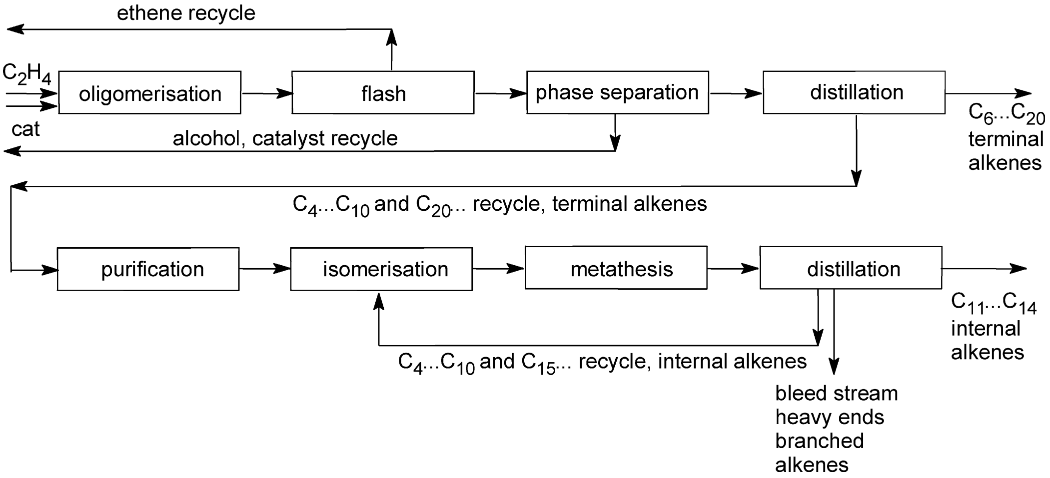
Table 1
Main uses of 1-alkenes.

Ethene	Polymers (PE), ethylene oxide, vinyl acetate, vinyl chloride, styrene
Propene	Polymers (PP), propene oxide, acetone, butanal, plasticizer alcohols, acrylonitrile, epichlorhydrin
1-Butene	Polymers, solvents
Butadiene	Polymers, oligomers, adiponitrile, sulfolane, chloroprene, vinylcyclohexene, cyclododecatriene
1-Hexene	Co-monomer in PE
1-Octene	Co-monomer in PE
C_{6-8}	Synthetic esters, plasticizer alcohols
C_{10-14}	Detergent alcohols
C_{14-16}	Sulfates and sulfonates in detergents

After 30 years of successful use of Ni catalysts, surprisingly iron and cobalt complexes containing pyridinediimine ligands were discovered that gave extremely fast catalysts simultaneously by the groups of Brookhart and Gibson, and workers at Dupont [4,5]. Turnover frequencies as high as several millions per hour were recorded! Catalyst activities are very high, and a separation of catalyst and product in a two-phase system as in SHOP may not be needed. The molecular weight distribution though will still require the isomerization/metathesis sequence as in the Shell Higher Olefins Process. Many industries have started investigations in this area, but apparently no commercializations were realized, probably because isomerized and branched products are obtained as well, exceeding the levels of SHOP products.

A much narrower distribution of products is obtained by a stoichiometric oligomerization with triethylaluminum as practiced by Ethyl Corporation (later Albemarle, BP, and now Ineos), which gives a Poisson distribution of higher alkenes. The stoichiometric growth reaction may be catalyzed by Group 4 metal complexes [6]. Especially hafnium functions well, because it does not undergo β-hydride termination [7]. A large excess of alkylaluminum, a hafnium catalyst smoothly inserting ethene molecules, and a fast exchange between the two metals leads to the desirable Poisson distribution. The average molecular weight is determined by the amount of ethene added per aluminum metal. After the reaction the alkylaluminum compound has to be destroyed, but the yield in desired products is high and the huge recycles of alkenes, typical of the nickel catalyzed oligomerization process are avoided. Thermal decomposition of the alkylaluminum compound gives 1-alkenes and oxidative destruction yields 1-alcohols.

1-Butene, 1-hexene, and 1-octene became important products over the years of the oligomerization processes because of their use as co-monomers in LLDPE, Linear Low Density Poly Ethylene. Butene can be made independently from ethene via dimerization, the only product that can be made with high selectivity in an oligomerization reaction. LLDPE containing 1-octene is made in a solution polymerization process (e.g. single site, metallocene catalyst, Dow), while the other two are made in gas-phase processes (Union Carbide, and Innovene from BP, now INEOS). It does not contain long chain branching, as LDPE, but contains ethyl, butyl, or hexyl branches, and has a narrow MW; it combines the density of HDPE with the linearity of LDPE. The material can be recycled for use in less demanding applications. Dow Chemical is the largest producer of LLDPE containing octene as the co-monomer; the world production in 2009 amounted to ~25 Mt/a. It is mainly used as a film in packaging. Together with PP it is a fast growing polymer in



Scheme 1. Simplified scheme of the Shell Higher Olefin Process.

the market. LLDPE was growing by 6% per year until 2008 and has overtaken the position of LDPE. Production of ethene from ethane by dehydrogenation contributes significantly to the growth of the (nameplate) PE production. The limited growth of the detergent range linear α-olefins made that during the 1990s a shortage of 1-hexene and 1-octene developed. Given the Schulz–Flory distribution the maximum weight percentage that can be obtained for 1-octene amounts to approximately 8%. Conversion of higher and lower homologues via metathesis into C_8, as is done for C_{11-12}, does not work out in this case, because for co-polymerization the alpha character is an absolute necessity. Since the mid-nineties new sources of 1-hexene and 1-octene have been explored. Three new catalytic routes to 1-octene will be reviewed here.

2. Overview of new routes to 1-hexene and 1-octene

Since 1994 Sasol has produced 1-hexene in their Fischer–Tropsch plant in Secunda, South Africa. Sasol mines coal in South Africa and converts it, along with Mozambican natural gas, into liquid fuels and chemical feedstock in its refineries in Sasolburg and Secunda. Sasol and their joint venture partners are building several other huge plants for the conversion of natural gas to liquid fuels (GTL) in places such as Quatar and Nigeria, using a cobalt catalyst, producing a high purity diesel fuel. In the Fischer–Tropsch process, syn gas is converted into a broad range of hydrocarbons and oxygenates over an iron catalyst in the South African plants. The process is operated in such a way that oxygenate production is very low and a large proportion of the hydrocarbons are 1-alkenes. The products are produced in the first place for use as fuels, but as in petroleum industry the lower products are valuable starting materials for chemicals. The product distribution obeys the Anderson–Schulz–Flory's equation (ASF) as in the ethene oligomerization reaction, with α's (the growth factor, the termination versus [growth + termination] ratio that may be close to the SHOP preferred values of around 0.8). Thus, the C_6 and C_8 content per weight is at most 8% each, and for linear 1-alkenes only, not counting branched products and oxygenates, the yield is probably lower. In addition, for various reasons – more sites, reinsertion of alkenes, condensation of products – the distribution is usually bimodal, and theoretically even higher [8–11]. Also, the selectivity for lower homologues deviates from the ASF distribution because of different α-values for the lower homologues, as is the case for C_4 and C_6 in ethene oligomerization, but now C_1 enters the scene showing large deviations. As in SHOP the content may be low of the desired 1-alkenes, but the scale now is at the fuels level, that is more than ten times above that of petrochemicals and thus percentages around 5% are an important source for chemicals. Sasol extracted 1-pentene and 1-hexene by distillation and extraction from the product stream and these products were brought on the market in 1994. In 1999 this was followed by the marketing of 1-octene, utilizing the world's highest distillation tower of >100 m in Secunda.

1-Heptene was also separated from the FT process stream, but as this is not desired as a feedstock for LLDPE Sasol decided to convert 1-heptene to 1-octene via a sequence of hydroformylation, hydrogenation, and dehydration. This chemistry will be discussed in Section 3.

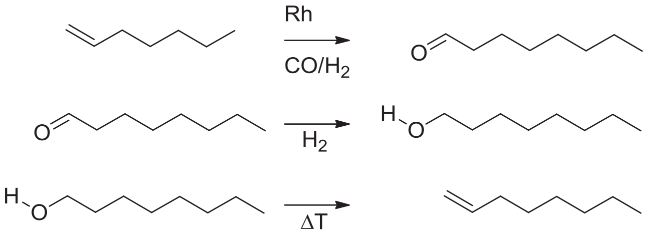
Selective Cr catalyzed trimerization of ethene to 1-hexene has been known since the 1970s and a process based on this catalysis was started up on a pilot scale by Phillips in 1995 and on a large scale as of 2003. A cyclic mechanism is involved that does not produce the usual Schulz–Flory distribution. Workers at British Petroleum invented phosphine ligands for the Cr catalyzed process, herewith lending this chemistry the control well known in late transition metal catalysis. This catalysis area was expanded later by Sasol to catalysts giving mainly 1-octene next to 1-hexene, an important breakthrough in oligomerization. This chemistry will be dealt with in Section 5.

Dimerization of a C_4 fraction to C_8 would potentially be a valuable route to 1-octene. Unfortunately there is no route for the conversion of 1-butene to linear product and for 2-butene this would seem even more difficult. 1,3-Butadiene can be dimerized in various ways to several products, one route being the cooligomerization with methanol which gives (E)-1-methoxyocta-2,7-diene (1-MOD). For decades butadiene has been a modestly priced "co-product" of the lower olefin production, but in the last decade the butadiene cost has risen due to a slowly increasing demand for butadiene based rubbers, while the production is under pressure because of the closure of steam crackers. The latter has to do with new capacity based on natural gas for propene and ethene coming on stream. Dow has developed a process based on the co-oligomerization reaction, followed by hydrogenation and demethoxylation to give 1-octene. This process came on stream in 2007 in Tarragona, Spain. The catalysis of the oligomerization step will be presented in Section 4.

3. Conversion of 1-heptene to 1-octene via hydroformylation

3.1. Overview

Sasol's conversion of Fischer–Tropsch derived 1-heptene to 1-octene comprises three steps, hydroformylation to octanal,



Scheme 2. One carbon chain extension of 1-heptene.

hydrogenation to 1-octanol, and dehydration to 1-octene as shown in Scheme 2.

Hydrogenation and dehydration are supposed to occur in almost quantitative yield and only hydroformylation will concern us here. Sasol's new 1-octene plant at Secunda in South Africa was completed in 2007. The 100,000 t/a plant uses technology licensed by Davy Process Technology in co-operation with Dow Chemical subsidiary Union Carbide. It employs the low pressure Rh hydroformylation technology. The production of Sasol's new plant added to the directly produced 1-octene doubles their capacity.

No details have been published, but since it uses Union Carbide's chemistry the catalyst most likely contains PPh_3 as the ligand, although the diphosphites developed in the late 1980s by the Bryant group [12] are also said to be used commercially [13]. PPh_3 as the ligand would give ~85% linear aldehyde (l/b ratio of 6) and only at the cost of lower rates this could be raised up to 92%. The diphosphite based catalysts may give a linear aldehyde content exceeding 97%, maintaining good rates. For the present purposes the latter would be the most attractive way, but more experience was obtained with the classic PPh_3 catalyst, also in catalyst separation and recycling.

Details on the separation of the catalyst from the product stream, also containing heptene and heavy ends, have not been published either; separation by distillation is feasible. Recently other separation methods for Rh hydroformylation have been published, such as adsorption of the catalyst on a solid bed [14] or separation by nanofiltration [15], in addition to the older ones [16]. The filtration method is not feasible in this case in view of the high costs for such a low-value product.

3.2. *Effect of impurities*

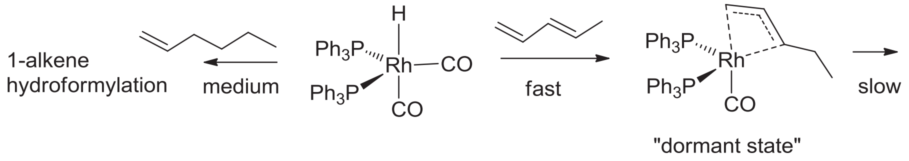
There is an important feature that distinguishes the present feed from other ones, namely their purity. Rhodium catalyzed hydroformylation may not be as sensitive to impurities as Ziegler–Natta polymerization catalysts, but still olefinic feedstocks are routinely freed form hydroperoxides for example, to avoid oxidation of the phosphine ligand. It was found, however, that alkenes must also be substantially free from compounds such as enones, dienes, and alkynes. These compounds may result in irreversible deactivation of the catalyst or have an incubatory effect on the reaction. A dramatic drop in activity may result, which in a batch reaction is noticed as incubation when the catalyst is able to convert slowly the bound impurity to an inert compound. In a continuous reaction the impurity will tie up part of the catalyst in an inactive state. Deactivation became particularly apparent when FT feedstocks were started to be used with Rh catalysts. Co catalysts used for detergent range alkenes are less sensitive, or the effect on the rate may not be noticed due to other processes that are taking place such as alkene isomerization. The influence of unsaturated impurities was not entirely unknown [17,18], as dienes were carefully removed from the alkene substrates by Garland and co-workers in his detailed kinetic and IR studies [19]. It was known that dienes are much more reactive towards rhodium hydride catalysts, while the overall hydroformylation of butadiene for instance is considerably slower than that of 1-alkenes; Rh/dppe catalyzes [20,21] hydroformylation of butadiene at 120 °C with a TOF of only 250 $mol\,mol^{-1}\,h^{-1}$ and the same catalyst hydroformylates 1-octene at 80 °C with a TOF in the order of 2000 $mol\,mol^{-1}\,h^{-1}$ (depending on CO pressure). Conjugated dienes could stop the reaction completely as was found in the hydroformylation of fatty acid esters [22].

A detailed study of inhibition by dienes, enones, and alkynes was undertaken by Walczuk et al. [23] for the PPh_3 based Rh catalyst, 1-octene as the substrate, and under standard laboratory conditions of pressure, temperature, and concentrations. For dienes and enones an unambiguous incubation was found that depended on the amount of methyl vinyl ketone or piperylene added, the more inhibitor added, the longer the incubation time. The progress of the reaction was monitored by infrared. After addition of the (hetero)diene the characteristic spectrum of the mixture of the two isomers of $HRh(CO)_2(PPh_3)_2$ disappeared and new CO bands were observed. As long as the new species were present only a slow uptake of syn gas was observed and hydroformylation of 1-octene did not occur. See Scheme 3; for piperylene the identity of the allylic intermediate could not be established with certainty.

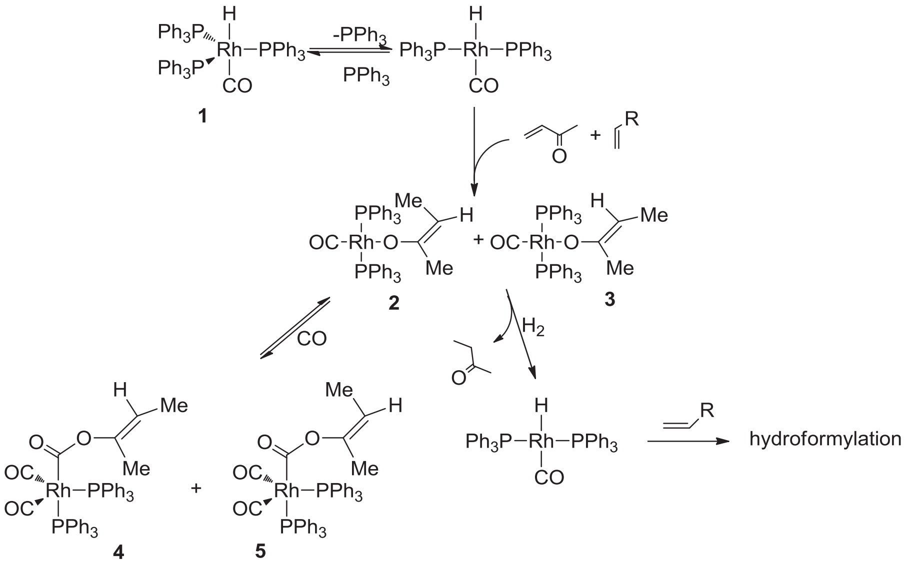
Once the new species had disappeared and the normal spectrum of the hydride species was observed again, a rapid hydroformylation of 1-octene took place. Octene conversion showed the typical S-curve over time, as is often observed in hydroformylation in the presence of impurities [24], and frustrates kinetic studies.

With very few exceptions the resting state of a hydroformylation catalyst is the rhodium hydride and the rate limiting step is the coordination of the alkene, or its insertion in the Rh–H bond, or a combination thereof [25]. The kinetics will show a negative order in CO pressure or phosphine ligand concentration in a phosphine rich system and a positive order in alkene concentration. This was coined Type I kinetics [26]. The other extreme case involves the hydrogenolysis step as the rate limiting one; in this case the resting state is the rhodium acyl species, Type II kinetics. Now the reaction is zero order in alkene concentration, has a negative order in CO, and a positive order in H_2. The latter case was encountered for very fast catalysts, using bulky phosphites as the ligand [27], in which CO dissociation and alkene coordination/insertion are fast, and the reaction of the acyl rhodium intermediate with H_2 is now slow. For dienes and enones the situation is different. Both react more readily with $HRh(CO)_2(PPh_3)_2$ than 1-octene and form stable intermediates that react very slowly to products, until they are consumed completely and hydroformylation of 1-octene can start. Dienes give an allyl intermediate that undergoes insertion of CO only sluggishly, giving a mixture a various aldehydes. The case for enones will be outlined below.

The reaction of a Rh/PPh_3 catalyst was studied in detail, in situ under hydroformylation conditions, but also at low temperature by



Scheme 3. Inhibition by piperylene.



Scheme 4. Reaction of $HRh(CO)(PPh_3)_3$ with methyl vinyl ketone.

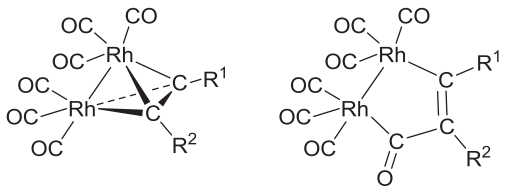
NMR using the stable precursor **1**, $HRh(CO)(PPh_3)_3$. The reactions and compounds found are shown in Scheme 4.

In the absence of syn gas two insertion products **2** and **3** were observed, two square-planar enolate complexes. When syn gas is admitted insertion of CO takes place and two substituted vinyl metallocarboxylates (carbovinyloxyrhodium) **4** and **5** were identified. Comparison with the in situ IR spectra showed that these species **4** and **5** were the dormant states of the catalyst during the incubation period of 1-octene hydroformylation and the appropriate inhibitor. The final product formed from methyl vinyl ketone (3-buten-2-one) is butanone, the hydrogenation product. Thus, the dormant states return to **2** and **3**, which are hydrogenated via the usual mechanism of dihydrogen oxidative addition. When all enone is hydrogenated hydroformylation of 1-octene will start.

Incubation by alkynes takes much longer and the S-curve is not so outspoken. It was found by Liu and Garland [28] in phosphine free rhodium catalysts that first adducts were formed as shown in Scheme 5. Terminal alkynes underwent rapid insertion of CO. Subsequently enones are formed and enones play the role of a second inhibitor as shown above. 1-Alkynes are much stronger inhibitors than internal alkynes. In general, steric bulk on potential inhibitor molecules reduced their inhibiting effect and species $HRh(CO)_2(PPh_3)_2$ remains the resting state.

Van Leeuwen and co-workers found that the inhibition strongly depends on the ligand or ligand mixture used [29]. For Xantphos no inhibition was noted and thus the continuation of the reaction of the inhibitors was now much faster than in the case of PPh_3. An interesting observation was that addition of small amounts of Xantphos, DPEphos, and BINAP to a Rh/PPh_3 catalyst reduced drastically the incubation time or even removed it. Hydroformylation of 1-octene at 15 bar and 100 °C in the presence of 100 equiv. of methyl vinyl ketone turned out to be sensitive to additional, bidentate ligands added. Without additional ligand the time to reach 50% conversion was 1 h 45 min ($Rh/PPh_3 = 1{:}170$). For a ratio Rh/PPh_3/Xantphos 1:90:5 the time needed under otherwise identical conditions was only 35 min, showing that Rh/Xantphos rapidly converts methyl ethyl ketone to butanone. In the presence of 100 equiv. of isoprene the activity dropped by 50% for the PPh_3 catalyst ($Rh/PPh_3 = 1{:}170$). In the presence of 5 equiv. of Xantphos no inhibition was recorded.

This seems to be an interesting area of further research, given the growing importance of FT feedstocks in the future, because “robust” catalysts need not be the same ones as those in the “SHOP era”.

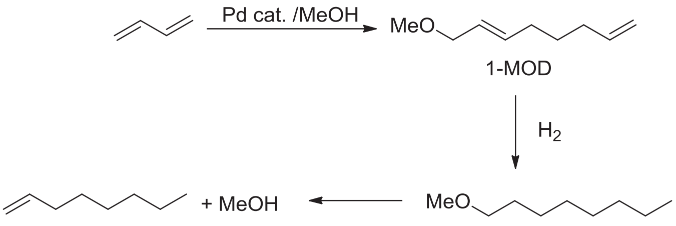


Scheme 5. Dimeric adducts formed between rhodium carbonyls and alkynes.

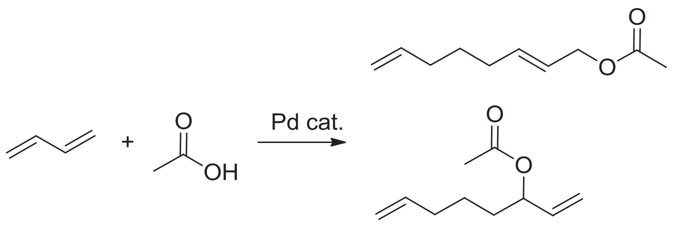
4. Dimerization of butadiene towards 1-octene

4.1. Introduction

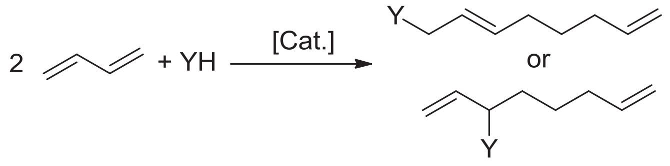
The commercial route to produce 1-octene based on 1,3-butadiene and MeOH as developed by Dow Chemical and patented in 1992 is presented in Scheme 6 [30]. The process came on stream in Tarragona in 2008 and is based on the use of the crude C_4 fraction of the cracker. A similar process was patented by Oxeno in 2002 and 2005 [31,32]. The telomerization of 1,3-butadiene with methanol in the presence of a palladium catalyst, presumably a palladium/triarylphosphine system, yields 1-methoxy-2,7-octadiene [33,34], which is fully hydrogenated to 1-methoxyoctane in the next step (>99% yield). Subsequent cracking of 1-methoxyoctane at high temperature gives 1-octene (up to 97% after distillation) and methanol for recycle. As reported by Dow, the second and third steps of the process are well controlled and highly selective using classical heterogeneous hydrogenation catalyst in the second step and an acidic alumina based catalyst in the third one. Thus, the first step of the process, the telomerization of 1,3-butadiene determines the overall efficiency of the process. The telomerization of 1,3-butadiene with methanol, potentially a 100% atomic efficiency



Scheme 6. Simplified view of the Dow process.



Scheme 7. Telomerization of 1,3-butadiene with acetic acid.



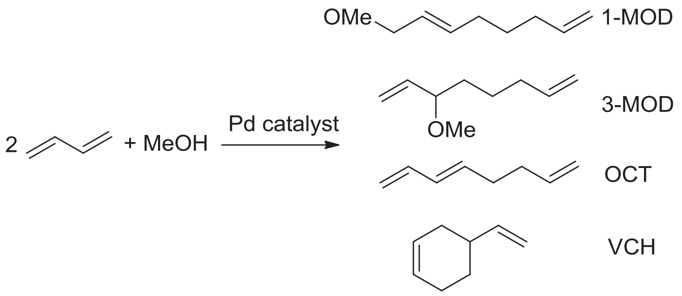
Scheme 8. General scheme for diene telomerization.

reaction, has been intensively studied by many industrial and academic laboratories.

Shell described the production of 1-octene from telomerization of 1,3-butadiene with acetic acid (Scheme 7) in the first step followed by hydrogenation and pyrolysis of acetoxyoctadiene [35,36].

Evonik reported the use of 1,7-octadiene as 1-octene precursor [37], and therefore interest in the telomerization of 1,3-butadiene with formic acid [38,39], giving a formate that after elimination of carbon dioxide gives 1,7-octadiene, has grown recently.

Telomerization reactions of butadiene were discovered by Smutny at Shell [40] and Takahashi et al. [41] at Osaka University in 1967. It refers to the oligomerization of 1,3-dienes, the taxogen, in the presence of a nucleophile, the telogen, containing an "acidic" hydrogen atom. A general equation involving the smallest 1,3-diene in the presence of any nucleophiles YH is depicted in Scheme 8.

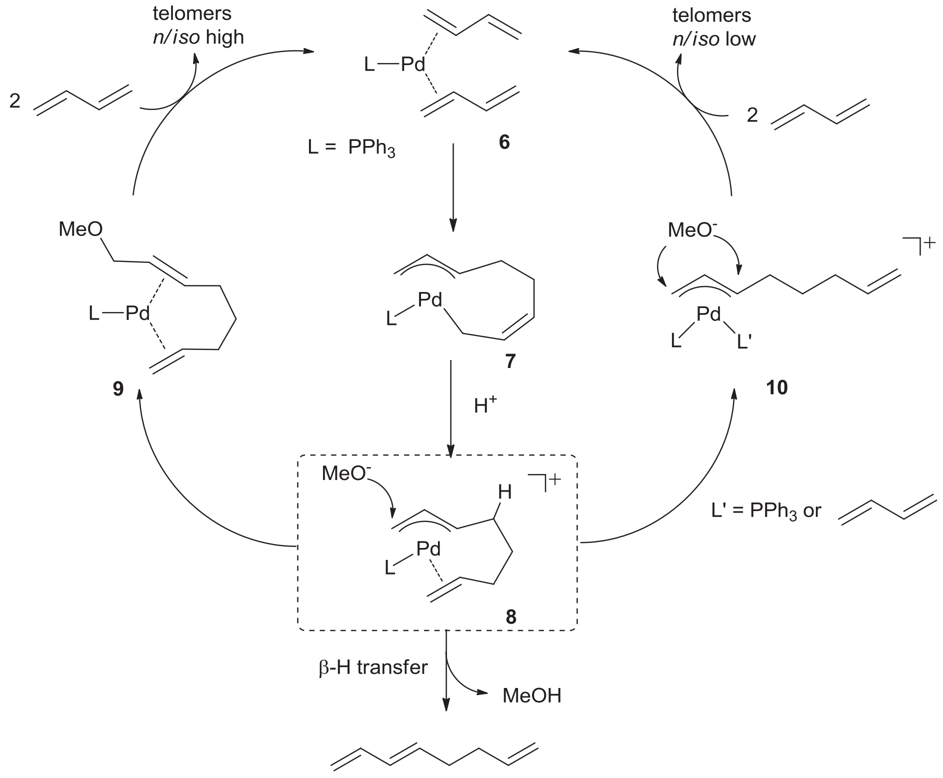


Scheme 9. Products formed in the telomerization of 1,3-butadiene with methanol.

More than 3000 articles, patents, and reviews about telomerization reactions were published over the years [42] and since 2000, more than 70 articles on 1,3-butadiene appeared. The most common dienes, 1,3-butadiene and isoprene, were studied with nucleophiles such as methanol [43], alcohols [44], polyols [45], acids [46], water [47], ammonia [48], amines [49], sugar based components [50]. Palladium complexes are the most widely used catalysts. Two telomers formed by the reaction of 1,3-butadiene and methanol or water, 1-methoxy-2,7-octadiene and 2,7-octadien-1-ol respectively are produced industrially as intermediates for the preparation of 1-octene and 1-octanol (Kuraray) as plasticizer alcohol [47c,47d,51,52].

4.2. *Telomerization of 1,3-butadiene and methanol; the mechanism*

The telomerization reaction of 1,3-butadiene and methanol leads to the formation of 1-methoxy-2,7-octadiene (1-MOD) (Scheme 9). Main by-products of the reaction are 3-methoxyocta-1,7-diene (3-MOD), 1,3,7-octatriene (OCT), and, less importantly, 4-vinylcyclohexene (VCH) formed by a thermal Diels–Alder reaction of two molecules of 1,3-butadiene.



Scheme 10. Extended mechanism for the telomerization of 1,3-butadiene with methanol.

Aspects related to engineering of the process such as catalyst recycling, biphasic conditions (water as solvent and sulfonated triphenylphosphine (tppts) as ligand), mini-plant scale, continuous reaction in loop reactors, were studied in depth by Behr et al. [43a–e]. Ionic liquids were also investigated as a solvent [43h].

The mechanism of the reaction was studied in detail by Jolly et al. [53], but factors explaining the changes in chemo- and regioselectivity remained unraveled. Recent studies from Beller et al. performed on the PPh_3-based system showed that increasing the L/Pd ratio led to systems with high productivity (high TON) due to stabilization of the Pd(0) species, although it had a detrimental effect on the selectivity [54].The extended reaction mechanism as proposed by Beller, based on Jolly's original one, is depicted in Scheme 10. Recently, computational studies of the telomerization intermediates for phosphine and carbene ligands were published by Beller and co-workers [55].

In the first step of the reaction, two molecules of butadiene, coordinated to a L-Pd(0) species **6**, couple oxidatively to form L-Pd-(η^3,η^1-octadiendiyl) complex **7**. Protonation with methanol at the C6 position of the octadiendiyl moiety leads to L-Pd-(η^3,η^2-octadiendiyl), **8**. Both intermediates **7** and **8** were isolated and characterized unambiguously and studied by Jolly or Beller with $L = PPh_3$. In the next step a methoxide anion attacks at the C1 or C3 position of the allyl moiety, giving the linear or the branched product respectively. Octatriene is formed by hydrogen abstraction at the C4 carbon atom in **8**. Beller's investigations indicated that a palladium complex containing two phosphines is mainly responsible for the formation of the (undesired) branched telomer. The formation of this palladium-bisphosphine or palladium-phosphine-butadiene species **10** is enhanced by higher L/metal ratios or by higher butadiene concentration respectively [54]. Low phosphine content renders the system less stable, because the basic conditions lead to phosphine oxidation and precipitation of Pd metal occurs.

A different mechanism involving dinuclear Pd species (Fig. 1) was reported by Behr et al. for the telomerization of butadiene with acetic acid [56]; the dimeric structure is not dictated by the octadiendiyl group, as π-allylpalladium acetate forms similar dimers [57].

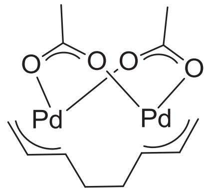


Fig. 1. Dinuclear Pd species as telomerization intermediate of butadiene with acetic acid.

4.3. Substituted triarylphosphines as ligands for the telomerization of 1,3-butadiene with methanol

As mentioned before, the ligand used industrially is triphenylphosphine, which is produced at low cost on a multi-ton scale. Unfortunately, triphenylphosphine gives a moderately active, productive, and selective catalyst system [58]. As a consequence, new ligand systems were developed and studied for the telomerization of pure 1,3-butadiene with methanol under different conditions, to improve the catalyst performance. All ligand systems must be compared under the same conditions, as subtle changes in concentration of reagents, solvent, promoter, and reaction progress influence the selectivity of the reaction [59]. This approach has a limitation, as Pd/phosphine complex formation will vary for one ligand and another and this will also influence the results.

Functionalized phosphines, possessing for instance oxygen or nitrogen donor atoms which can act as hemilabile moieties to vary the electronic and steric properties of the ligand, were employed and examples are presented in Fig. 2.

Catalytic performances of these ligands or their derived Pd complexes are summarized in Table 2. At low temperature (60 °C), triphenylphosphine gives 88% selectivity towards 1-MOD [44e] (Entry 1). Raising the temperature up to 90 °C, the productivity and activity of the catalyst increase, but the formation of octatriene (OCT) also increases, thus resulting in a lower 1-MOD yield (Entry 2). At 90 °C, arylphosphines ligands containing methoxy substituents strongly improve the catalytic system in terms of selectivity and productivity. Adding only one o-MeO moiety on one phenyl as in **16** increased butadiene conversion from 39 to 65% and 1-MOD selectivity from 73.5 to 88% at the cost of OCT [34]

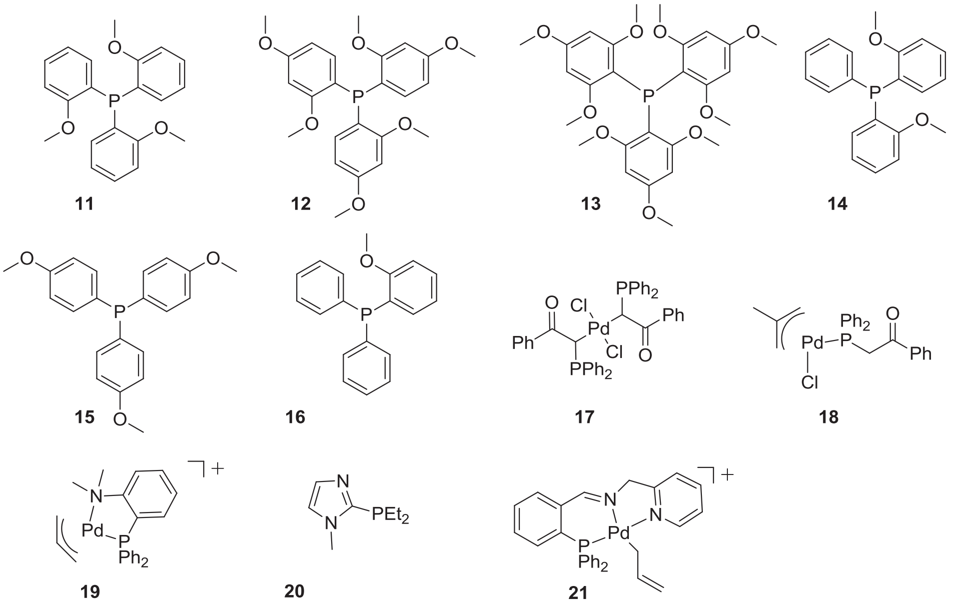


Fig. 2. Functionalized phosphines or derived Pd complexes.

Table 2
Functionalized phosphines in telomerization of 1,3-butadiene with methanol.

Entry [Ref.]	Ligand or complex	L/Pd	Bd/Pd	*T* (°C)	*t* (h)	Conv. (%)[a]	TON	1-MOD (%)	*l*/*b* (%)[b]	Chemo. (%)[c]
1 [44e]	PPh_3	2	2000	60	0.5	76	1337	88	94	94
2 [34]	PPh_3	2	32,000	90	2	39	9110	73	94	78
3 [34]	**11**	2	32,000	90	2	30	9024	94	96	97
4 [34]	**12**	2	32,000	90	2	2	–	85	96	88
5 [34]	**13**	2	32,000	90	2	1	–	9	98	10
6 [34]	**14**	2	32,000	90	2	65	19,552	94	96	97
7 [34]	**15**	2	32,000	90	2	80	22,784	89	94	94
8 [34]	**16**	2	32,000	90	2	65	18,304	88	95	93
9 [44d]	**17**	–	2000	60	5	51	795	78	96	82
10 [44d]	**18**	–	2000	80	4	22	387	88	94	92
11 [43l]	**19**	–	2000	60	3	58	1044	90	93	97
12 [44d]	**20**	2	2000	60	4	57.5	1058	92	93	98
13 [44d]	**21**	–	2000	60	18	100	1700	85	92	93

[a] Conv. is butadiene conversion.

[b] *l*/*b* = (1-MOD)/[(1-MOD) + (3-MOD)] in %.

[c] Chemoselectivity (Chemo.) = [(1-MOD) + (3-MOD)]/[(1-MOD) + (3-MOD) + OCT] in %. NaOMe is used as promoter (except entry 1, no base was added). TON is 1-MOD/Pd (mol). MeOH/Bd molar ratios are 1.5 for Ref [44d,e], 2.5 for Ref. [43l] and 2 for Ref. [34].

Table 3
Trihydrocarbylphosphines in telomerization of 1,3-butadiene with methanol.

Entry [Ref.]	Ligand	L/Pd	Bd/Pd	*T* (°C)	*t* (h)	Conv. (%)[a]	TON	1-MOD (%)	*l*/*b* (%)[b]	Chemo. (%)[c]
1 [44e]	PPh_3	2	2000	60	0.5	76	1337	88	94	94
2 [54]	PPh_3	3	10,000	50	2.5	63	5922	94	96	97
3 [43m]	PPh_3	3	55,000	90	2.5	58	27,115	85	95	90
4 [44e]	$P(nBu)_3$	2	2000	60	0.5	96	1747	91	94	97
5 [42h]	$P(nBu)_3$	3	100,000	90	16	63	51,660	82	91	90
6 [44e]	$P(Et)_3$	2	2000	60	0.5	99	1831	92.5	94	98
7 [44e]	$P(iPr)_3$	2	2000	60	0.5	100	1460	73	93	77
8 [44e]	$P(Cy)_3$	2	2000	60	0.5	95	1444	76	92	82
9 [43m]	$P(Cy)_3$	3	50,000	90	2.5	22	8030	73	91	80

[a] Conv. is butadiene conversion.

[b] *l*/*b* = (1-MOD)/[(1-MOD) + (3-MOD)] in %.

[c] Chemoselectivity (Chemo.) = [(1-MOD) + (3-MOD)]/[(1-MOD) + (3-MOD) + OCT] in %. Base used: NaOH for Ref. [42h], $N(Et)_3$ for Ref. [43m,54], no base for Ref. [44e]. MeOH/Bd molar ratios are 1.5 for Ref. [44e], 2.2 for Ref. [43m] and 2 for Ref. [42h,54].

(Entry 8). The highest selectivity (94%) is obtained with ligands **11** and **14**, possessing three *o*-MeO or two *o*-MeO groups respectively (Entries 3 and 6). Phosphine **15** gives the most productive catalyst of the series (butadiene conversion = 80) (Entry 7). Phosphines **11** and **13** give catalysts of low productivity and selectivity (Entries 3 and 6). Thus, very bulky methoxy substituted phosphines give poorly selective catalysts. The basicity of the phosphine ligand, and hence its ease of oxidation, increases substantially with the number of methoxy substituents, especially with those in *ortho*-position [60], and therefore the loss of productivity of the catalyst could be explained by a larger loss of the phosphine ligand by oxidation during the catalysis. At 60 °C for P-N or P-N-N ligands **19** and **20** only a slight improvement is observed in selectivity (Entries 11 and 12). Unfortunately, butadiene conversion is significantly lower. Bipyridine as ligand was also tested for the telomerization of butadiene with methanol but the catalyst gave very poor selectivity towards linear telomer and low conversion [44d].

Trialkylphoshines were also studied at low ratio butadiene/Pd and under these conditions more productive catalysts are formed as reported by Carlini and co-workers [44d,e]. At 60 °C with a ratio of butadiene/Pd of 2000, all trialkylphosphines tested (Table 3) gave more productive systems than Pd/PPh_3 (Entries 1, 4, 6, 7 and 8). Concerning the selectivity towards 1-MOD, the steric hindrance of the ligand remains crucial. Small trialkylphosphines such as $P(Et)_3$ and $P(nBu)_3$ give more a selective system than PPh_3 towards the production of 1-MOD, while bulky ones such as $P(iPr)_3$ and $P(Cy)_3$ formed more OCT (Entries 7–9). At lower catalyst amount as reported by Beller, trialkylphosphine based catalyst are less productive and even less selective in the case of $P(nBu)_3$ presumably because of the higher ligand loss during catalysis by oxidation, as mentioned previously (Entry 5).

4.4. Diphosphines as ligands for the telomerization of 1,3-butadiene with methanol

Classical diphosphines such as dppm, dppe, etc. were studied for the telomerization reaction or more sophisticated diphosphines such as **22** or **23** (Fig. 3) and were studied mainly at low temperature (60 °C) (Table 4). Beller et al. patented diphosphines based on binaphthyl skeleton similar for the telomerization of olefins under biphasic conditions [61].

In the case of this kind of ligands, a comparison to allylic substitution could be made, as in the case of diphosphine, the mechanism of the reaction goes through intermediate **10**, the L_2-Pd-(allyl) complex (Scheme 10). As reported by Sinou and co-workers [62], for Pd-catalyzed allylic etherification of 3-ethylcarbonate-1-hexene with phenol, diphosphines such dppm, dppe, dppp (*n* = 1–3) form less active catalysts than PPh_3. However increasing the bite angle β_n of the diphosphine increases the activity until *n* = 10 (from *n* = 4, the catalyst exhibits same activity than PPh_3). This trend was reported also for the allylic alkylation [63] but in this case increasing too much the bite angle (>100 °C) decreases the activity. In the telom-

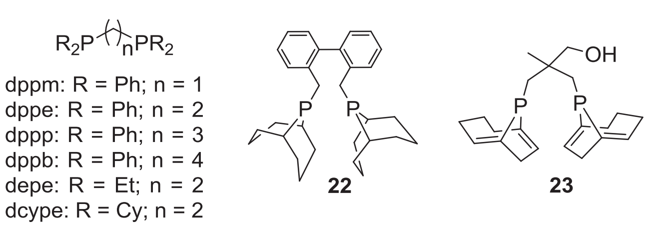


Fig. 3. Diphosphines for the telomerization of butadiene with methanol.

Table 4
Diphosphines in telomerization of 1,3-butadiene with methanol.

Entry [Ref.]	Ligand	L/Pd	Bd/Pd	*T* (°C)	*t* (h)	Conv. (%)[a]	TON	1-MOD (%)	*l*/*b* (%)[b]	Chemo. (%)[c]
1	PPh_3	2	2000	60	0.5	76	1337	88	94	94
[44e]	PPh_3	2	2000	60	2	93	1636	88	94	94
2 [44e]	dppm	2	2000	60	4	93	1674	90	95	95
3 [44e]	dppe	2	2000	60	4	64	1164	91	93	98
4 [44e]	dppp	2	2000	60	4	46	791	86	92	93
5 [44e]	dppb	2	2000	60	0.5	83	1543	93	96	97
6 [43m]	dppb	5	50,000	90	2.5	7	–	7	0	7
7 [44e]	depe	2	2000	60	4	37	636	86	95	92
8 [44e]	dcype	2	2000	60	4	11	143	65	93.5	76
9 [64]	**22**	1.2	–	70	0.25	–	–	94	–	–
10 [64]	**23**	1.2	–	70	0.25	–	–	95	–	–

[a] Conv. is butadiene conversion.
[b] *l*/*b* = (1-MOD)/[(1-MOD) + (3-MOD)] in %.
[c] Chemoselectivity (Chemo.) = [(1-MOD) + (3-MOD)]/[(1-MOD) + (3-MOD)+OCT] in %. No base was used except $N(Et)_3$ for Ref. [43m]. MeOH/Bd ratios are 1.5 for Ref. [44e] and 2.2 for Ref. [44m].

erization reaction, increasing the bite angle of the diphosphine such as dppm, decreases the productivity of the catalyst with the notable exception of dppb that gives a more active, productive and selective catalyst than PPh_3 at 60 °C (Entries 2–5). The trend observed here is different from the classical allylic substitution reaction. This could be explained by the fact that for the telomerization of butadiene, increasing the bite-angle thus the steric hindrance around the Pd atom probably slows down the oxidative coupling of butadiene in the first step of the reaction. However all catalysts derived from dppm until dppb gives more selective system than PPh_3, but no trend could be observed for the selectivity as amounts of 3-MOD and OCT vary randomly (Entries 2–5). Increasing the steric bulk of the substituent at the phosphorus atoms such as depe and dcype affects strongly the productivity and selectivity of the catalyst (Entries 7 and 8). Unfortunately at 90 °C and higher butadiene/Pd ratio, dppb gave an almost inactive and poorly selective catalyst compared to PPh_3 under the same conditions (Entry 6). The highest selectivity towards 1-MOD with diphosphines as ligands was reported with **22** and **23** at 70 °C (95%, Entries 9 and 10) [64].

4.5. *Bulky monophosphines and NHC as ligand for the telomerization of 1,3-butadiene with methanol*

Recently, several enhancements were made for the telomerization of butadiene with methanol by using new catalyst precursors and ligand systems. Mono-phosphine-Pd(0)-(1,6-diene) complexes are efficient catalysts for several C–C cross coupling reactions of arylchloride [65] and nucleophiles; they can be easily prepared via an elegant method reported by Pörschke and co-workers [66]. Inspired by the use of these complexes Beller et al. reported PPh_3-Pd-(η^2,η^2-allylether) complexes active in the telomerization reaction at low temperature (−10 °C). Unfortunately, at temperatures higher than 60 °C, no significant differences were observed in activity, productivity and selectivity compared to classical Pd(II)/PPh_3 system. As mentioned by Pörschke, use of 1,3-divinyltetramethyldisiloxane (dvds) as diolefin leads to more stable monophosphine-Pd(0)-(1,6-diolefin) complexes, which can easily be handled, even under air.

N-heterocyclic carbenes as ligand, often used as alternative to highly basic phosphines are useful in numerous metal-catalyzed reactions [67] and were investigated by Beller et al. for the selective telomerization of butadiene with alcohols [44a–c]. Another approach was recently studied by van Leeuwen and co-workers [68] inspired by the work of Buchwald and the development of bulky and basic phosphines such as SPhos, for C–C and C–N cross coupling reactions [69]. Thus a series of air-stable L-Pd-(dvds) containing NHC or bulky phosphines were developed and studied by Beller and van Leeuwen respectively and selected examples are presented in Fig. 4.

Catalytic performances of the L-Pd-dvds are presented in Table 5. It can be noticed that in the case of PPh_3 and NHC catalysts, the chemoselectivity is lower at low butadiene conversion (Entries 1 and 4). For the NHC series, **24** is highly productive and selective at 70 °C (Entry 3); introducing electron-withdrawing substituent in **25** increases the activity of the catalyst without affecting

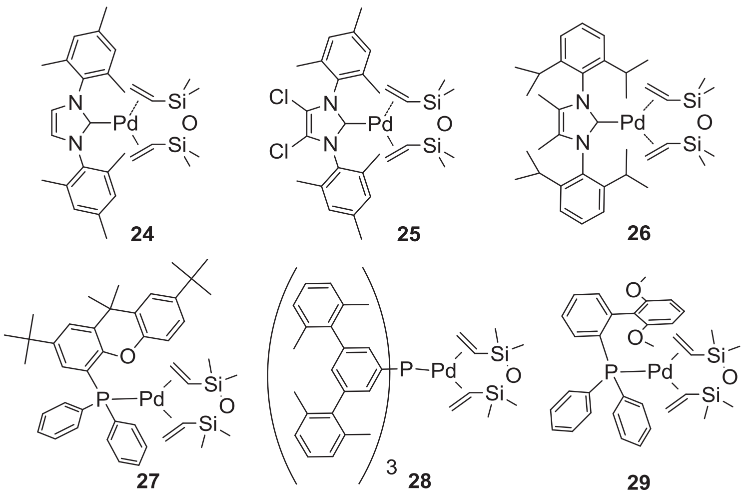


Fig. 4. NHC and phosphine palladium complexes.

Table 5
Carbenes and bulky phosphines in telomerization of 1,3-butadiene with methanol.

Entry [Ref.]	Complex	Bd/Pd	*T* (°C)	Conv. (%)[a]	TON	1-MOD (%)	*l/b* (%)[b]	Chemo. (%)[c]
1 [44a]	Pd/PPh_3 (1/3)	100,000	70	27	22,680	84	96	87
2 [68]	Pd/PPh_3 (1/2)	20,000	60	90	15,660	87	92	95
3 [44a]	**24**	100,000	70	97	94,090	97	98	99
4 [44a]	**24**	1,000,000	90	23	200,100	87	98	89
5 [44a]	**25**	100,000	70	97	94,090	97	98	99
6 [44a]	**26**	100,000	70	2	–	1.8	91	–
7 [68]	**27**	20,000	60	99	18,414	93	95	98
8 [68]	**28**	20,000	60	96	14,688	76	86	89
9 [68]	**29**	20,000	60	99	17,820	90	92	98

[a] Conv. is butadiene conversion.
[b] *l/b* = (1-MOD)/[(1-MOD) + (3-MOD)] in %.
[c] Chemoselectivity (Chemo.) = [(1-MOD) + (3-MOD)]/[(1-MOD) + (3-MOD) + OCT] in %. NaOMe was used as base. MeOH/Bd molar ratio is 2. Reaction time: 16 h.

the selectivity to 1-MOD [44a]. Beller showed that steric hindrance of the carbene is also important as the very bulky carbene ligand possessing *o,o′-iso*propyl substituents on both phenyl groups gave an inactive telomerization catalyst (Entry 6), but the complex was reported to efficiently catalyze the dimerization of butadiene to produce OCT with high yield and high selectivity using *i*PrONa as promoter instead of MeONa [70]. Nowadays, best results in terms of selectivity and productivity for 1-MOD synthesis from pure 1,3-butadiene and methanol were reported by Beller et al. with **24** at 90 °C in the presence of an excess of 80 equiv. of the ligand, exhibiting a productivity of 1,540,000 in 16 h with 97% selectivity to 1-MOD [44a–c,71]. The remarkable property of carbene based systems is that the selectivity towards 1-MOD stays close to 97% independent of the reaction temperature.

In the bulky phosphine series, bowl shape phosphine (BSP) [72], SPhos [69], and monoxantphos [68] were studied. In the case of **28**, containing BSP, the catalyst is productive but both chemo- and regioselectivity are very low compared to PPh_3 probably because of the large steric bulk of the BSP (Entry 8). Complex **29**, containing the diphenyl analogue of SPhos [73] did not show significant improvement over PPh_3 under the same conditions. Sphos based systems exhibit lower selectivity (1-MOD = 83.5%, Entry 9) [68]. The most promising systems remain the monoxantphos ones, **27**, giving a more productive and selective system (up to 93% for 1-MOD) (Entry 7).

in situ formed catalytic systems were also studied in the case of the NHCs from Pd(II) precursor and imidazolium salts and they gave similar results as the corresponding NHC-Pd-dvds complexes [43m]; a similar trend was observed for bulky phosphines [68]. The testing of monoxantphos under “Dow production conditions” (scale-up, crude C_4 fraction, 90 °C, Butadiene/Pd = 40,000) reveals the high potential of this phosphine (1-MOD = 89% at 90 °C; 83% with PPh_3). Remarkably, monoxantphos gives a highly active catalyst, one of the most active reported, reaching TOF (5 min.) up to 140,000 h^{-1} at 100 °C with high selectivity (up to 84%) for the production of 1-MOD. Moreover, monoxantphos also highly stabilizes the catalytic active species as the loss of palladium during the catalytic reaction is much lower than that of the catalyst based on PPh_3.

5. Selective tetramerization of ethylene to 1-octene

5.1. Homogeneous chromium-based catalysts for the selective production of linear alpha-olefins: main historical developments

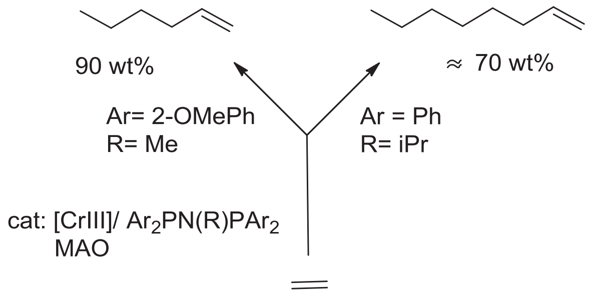
It has been more than four decades since the first discovery of the chromium based catalysts in selective ethylene oligomerization. It was in 1967 that Manyik, Walker, and Wilson from Union Carbide Corporation first observed that during ethylene polymerization with Cr(III)-tris-2-ethylhexanoate, activated with partially hydrolyzed tri-isobutylaluminum, some amounts of 1-hexene (1-C_6) were formed in the reaction mixture, which then co-polymerized with ethylene [74]. Later, in 1977, the same authors were also the first to propose a possible mechanism to account for the selective formation of this olefin involving chromium metallocyclic intermediates [75] (vide infra).

It was only much later though, in the early 1990s, that Reagan from Phillips Petroleum Company picked up on this discovery and developed in the years that followed an industrially viable process for the production of 1-hexene [76–78]. Using the same Cr-tris-2-ethylhexanoate and adding 2,5-dimethylpyrrole as a ligand together with Et_2AlCl and $AlEt_3$ as co-catalysts, a high productivity of 155,000 g/gCr/h was achieved with 93 wt% selectivity for 1-hexene at 115 °C, 100 bar of ethylene and with cyclohexane as solvent [79,80]. In 2003, the first and only operative plant to date to produce commercially and selectively 1-hexene via trimerization of ethylene using homogeneous chromium metal catalysts was build in Qatar [81]. It is operated by the Quatar Chemical Company (Chevron Phillips/Qatar Petroleum joint venture) and has a capacity of 47,000 t/a. Meanwhile, other catalytic systems using alternative protocols and co-catalysts giving higher productivities [82,83], or systems based on chelating bi- and tridentade ligands bearing phosphorus, nitrogen, or sulfur donors have also been developed for the selective trimerization of ethylene (for a review see [84]).

In 2002, following encouraging results using PNP or *N,N*-bis(diarylphosphino)amine ligands – $Ar_2PN(R)PAr_2$ – in the Ni-catalyzed olefin polymerization [85] and Pd-catalyzed ethylene/CO copolymerization [86], Wass and co-workers at British Petroleum patented and published the use of these small and tight bite angle diphosphine ligands in the selective trimerization of ethylene [87,88]. When using $[(2\text{-OMePh})_2PN(Me)P(2\text{-OMePh})_2]$ as a ligand in combination with $CrCl_3(THF)_3$ and MAO as the activator, a productivity of 1,033,200 g/gCr/h with a selectivity for 1-C_6 = 90 wt% was achieved at 80 °C and 20 bar ethylene. Apart from the high productivity obtained, this system had also the advantage that it could be operated at relatively low temperature and ethylene pressure.

Not long after this report, Bollmann and co-workers from Sasol Technology reported the use of similar Cr(III)/PNP/MAO systems for the first highly selective and highly productive ethylene tetramerization process to give 1-octene, 1-C_8 (Scheme 11) [89,90].

Importantly, contrary to the system reported by Wass which the presence of ortho-methoxy groups on the arylphosphino moiety (Ar = 2-OMePh) was believed to be crucial to obtain efficient trimerization catalysts [88], Bollmann and co-workers used $Ph_2PN(iPr)PPh_2$ ligand in which no ortho-substitution is present on the aromatic P-substituents [90]. The use of this ligand together with $Cr(acac)_3$, 300 equiv. of MAO and when operating the reaction at 45 °C with 45 bar ethylene pressure in cyclohexane, gave rise to an unprecedented productivity of 591,000 g/gCr/h with a selectivity for 1-C_8 amounting to 67 wt% (98.7 wt% of the C8 products). Alongside with 1-octene, 1-hexene was the main side-product



Scheme 11. Selective trimerization [88] and tetramerization [90] of ethylene using Cr(III)/PNP/MAO system.

formed under these reaction conditions (around 9 wt%, 63.0 wt% of C_6 products). Other oligomers produced consisted mainly of methylcyclopentane and methylenecyclopentane, both less than 3 wt%. The amount of polymeric material formed was quite low (PE = 1 wt%).

Since this landmark report various studies from both academia and industry have been undertaken to investigate the influence of the ligand structure, the chromium source, the co-catalyst effect, and/or other experimental variations on the outcome of the reaction.

5.2. Ligand structure effect of the Cr/PNP/MAO system

5.2.1. Substitution at the phosphorus donor atoms

Several studies carried out by researchers at Sasol, have demonstrated that the steric and coordinative properties of the PNP ligand were not only crucial to the activity but most importantly to the 1-octene versus 1-hexene selectivity of the catalytic system. For example when testing a series of *N*,*N*-bis-(diarylphosphino)amine ligands with different steric bulk by having different number of alkyl groups at the ortho position of the aryl-substituents (Fig. 5), results from the selective ethylene oligomerization experiments revealed that relative ratio 1-C_8/1-C_6 changed dramatically with the bulk of the ligand (Table 6) [91,92].

As a general trend, on keeping the same N-substitution, increasing the number of the ortho-alkyl groups (Ligands **30**–**34**; **35**, **36** or **37**–**39**), thereby increasing the steric bulk around the metal centre, gives rise to an increased formation of 1-hexene at the expense of 1-octene (1-C_8/1-C_6: L**30**–**34** = (16.5, 4.3)–0.1; L**35**, **36** = 2.4, 0.03; L**37**–**39** = 4.2–0.5). This ligand steric effect on the selectivity of the catalyst was also observed when increasing the size of the alkyl-substituents on the P-Ar moiety, e.g. going from ortho-Me to ortho-Et substitution (1-C_8/1-C_6: L**32**, **35** = 4.4, 2.4; L**34**, **36** = 0.1, 0.03). Similarly, changing the N-alkyl substituent from N-Me to N-*i*Pr led to a dramatic change in selectivity (1-C_8/1-C_6: L**35**, **39** = 2.4, 0.5). These results led the authors to the conclusion that overall steric bulk of the Ar$_2$PN(R)PAr$_2$ ligand is the key factor in determining the relative selectivity to 1-octene or 1-hexene, with more sterically encumbered ligands favouring trimerization over tetramerization. In a similar study, in order to determine the role of the P-Ar methoxy substitution in the system reported by Wass for the trimerization of ethylene, the same researchers from Sasol tested Ar$_2$PN(Me)PAr$_2$ ligands bearing methoxy groups at different positions on the aryl substituents. When changing the methoxy substitution from ortho to meta and finally to para a drastic shift from selective trimerization to mainly tetramerization was observed [92]. Under standard reactions conditions (45 °C, 45 bar) the relative ratio 1-C_8/1-C_6 changed from 0.12 for

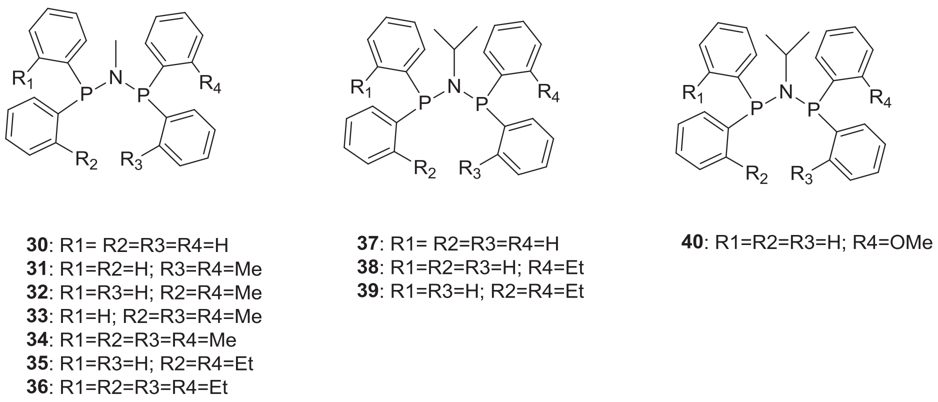


Fig. 5. PNP ligands with different steric bulk tested in selective ethylene oligomerization.

Table 6
Selective catalytic oligomerization of ethylene with ligands **30–40**,[a] adapted from [91,92].

Ligand	Productivity (g/g Cr/h)	C_6 (wt%)	1-C_6 in C_6 (wt%)	C_8 (wt%)	1-C_8 in C_8 (wt%)	PE (wt%)	C_6 + C_8 (wt%)	1-C_6 + 1-C_8 (wt%)	1-C_8/1-C_6 (molar)
30	44,000	4	23	22	92	40	26	21	16.5
30[b]	26,500	25	39	59	94	1	84	65	4.3
31	37,470	17	55	66	98	8	83	74	5.2
32	26,460	30	26	48	95	9	78	53	4.4
33[c]	96,940	42	82	42	98	12	84	76	0.9
34[c]	298,800	86	99	11	99	3	97	96	0.1
35	52,360	38	39	49	96	4	87	62	2.4
36[c]	324,110	91	100	4	99	3	95	95	0.03
37[c]	272,400	17	70	68	99	1	85	79	4.2
38	159,300	27	72	63	98	1	90	81	2.4
39	110,010	59	94	34	99	3	93	89	0.5
40	243,900	63	98	17	98	1	80	78	0.2

[a] Standard reactions conditions: 0.033 mmol [Cr(acac)$_3$], 2 equiv. ligand, 300 equiv. MAO, 100 mL toluene, 45 °C, 45 bar, 30 min. or less.

[b] 0.033 mmol Cr(THF)$_3$Cl$_3$, 65 °C, 30 bar.

[c] 0.022 mmol [Cr(acac)$_3$].

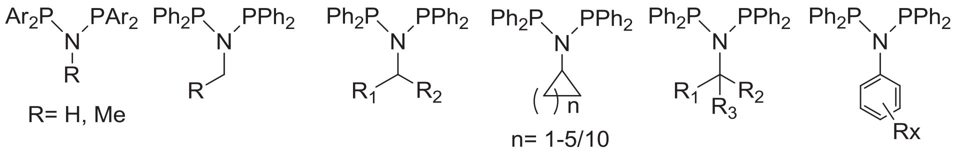


Fig. 6. N-substituted PNP ligands tested in the selective ethylene oligomerization.

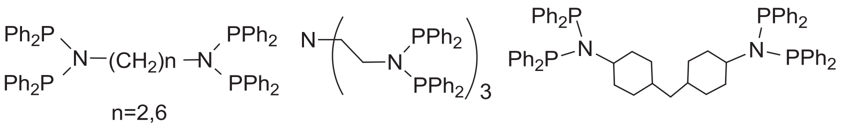


Fig. 7. Multi-site PNP ligands tested in the selective ethylene oligomerization.

Ar = 2-OMePh to 1.7 for Ar = 3-OMePh and finally 4.4 when Ar = 4-OMePh. These selectivities were consistent with the previously found trend in that removing steric encumbrance from the metal centre favours tetramerization. However, after further investigations and comparing the selectivities obtained with ligand **40** (Fig. 5), bearing only one ortho-methoxy group, with those of ligand **38** with only one ortho-ethyl group ($1\text{-}C_8/1\text{-}C_6$: L**40** = 0.2; L**38** = 2.4) the authors concluded that with relatively similar steric bulk, the methoxy group on the P-aryl substituents must have an additional special effect, probably a pendant donor effect, that may account for predominantly selective trimerization with ligand **40**. The potential coordination of the ether group to the metal centre in this type of ligand system has been seen in various X-ray structures obtained by Bercaw and co-workers in a series of isolated $[(Ar_2PN(Me)PAr_2)CrX_3]$ complexes (Ar = 2-OMePh) where one methoxy group was coordinated to the Cr(III) metal centre [93,94]. The variable-temperature ^{2}H NMR spectra of these complexes also revealed a dynamic behaviour of these complexes in solution due an exchange of coordinating ether groups. These isolated Cr(III) complexes were active trimerization catalyst to 1-hexene upon activation.

Finally other $Ar_2PN(R)PAr_2$ type ligands with different aryl substituents have been tested in the selective ethylene oligomerization [90]. For example PNP systems with Ar = 2-naphthyl (R = Me) or Ar = 4-biphenyl (R = Me) gave higher productivities than the system with Ar = Ph (R = Me), although slightly lower selectivities were observed. Other systems with Ar = 2-thiophenyl (R = iPr) and Ar = Et (R = Me) did not show better selectivities and productivities than the P-Ph system (R = iPr).

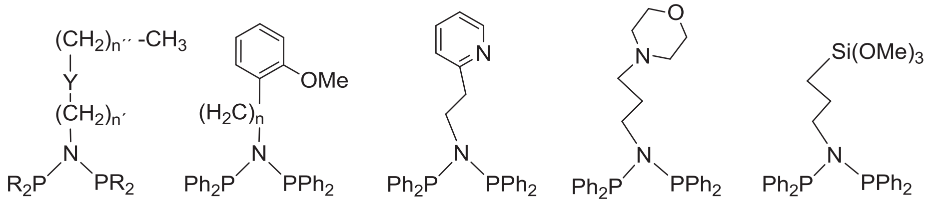
5.2.2. Substitution at the nitrogen atom

Extensive studies have been undertaken on varying the central nitrogen substituent of the PNP system to study the effect on the performance. Researchers from Sasol in collaboration with the group of Wasserscheid have investigated a large range of N-R variations (Fig. 6) [90,95–97].

The results of these studies allowed one to draw the following main conclusions: protection of the nitrogen is essential, as unprotected N-H lead to poor selectivity and moderate activity, probably due to side reactions during catalysis [96]. The secondary alkyl-N substituents iPr, Cy or larger than cyclohexyl, are better than primary alkyl or aryl substituents, giving slightly higher overall selectivity to 1-octene, but most importantly the total $1\text{-}C_8 + 1\text{-}C_6$ selectivity increases by increasing the selectivity of 1-hexene in the C_6 products (the amount of C_6-cyclic products decreases). A further increase of the steric demand of the iPr, Cy, etc. groups leads to a decrease in 1-octene selectivity, although the $1\text{-}C_8 + 1\text{-}C_6$ selectivity increases due to more selective production of 1-hexene, in other words the catalytic system moves from selective tetramerization towards trimerization. The same steric effects were also observed when the steric bulk of the N-Ar substituents was increased [97,98]. These observations are again consistent with the previously described finding that increasing the steric bulk of the $Ar_2PN(R)PAr_2$ ligand favours trimerization over tetramerization. It was also established in these studies that the steric bulk and not the basicity of the N-substituent is responsible for the selectivity of the catalytic system [96].

Several multi-site PNP type ligands were also tested in the selective oligomerization of ethylene (Fig. 7) [96,99]. When compared to their single-site analogues, similar catalytic results were usually obtained and in general this type of ligands do not offer better selectivities and productivities.

N-functionalized ligands have been tested in order to investigate the possible pendant donor effect of functional groups on the back on the ligand [96,100,101a] (Fig. 8). In general, at the conditions used, no specific influence on the selectivity of the catalytic system such as the ratio $1\text{-}C_8/1\text{-}C_6$ was found on introducing these N-functionalizations. Only improved stability and productivities



41 **42** **43** **44** **45**

R= Ph, Et Y= O, S
n´= 2,3 n´´= 0,1,3

n= 0,1

Fig. 8. PNP ligands with pending functionalities.

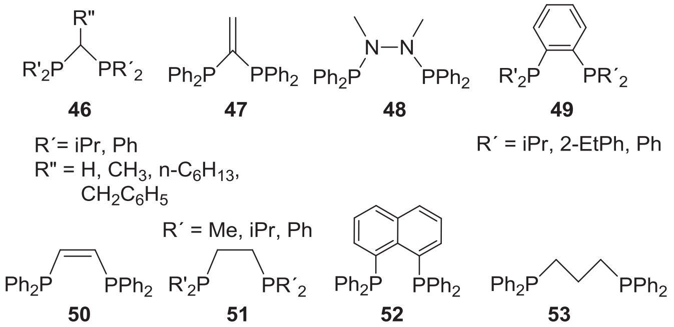


Fig. 9. Diphosphine ligands tested in the selective ethylene oligomerization.

of the catalyst as compare to the non-functionalized ligand were seen with ligand **41** (R = Et, Y = S, *n′* = 3, *n″* = 0) and ligand **42** (*n* = 1) [100,101a].

5.3. Other diphosphine ligands tested in the selective tetramerization of ethylene

In addition to the PNP system (Section 5.2), other diphosphine ligands have been investigated for the selective tetramerization of ethylene, with different bite angles and chelating bridge systems (Fig. 9) [102,103]. The closest analogue to the PNP system is the PCP ligand, both in terms of bite angle and in terms of steric constraint. Surprisingly, bis-(diphenylphosphino)methane ligand **46** (R′ = Ph, R″ = H) and ligand **47** were poor ligands in the selective oligomerization giving mainly a Schulz–Flory distribution of oligomers [102,103a]. It was suggested that possible side reactions on these unprotected 1-carbon spacer ligands could be the reason of such poor performance. To minimise these possible side reactions on the backbone of the ligand, Wass and co-workers made a series of cationic chromium(I) carbonyl complexes bearing substituted PCP type ligands **46** (R′ = Ph, R″ = CH_3, n-C_6H_{13}, $CH_2C_6H_5$). When tested in ethylene oligomerization, these substituted PCP catalysts gave some selectivity for 1-octene and 1-hexene, but the observed productivities and selectivities were still far from the same cationic Cr(I)PNP type complex [PNP = Ph_2PN(*i*-pentyl)PPh_2] [103a]. Substantial amount of polymeric product was formed (R″ = CH_3, $CH_2C_6H_5$), although this problem could be subsequently reduced, as well as the productivity increased, when generating the catalyst in situ; for example mixing ligand **46** (R″ = CH_3) with $Cr(acac)_3$ in the presence of an excess MMAO as activator. In a different approach, Overett and co-workers from Sasol [102], used a basic phosphine ligand **46** in order to reduce the acidity of the methylene hydrogens of these unsubstituted PCP systems. When tested in a pre-formed Cr(III) catalyst, ligand **46** (R′ = *i*Pr, R″ = H) gave very high selectivities (1-C_8 = 62.3 wt%, 1-C6 = 14.5 wt%, PE = 4.7 wt%) with values close to the PNP system, although the catalyst activity was an order of magnitude lower. This result demonstrated the potential of PCP ligands in the selective oligomerization of ethylene.

Enlarging the bite angle of the PNP ligand and moving to a hydrazyl-bridged PNNP ligand **48**, gave rise to a catalytic system with high selectivity for 1-octene (1-C_8 = 58.8 wt%, 1-C_6 = 17.5 wt%) at 45 °C and 45 bar in toluene with 300 equiv. MAO. Unfortunately a relatively high amount of polymeric material formed (PE = 8 wt%) and the productivity was an order of magnitude lower than that of the PNP system [90]. A similar modification with the carbon-bridged diphosphine ligands and using a PCCP type ligand (**49**, R′ = Ph; **50**; **51**, R′ = Ph) coordinated to a Cr(III)-chloride complexes, also rendered catalysts with high selectivities for 1-octene [102]. The best PCCP ligand both in terms of activity and in terms of selectivities was ligand **49** (R′ = Ph) with a rigid aromatic backbone. Using this ligand selectivities were 1-C_8 = 56.8 wt%, 1-C_6 = 13.0 wt% and PE = 0.9 wt% together with an impressive productivity of 2,240,000 g/gCr/h at 60 °C, 50 bar ethylene pressure in methylcyclohexane with 500 equiv. MMAO-3A. Under the conditions tested this productivity was higher than the best PNP ligand coordinated to the same preformed Cr(III) catalyst. This productivity was even further increased to 7,200,000 g/gCr/h at 80 °C with 70 bar ethylene with selectivities for 1-C_8 = 54.8 wt%, 1-C_6 = 24.7 wt% and PE = 0.8, giving one of the highest productivities ever reported for selective oligomerization of ethylene. Disappointingly, when **49** (R′ = Ph) was tested in situ with $Cr(acac)_3$ to generate the active catalyst, a dramatic fall in productivity was observed to only 48,000 g/gCr/h (60 °C, 50 bar ethylene) as well as a dramatic increase of polymeric products (PE = 21.3 wt%), although the selectivities for 1-octene and 1-hexene were maintained. This is in contrast with the PNP system where usually the in situ generation of the catalyst gives better performance [90]. Interestingly changing the P-substituents of this PCCP system from R′ = Ph to *i*Pr or 2-EtPh for ligand **49** or for ligand **51** from R′ = Ph to *i*Pr or Me, resulted in a complete change in performance from selective tetramerization to selective trimerization, as well as lower productivities. The fact that even an unhindered P-methyl substituent in ligand **51** gave rise to mainly trimerization to 1-hexene revealed that not only steric but also electronic factors play an important role in the selectivity of these PCCP ligands for ethylene oligomerization [102].

Changing the carbon chelating bridge to a 3-carbon spacer such as **52** with a naphthyl backbone, produced mainly 1-hexene with selectivities for 1-C_6 = 61.9 wt% with 1-C_8/1-C_6 = 0.51 (60 °C, 50 bar, MMAO-3A in methylcyclohexane). The use of a more flexible 3-carbon spacer backbone such as in ligand **53** gave relatively low productivity, low selectivity towards 1-octene (1-C_8 = 30.3 wt%) as well as a higher amount of polymers (PE = 24.3 wt%) [102]. Other ligand systems with PC_nNC_nP (n = 1, 2) revealed to be very good ligands in the selective trimerization of ethylene to 1-hexene when coordinated to Cr(III) complexes [104,105].

In conclusion, these studies have certainly demonstrated that numerous structural ligand parameters such as the steric bulk, pendant effect, phosphine basicity, chelating bite angle or backbone rigidity of the different diphosphine ligands have an important role in the performance of the catalytic system for the selective ethylene oligomerization. Each ligand system PNP, PCP, PNNP, PCCP or higher bridging system has its own behaviour and will influence the outcome of the catalyzed-reaction in its own way. Further studies should certainly focus on systematic structural variation of these ligands and particularly the promising benzene based PCCP ligand **49** deserves further attention as it combines high selectivity and high activity in the selective tetramerization of ethylene, similar to the PNP system [103b].

5.4. The chromium source and the co-catalyst effect on the Cr/PNP system

Usually ethylene oligomerization experiments are performed by generating the catalyst in situ, which is by mixing the ligand with the chromium(III) source with or without the co-catalyst(s), and then the mixture is transferred into the pressure vessel containing, if not previously added, the co-catalyst(s) in the solvent of the reaction. The vessel is then pressurised with ethylene and the reaction run at the given temperature under constant ethylene pressure. Main source of Cr(III) salts used are $Cr(acac)_3$, $CrCl_3(THF)_3$, or Cr(tris-2-ethylhexanoate) and comparative studies of their catalytic performances were reported to exhibit no significant differences between them [96]. Some pre-formed Cr(0,I,II,III) complexes have also been tested as catalysts [90,96,101,106], and when compared with the in situ system, in only one example, when using $Ph_2PN[Si(CH_3)_3]PPh_2$ ligand, the use of a pre-formed Cr(III) revealed to be superior to the in situ system [96]. In all other examples the in situ method appeared to be better in terms of activity and selectivity. The insoluble nature of the pre-formed complexes was reported as a possible cause for the poor performance, although other mechanistic parameters are certainly involved.

Whether in situ or pre-formed catalysts are used, in all cases an activator is needed, such as an excess of alkylaluminoxane or a combination of excess trialkylalumium with an anion-containing co-catalyst, to generate the active cationic metal catalyst.

Various alkylaluminoxanes have been tested and compared such as methylaluminoxane (MAO), modified MAO (MMAO), silica-supported MAO in combination with trimethylaluminum (TMA), ethylaluminoxane (EAO), or isobutylaluminoxane (*i*-BAO). In general MAO and MMAO (200–500 equiv./Cr) performed better than other alkylaluminoxanes giving better selectivity and activity [90,107,108].

In an effort to reduce the cost of the Cr/PNP catalyst system for large-scale production, researchers from Sasol have intended to substitute the alkylaluminoxane activator, such as MAO, with a cheaper co-catalyst system such as mixture of alkylalumium/anion-containing co-catalyst such as a borane, borate or aluminate compound [106,109,110]. It was found that the use of fluorinated borane and borate co-catalysts, together with excess trialkylalumium can give rise to relatively high selectivity for 1-octene, close to the results obtained with MAO activation, but the observed productivities were much lower and higher proportions of polymers were formed. The rapid deactivation of the catalyst observed when using this co-catalyst combination was proposed to be due to the degradation of borane/borate co-catalyst anion with excess of trialkylalumium [106]. Therefore chemically more robust co-catalyst anions were tested and the well-defined Cr(I)[$Ph_2PN(iPr)PPh_2$]-carbonyl complex with a bulky [$Al\{OC(CF_3)_3\}_4$] anion revealed to be a very good catalyst for the selective tetramerization of ethylene to 1-octene with selectivities similar to the in situ prepared Cr/MAO system and with low production of polymers (PE = 1 wt%) [110]. A more systematic study on a wider range of anions and particularly fluorinated aluminates with excess trialkylalumium, revealed the importance of the anion's stability and coordinating property [109]. For example, using an in situ generated catalyst $Al(OC_6F_5)_3$ afforded mainly selective trimerization, while the use of [Ph_3C][$Al\{OC(CF_3)_3\}_4$] as co-catalyst gave rise to a highly selective tetramerization catalyst. This dramatic shift in selectivity according the type of aluminate co-catalyst was proposed to depend on the anion coordination strength to the active chromium species; $Al(OC_6F_5)_3$ forms presumably a more strongly coordinating anion favouring trimerization. This trend of anion coordinating strength in relation to 1-C_8/1-C_6 selectivity correlated with other type of aluminate co-catalysts [110]. In conclusion, these studies have clearly demonstrated the potential of bulky, non-coordinating, fluorinated, aluminate/trialkylalumium-based co-catalysts for the selective tetramerization of ethylene to 1-octene in the absence of the more expensive alkylaluminoxane co-catalyst.

Other co-catalysts such as halogen containing compounds have also been tested in the Cr/PNP/MAO system [111,112]. Although selectivities towards 1-octene were slightly increased in some cases, productivities were greatly reduced upon addition of these halogenated co-catalysts.

5.5. Other experimental variations of the Cr/PNP system

Other parameters such as the solvent, the reaction temperature, the pressure as well as the ratio Cr/PNP influence the outcome of the selective tetramerization of ethylene.

Most common solvents used are toluene, cyclohexane, and methylcyclohexane. Some studies have shown significant rate improvement using aliphatic solvent such as methylcyclohexane instead of toluene [90,96]. It was reported that reactions performed in methylcyclohexane containing only 1% of toluene led to more than 50% reduction in the reaction rate as compared to reactions in pure methylcyclohexane [96]. This suggests that solubility is not the only parameter to explain this difference in reactivity between the two aliphatic and aromatic solvents and toluene probably interferes with the active catalyst. The formation of cationic Cr(tolyl)$_2$ type complex has been suggested [96]. Another study using pre-formed Cr(III)Cl_3(PNP) complexes bearing for example $Ph_2PN(iPr)PPh_2$ as ligand, revealed that changing the solvent from toluene to chlorobenzene led to a change in the catalyst selectivity from tetramerization to trimerization (1-C_8/1-C_6, toluene = 1.73, chlorobenzene = 0.55) together with an increase of productivity (toluene = 903 g/gCr/h, chlorobenzene = 5331 g/gCr/h) when the catalytic experiments were performed at 25 °C with a low ethylene pressure of 4 bar [100].

In general the selective ethylene tetramerization experiments are performed in the temperature range of 40–60 °C. Various studies on both semi-batch and continuous miniplant have shown a strong dependency of the reaction temperature on the activity and selectivity of the Cr(III)/$Ph_2PN(R)PPh_2$/MAO catalytic system [99,107,113–115]. High reaction temperatures (>60 °C) significantly reduced the catalyst productivity as compared to reactions performed at lower temperature under the same ethylene pressure [113]. Similarly increasing the reaction temperature also led to a decrease in the reaction selectivity for 1-octene (as well as a decrease in the selectivity for the minor cyclic C_6-products), which is accompanied by a simultaneous increase in the selectivity for 1-hexene [99,107,113–115]. Therefore in general an increase of the reaction temperature does not affect the selectivity $C_8 + C_6$. By calculating ethylene concentration in the liquid phase under different temperature and pressure conditions in semi-batch experiments, it was found that the temperature affects both the productivity and the selectivity of the catalyst at constant ethylene concentration [113]. Consequently catalyst decomposition with increasing temperature is probably the main reason for lower productivities at high temperatures, whereas an increase in the rate of formation of 1-hexene with the temperature would explain the change in catalyst selectivity with increasing temperature [113,114].

Conversely, increasing ethylene pressure increases catalyst activity as well as the selectivity for 1-octene while the selectivity for 1-hexene decreases [99a,100,107,113,114,115]. The rates of formation of 1-octene and 1-hexene as a function of ethylene pressure (15–45'bar at 60 °C) revealed to have different orders (1-C_8 = 2.05, 1-C_6 = 1.29), which explains the increase formation of 1-octene with increasing pressure [115].

Finally, the ratio PNP/Cr of the in situ generated catalyst was also found to affect both the activity and the selectivity of the catalytic system. Usually catalytic experiments are performed with a PNP/Cr molar ratio of 1–2. Some studies have demonstrated that an increase of this ratio to 2 or higher led to a reduction in the catalyst productivity of the catalytic system studied, although the selectivity was usually maintained [99b,107,116a]. However, reducing this ratio PNP/Cr to sub-stoichiometric amounts led to a progressive change in catalyst selectivity. For example, a catalytic system generated in situ with a molar ratio of 1 of $Ph_2PN(i\mathrm{Pr})PPh_2$ to Cr(III) metal salt gave rise to a selective tetramerization catalyst, whereas the same catalytic system with a PNP/Cr molar ratio of 0.5 or lower gave a Schulz–Flory-like oligomer distribution [116]. A residual selective reaction to 1-octene still took place at these sub-stoichiometric ratios as shown by the higher quantities of 1-octene produced compared to a typical Schulz–Flory distribution. Interestingly, amounts of odd-numbered olefins that follow a Schulz–Flory distribution are also produced under these conditions. The formation of methylidene chromium species from MAO that react with even-numbered

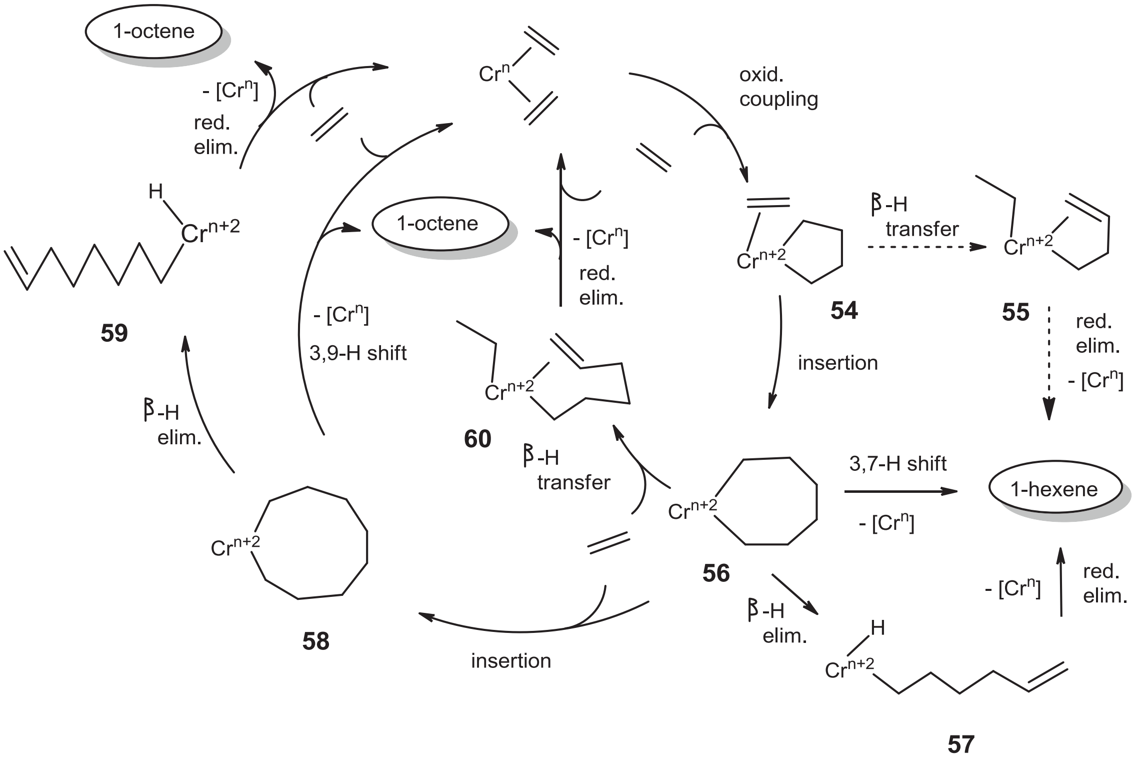


Fig. 10. Proposed catalytic cycle for the selective trimerization and tetramerization of ethylene adapted from cited references.

olefins was proposed to explain such a distribution of oligomers at these low PNP/Cr molar ratio [116a], although recent experimental evidences support more a direct chain transfer reaction between the aluminum co-catalyst and the ligand free chromium species [116b].

5.6. Mechanistic aspects

Manyik, Walker, and Wilson, in their first studies on the selective formation of 1-hexene during ethylene polymerization experiments, observed significant differences in the pressure and temperature dependence of the rate of formation of 1-hexene and polyethylene [74,75]. Based on these observations these authors were the first to suggest in 1977 a mechanistic pathway other than the normal Cossee–Arlman linear chain growth reaction [117]. To account for the selective production of 1-hexene they proposed the formation of chromium metallocycles as intermediates (Fig. 10) [75]. After activation, the chromium metal centre was proposed to coordinate to two molecules of ethylene and undergo an oxidative coupling to form a chromacyclopentane intermediate **54**. Further growth of the metallacycle, however, was not proposed at that time by these researchers and instead they suggested a β-H transfer to another coordinated ethylene molecule to give chromium ethyl butenyl species **55** that subsequently reductively eliminates 1-hexene. This mechanism was supported by previous studies by McDermott and co-workers of metallocycles and their thermal decomposition in platinum chemistry [118]. Later, the same platinum chemistry led also Briggs from Union Carbide Corporation to propose a slightly different mechanism for the formation of 1-hexene from chromacyclopentane intermediate **54**. Since the decomposition of platinacycloheptane gave 1-hexene as the main product, in the same way Briggs concluded that insertion of ethylene into chromacyclopentane **54** would give a chromacycloheptane **56** from which 1-hexene could be liberated by β-hydride elimination, to form chromium hexenyl hydride species **57**, followed by reductive elimination [119]. The isolation of chromacyclo-pentane and -heptane complexes later by Jolly and co-workers and the easy decomposition of the latter to 1-hexene further supported the viability of such metallocycle intermediates during the catalytic cycle [120]. More evidence for the metallocycle mechanism to 1-hexene was then given by the group of Bercaw with elegant deuterium labelling experiments using mixture of deuterated and non-deuterated ethylene with activated $[(Ar_2PN(Me)PAr_2)CrR_3]$ type catalysts (Ar = 2-OMePh). Analysis of the obtained C_6 isotopomer distribution allowed one to rule out a Cossee–Arlman type mechanism with this trimerization system [93,121]. Similarly, the results obtained by researchers from Sasol of analogous labelling experiments using the ethylene tetramerization system were also consistent with the formation of metallocyclic intermediates during catalysis. For example when exposing the $Cr(acac)_3/Ph_2PN(iPr)PPh_2$/MMAO catalytic system to a mixture of deuterated and non-deuterated ethylene ($C_2D_4/C_2H_4 = 1:1$), the authors observed the formation of C_6 and C_8 isotopomers having a distribution matching the predicted pattern for a metallacycle mechanism and not the one for a linear chain growth mechanism. The authors observed C_6 and C_8 isotopomers with only even numbers of deuterium atoms [122]. Indeed, in a Cossee–Arlman mechanism, H/D scrambling occurs, and isotopomers with odd numbers of H or D are expected. Thus, the H-transfer step is an intramolecular process. These results led to the conclusion that the formation of both 1-octene and 1-hexene using the Cr(III)/PNP/MAO system proceeds via chromium metallocyclic intermediates **58** and **56**, chromacyclononane **58** resulting from further ethylene insertion into **56**. The deuterium labelling studies did not permit to distinguish the mechanism by which the linear alkenes are released from their metallocycles. Theoretical calculations suggested the formation of 1-hexene from different chromacycloheptanes via a concerted 3,7-hydrogen shift with formal two-electron reduction of the metal [104,123]. A similar 3,9-H shift from **58** would give 1-octene, although no theoretical calculations have yet been published on such a catalytic step [124]. Also, complex **58** can undergo β-hydride elimination similar to that of **56** to give chromium octenyl hydride species **59**, from which 1-octene can reductively eliminate. Another pathway for the formation of 1-octene from **56** could be the formation of a chromium ethyl hexenyl species **60** via a β-H transfer to a coordinated ethylene molecule that can subsequently undergo reductive elimination of 1-octene [122].

With regards to the oxidation state of active catalyst, the metallocycle mechanism implies necessarily a two-electron redox couple for the chromium metal centre (Fig. 10). Due to the instability of the different chromium metallocycle intermediates involved, no catalytic intermediates that could confirm the exact nature of the different tetramerization active species have been isolated until now. Rucklidge and co-workers at Sasol compared the ethylene oligomerization results of isolated cationic $Cr(I)[Ph_2PN(iPr)PPh_2]$-carbonyl complex bearing a weakly coordinating counteranion with those of the neutral parent Cr(0) complex (both with the addition of $AlEt_3$ as CO scavenger). Only the Cr(I) complex gave efficient tetramerization suggesting that the Cr(I) cation could be the active catalyst and thereby a Cr(I)/Cr(III) redox couple would be operating during catalysis [110]. in situ EPR spectroscopy of $Cr(acac)_3$/PNP/MMAO mixture during catalyst formation and in the presence of ethylene have also shown the generation of Cr(I) species, but these were only minor components compared to other, EPR-silent active chromium species [125]. In addition, although a mononuclear metallocyclic mechanism is usually considered for the selective ethylene oligomerization, a bimetallic mechanism has also been proposed for the formation of 1-octene [126].

In conclusion high selectivity to 1-hexene or 1-octene of homogeneous chromium-based catalyst bearing PNP type ligands seems to lie in their propensity to form energetically favoured seven and/or nine membered ring metallocycles. Constrained geometry of chromacyclopentane **54** probably allows further ring expansion via ethylene insertion rather than other β-H type reactions. The formed metallocycles **56** and **58** are then sufficiently flexible to release linear α-olefins instead of undergoing ring expansion [127]. More mechanistic investigations are certainly needed on the Cr/PNP/MAO system to clarify some of these catalytic steps such as the release of 1-octene from its metallocyclic intermediate.

6. Concluding remarks

Three processes have been reviewed for the direct synthesis of 1-octene, two are already on stream and the third is expected to become operative within a few years [128]. The scale of the dedicated 1-octene plants is in the order of 100,000 t/a and it is always surprising to see that multistep processes for such low-cost basic chemicals are economically viable. The situation is comparable to SHOP for which the overall sequence is cracking of hydrocarbons to lower alkenes, oligomerization of ethene, hydroformylation of alkenes, and hydrogenation, while a direct selective terminal oxidation of separated alkanes would have sufficed. The first route to 1-octene concerns the hydroformylation of 1-heptene, coming from the FT process, followed by hydrogenation and dehydration, which is commercial because there is “no market” for 1-heptene as a co-monomer in LLDPE (probably because Sasol would be, as yet, the sole producer of it).

The second route presented is of similar complexity, viz. the telomerization of butadiene with methanol, hydrogenation of 1-MOD to 1-methoxyoctane, and thermal cracking to 1-octene and methanol. The reaction has been known for more than 40 years and yet enormous improvements in selectivities were reported compared to the old PPh_3 ligands (NHC ligands and substituted arylphosphines ligands). The latter ligands, although not as selective as the best NHC ligands for pure butadiene but less expensive, seem to be the ligands of choice for the next generation of processes using C_4 mixtures as a feedstock.

The third route involves the selective tetramerization of ethene to 1-octene, together with up to 30 wt% of 1-hexene. In this instance a production of two products may not pose a problem, as several other sources are available to compensate unbalanced production. Tetramerization to 1-octene came as a surprise after trimerization had been known for 30 years; it was the introduction of bidendate chelating phosphine ligands in the Cr catalyzed trimerization that enabled further chain growth. It proves once again that in homogeneous catalysis all possibilities that can be imagined may be realized some day; never say never.

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