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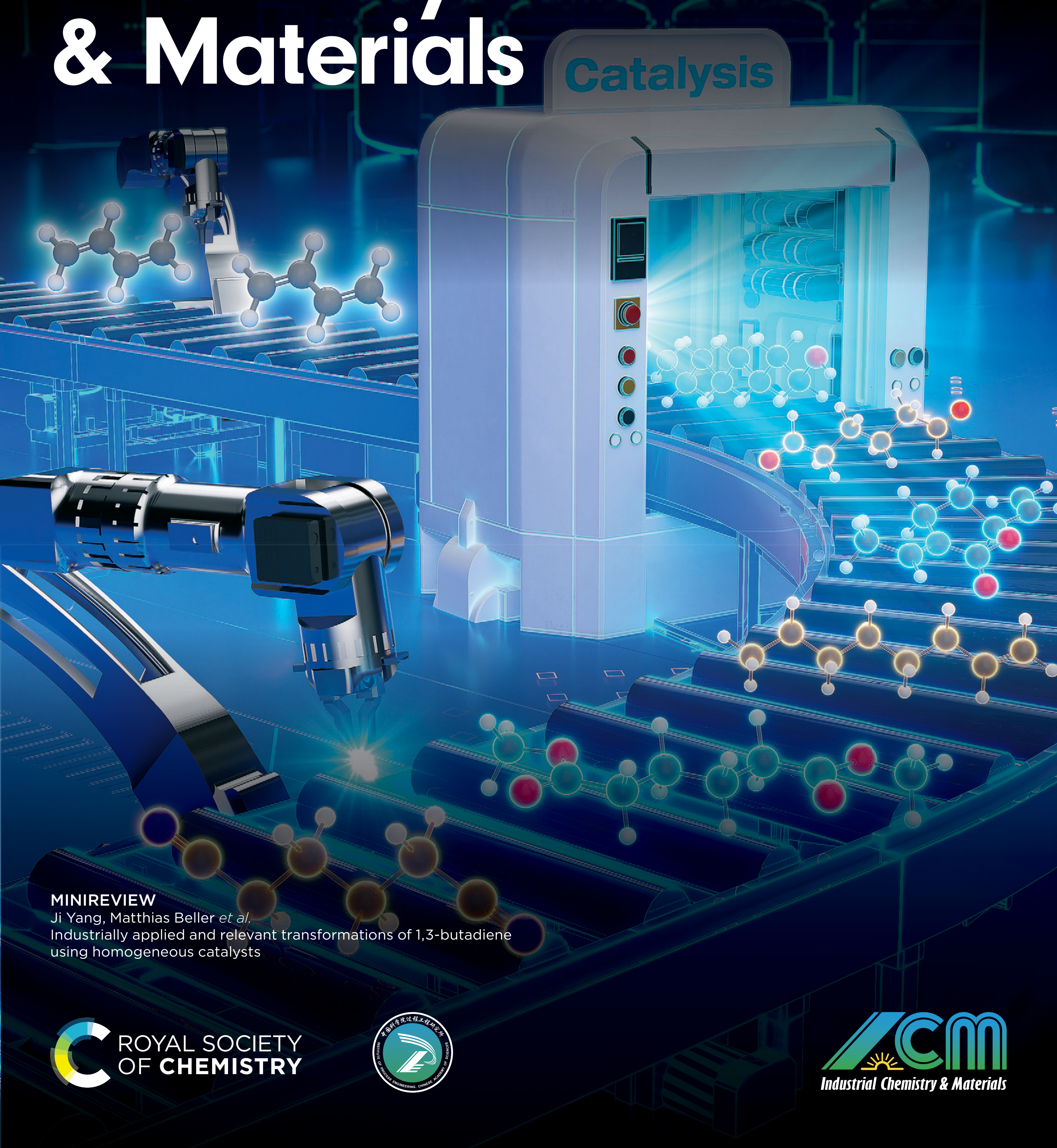

MINIREVIEW
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Industrially applied and relevant transformations of 1,3-butadiene using homogeneous catalysts

Ji Yang,†* Peng Wang,† Helfried Neumann, Ralf Jackstell and Matthias Beller *

In recent decades, the use of 1,3-butadiene as a comparably cheap and abundant raw material for new applications has attracted more and more interest, specifically in the chemical industry. The present review covers several of the most important homogeneously catalyzed processes and technologies which are currently used or have the potential to produce fine and bulk chemicals from 1,3-butadiene. As an example, palladium-catalyzed telomerizations provide valuable chemicals through the selective dimerization of 1,3-dienes with the simultaneous addition of various nucleophiles, which can be used for the synthesis of 1-octene, 1-octanol, and various lactones. On the other hand, direct carbonylation allows the selective introduction of functional groups onto 1,3-dienes, such as carbonyl, carboxyl or ester groups. The key to success in achieving these industrially relevant conversions of 1,3-butadiene was mainly the development of innovative efficient catalysts. We hope this review will make readers familiar with the industrially applied and relevant transformations of 1,3-butadiene and inspire them to further explore new and advanced systems.

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1 Introduction

1.1 General properties of 1,3-butadiene

In the chemical industry, the term butadiene (BD) generally refers to 1,3-butadiene with CAS number 106-99-0, which can be regarded as the most simple conjugated 1,3-diene with the chemical structure $H_2C{=}CH{-}CH{=}CH_2$.[1] As a comparison, the thermodynamically less stable 1,2-butadiene with CAS number 590-19-2, which has two cumulated double bonds with the formula $H_2C{=}C{=}CH{-}CH_3$, has only minor importance.[2] Considering the physical properties, its flash point (85 °C) and ignition temperature (415 °C) are relatively low. When mixed with atmospheric oxygen at 101.3 kPa and 20 °C, unstable 1,3-butadiene tends to form explosive peroxides between the concentrations of 1.1 and 16.3 vol%.

Regarding its special structure and configurations, the planar σ-*trans* conformer of 1,3-butadiene is more stable, in

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which case the two pairs of double bonds are facing opposite directions.[3] This configuration not only minimizes the steric hindrance but also maximizes the orbital overlap between double bonds. In contrast, the σ-*cis* configuration with a 0° dihedral angle is approximately 3.9 kcal mol^{-1} higher in energy than the σ-*trans* conformation with a C2–C3 dihedral angle of 180°.[4] However, 1,3-butadiene needs to adopt this s-*cis* configuration to participate in concerted addition reactions. Similarly, a collaborative study combined with experiments and DFT calculation has revealed that the double bond length of σ-*trans*-butadiene is 133.8 pm. Compared to the bond length of 133.0 pm in ethylene, the slight change in bond length is taken as evidence of a delocalized π structure and a modest degree of partial double bond quality in the middle C2–C3 single bond, in consensus with the resonance theory. A comparison of bond energies also reveals that 1,3-butadiene is stabilized thermodynamically. When comparing the hydrogenation energy, 57.1 kcal mol^{-1} released by 1,3-butadiene is slightly less than 60.6 kcal mol^{-1} of twice isolated C=C bond energy, which can be taken as a resonance stabilization energy of 3.5 kcal mol^{-1}.[5,6]

1.2 Discovery and history of 1,3-butadiene

In 1863, 1,3-butadiene was first isolated by the French chemist Joseph-Bienaimé Caventou from the pyrolysis of pentanol. Then, in 1886, the structural formula was identified with conjugated double bonds.[7] 1,3-Butadiene was also obtained and analyzed by Henry Edward Armstrong when he investigated the pyrolysis of petroleum.[8] An important milestone of butadiene chemistry was the discovery of the Russian chemist Sergei Lebedev in 1910, who found that 1,3-butadiene could be polymerized to obtain an elastic material with properties similar to those of natural rubber. This discovery opened the door for the use of 1,3-butadiene in the chemical industry.[9] Following in 1929, chemists Walter Bock and Eduard Tschunker at IG Farben in Germany invented a novel material by copolymerizing styrene and 1,3-butadiene that can be used as automobile tires.[10,11] The widespread convenience of this material led to a flow in demand for 1,3-butadiene, so processes of manufacturing 1,3-butadiene were developed rapidly at that time, including catalytic processes through alcohols developed in Russia and the USA, and acetylene synthesis routes developed in Germany.

1.3 Today's industrial production

Despite the delicate structure of 1,3-butadiene, especially the easily converted unsaturated double bonds, it is the 36th highest industrially produced chemical and economically the most important unsaturated C4 hydrocarbon. The production capacity of 1,3-butadiene is expected to increase from 14.2 million metric tons in 2020 to almost 16 million metric tons worldwide by 2025 (Fig. 1).[12–16]

Currently, 1,3-butadiene is favorably produced from C4 fractions isolated by cracking of naphtha and crude oil.

Helfried Neumann

Dr. Helfried Neumann studied chemistry at the University Erlangen, Germany, and finished his PhD studies there in 1995 under the supervision of Rainer Herges and Paul Rague von Schleyer. In 1996, he joined the Institute of Organic Catalysis in Rostock (IfOK, which was later renamed to Leibniz-Institute für Katalyse e.V.) and became project leader since 1998. His current research activities are concerned with carbonylation reactions, "hydrogen-borrowing" concept, perfluoroalkylation of arenes and the development of new ligands.

Ralf Jackstell

Dr. Ralf Jackstell received a teacher degree in chemistry and mathematics at the University of Rostock in 1994. In 1998 he received his PhD degree in phosphororganic chemistry at the University of Rostock. Since that time, he has been working at LIKAT in Rostock as group and currently topic leader in "Applied carbonylations". His main research studies are related to carbonylation and hydrogenation reactions and have been published in >170 publications.

Matthias Beller

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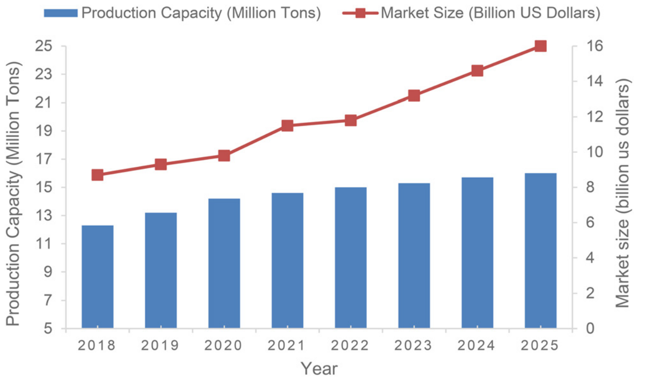


Fig. 1 Production volume and market size of 1.3-butadiene.

When heated to a high temperature of 900 °C, these feedstocks are dehydrogenated to obtain unsaturated hydrocarbons containing 1,3-butadiene.[17] In addition, 1,3-butadiene can also be prepared by heterogeneous dehydrogenation of *n*-butane. As a representative example, the first such industrialized plant, manufacturing 65 000 tons of 1,3-butadiene annually, began operations in Houston in 1957.[18,19] This plant commercially used the Houdry Catadiene process (HCP), which involves treating butane at high temperatures with an aluminum and chromium catalyst.[1] Additionally, 1,3-butadiene is also produced from ethanol in some parts of the world including China, Eastern Europe and India. In this latter process, 1,3-butadiene is manufactured at 400–450 °C by utilizing various metal oxide catalysts, and alternatively at 325–350 °C using tantalum catalyst supported on porous silica.[20] It is noteworthy that significant development studies are currently underway to produce 1,3-butadiene from renewable resources *via* not only classical chemocatalytic but also biocatalytic transformations.

1.4 Main uses and applications

Nowadays, 1,3-butadiene is one of the most important bulk chemicals, which has a wide range of applications and has penetrated all aspects of our daily life. There are 16 211 publications/patents from 2010 to 2022 published with the key word 1,3-butadiene in the Web of Science Core Database (Fig. 2, search time on November 1, 2022). These publications show a trend that research on 1,3-butadiene is becoming more and more emphasized. Also, after analyzing these data it is obvious that the main applications of 1,3-butadiene lie in the field of polymer materials. As a representative product, polybutadiene rubber (PBR) has adjustable tough or elastic properties depending on the proportions of raw materials used in its preparation.[21,22] Meanwhile, styrene–butadiene rubber (SBR) is the most common material for making automobile tires.[23–25] The powerful properties of these rubber polymers bring tires with performance-enhancing components in terms of rolling resistance and traction. With the rapid development of the electronic industry, acrylonitrile–butadiene–styrene (ABS) has become the largest engineering thermoplastic resin, widely used in mobile phones, household appliances, computers, and office products.[26,27] Simultaneously, numerous chemicals produced from 1,3-butadiene are also widely used to manufacture paper coatings, turf, carpets, gloves, wetsuits, toys and other consumer products. Considering that there are already

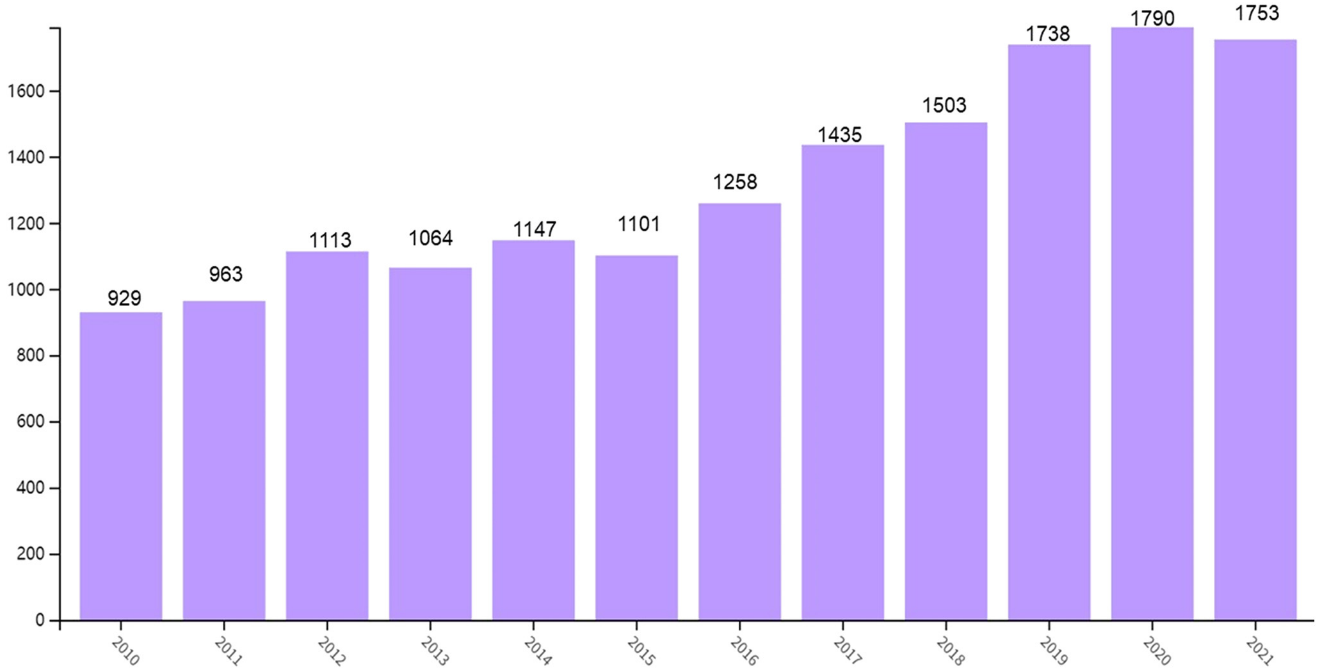


Fig. 2 Number of publications from 2010 to 2021 with the key word butadiene.

various reviews/books on industrial polymers based on 1,3-butadiene for readers to refer to,[21–27] this review will not duplicate this section but center on industrial transformation examples and some promising progress in recent research to produce other bulk chemicals. In particular, we will focus on the development of catalytic systems achieving transformations of 1,3-BD towards functionalized products with high atom economy and avoiding environmental pollution.

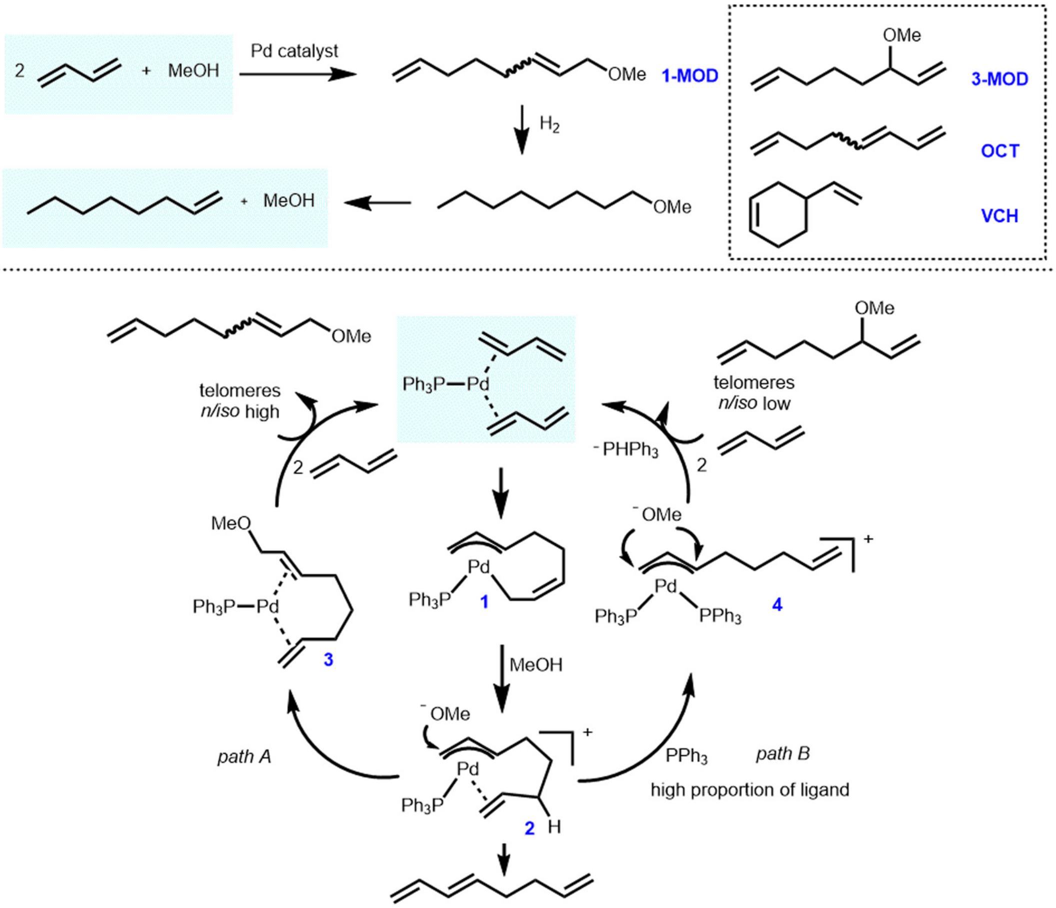
2 Selected current applications in industry

2.1 1-Octene *via* telomerization with methanol (Dow process)

Dow Chemical developed and patented a commercial route in 1992 to produce 1-octene based on the telomerization of 1,3-butadiene and MeOH as shown in Scheme 1.[28] The process has been in industrial operation in Tarragona since 2008 using crude C4 fractions from cracking furnaces as raw materials. The key intermediate in this process is 1-methoxy-2,7-octadiene (1-MOD), which was synthesized in the presence of a palladium/triarylphosphine catalytic system.[29,30] Later on, Oxeno Ind. (now Evonik Industries) patented and applied similar processes utilizing palladium salts in the presence of *N*-heterocyclic carbenes in 2002 and 2005.[31,32] Overall, the relevant process can be described as follows: the initially obtained telomerization product 1-MOD is completely hydrogenated to 1-methoxyoctane with >99% yield. Subsequently, base-catalyzed cracking at high temperature leads to 1-octene with 97% yield and methanol for recycling. According to the information of relevant patents,[28–30] great reaction efficiency and high selectivity were obtained in the second and third steps, and related products could be basically obtained by quantitative conversion. Therefore, the first step, *i.e.*, the telomerization of 1,3-butadiene with methanol, determines the overall efficiency of the process.

Originally, the telomerization reaction of 1,3-butadiene was discovered in 1967 by Smutny at Shell and Takahashi at Osaka University independently.[33,34] The name telomerization refers to the oligomerization of 1,3-dienes with a nucleophile (in terms of "telogen"). Interestingly, the nucleophile can be of various proton-containing types such as alcohols,[35–51] polyols,[52–58] acids,[59–62] water,[63–77] ammonia,[78,79] amines,[80–90] and biomass-based components.[91–100] Therefore, this highly efficient and promising reaction has been intensively studied in many renowned industrial and academic laboratories.[101]

2.1.1 Mechanism. In the presence of a suitable catalyst, the telomerization of 1,3-butadiene and MeOH produces



Scheme 1 Simplified Dow process and mechanism for the telomerization of 1,3-butadiene with methanol.

initially 1-methoxyocta-2,7-diene (1-MOD) as the main product. Simultaneous formation of 3-methoxyocta-1,7-diene (3-MOD) and 1,3,7-octatriene (OCT) as dimerization products and 4-vinylcyclohexene (VCH) produced by a concerted pericyclic Diels–Alder reaction are often observed, too.

With the aim of improving the efficiency and selectivity, the mechanism of this reaction has attracted extensive attention. Jolly and colleagues first investigated this process, specifically the η^3-allylpalladium intermediate analyzed by NMR.[102] Later on, some of us have also conducted in-depth research on the mechanism utilizing representative palladium/phosphine catalysts. Thereby, we not only clearly revealed the related side reactions but also showed the multiple roles of phosphine ligands in this catalytic process.[103–105] The extended reaction mechanism is as follows (Scheme 1).[104,105] Initially, two molecules of 1,3-butadiene are oxidatively coupled at a low-coordinated ligand–palladium(0) center to form ligand–palladium–(η^3,η^1-octadiendiyl) active species **1**. Selective protonation of species **1** by MeOH at the C6 site results in the ligand–palladium–(η^3,η^2-octadiendiyl) complex **2**. Subsequent attack of the methoxy group at the allylic position (site 1 or 3) leads to linear or branched (1- or 3-substituted) products, respectively. Both intermediates **1** and **2** were characterized and studied in detail. More specifically, the linear/branched selectivity of this reaction was significantly affected by the nature of the phosphine ligand. The formation of Pd–bimolecular phosphine or Pd–PPh_3–butadiene complex **4** was enhanced respectively by increased triphenylphosphine/Pd ratio or increased concentration of 1,3-butadiene, leading to a larger extent of branched product 3-MOD. At the same time, an insufficient amount of phosphine makes the system less stable, resulting in irretrievable phosphine oxidation and precipitation of palladium metal. Furthermore, some of us were involved in computational studies on telomerization intermediates to assist in further understanding of this process.[106]

2.1.2 Catalyst developments. The ligand presumably used in the Dow process is a triarylphosphine, which is available relatively inexpensively on an industrial scale.[107] Simple triphenylphosphine generally leads only to a moderately efficient catalyst with unsatisfactory linear/branched selectivity.[94] Therefore, extensive research has been devoted to the development of novel catalysts with improved performance.

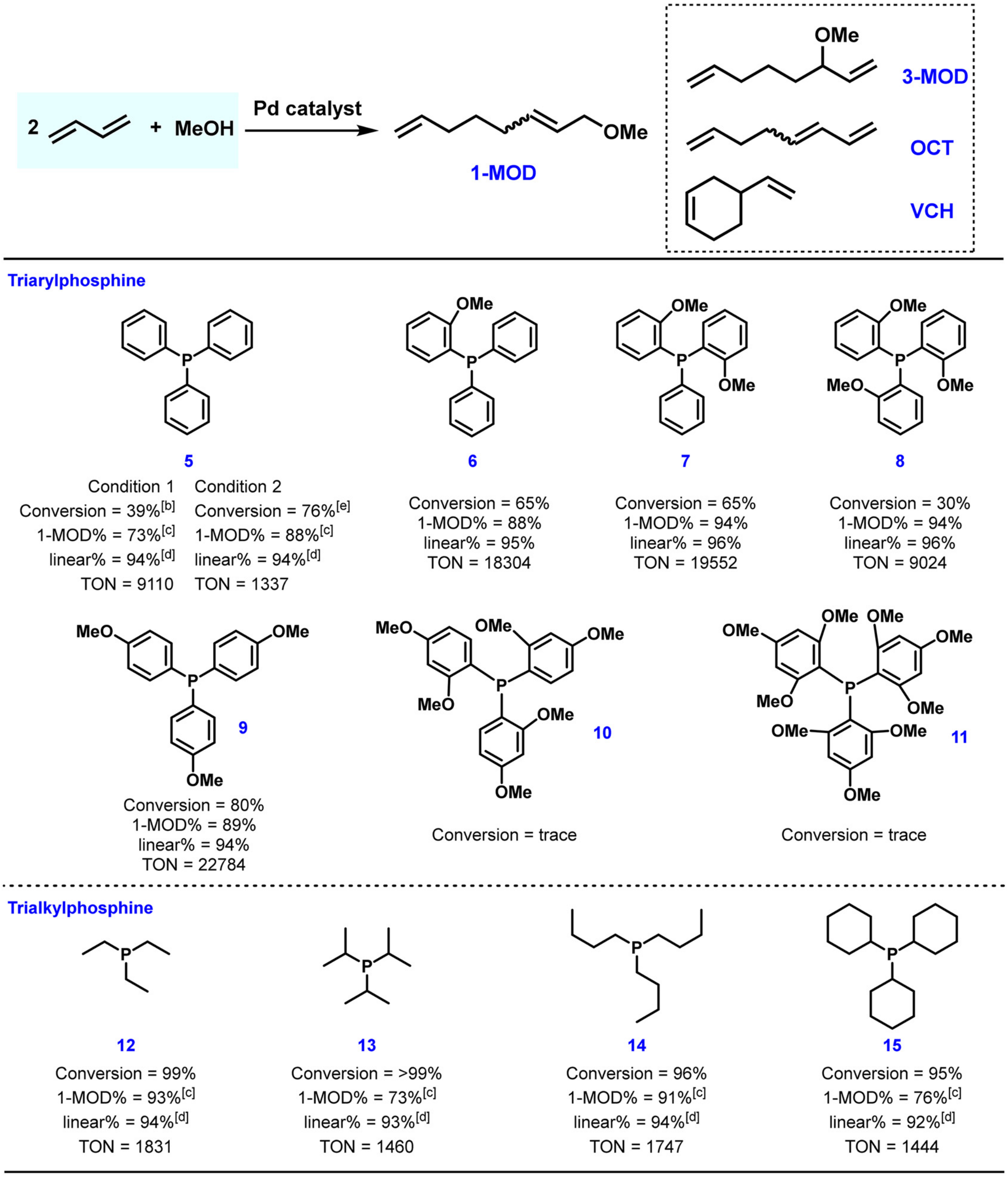
Several functionalized triaryl phosphines containing oxygen atoms were employed in this reaction and selected results are summarized in Fig. 3. By altering the electronic and steric properties of the ligand as well as the position and amount of hemilabile coordination groups, the catalytic efficiency of triaryl phosphine ligands substituted with methoxy groups was determined. For example, introducing one methoxy substituent on the aryl ring of the phosphine could increase the conversion of 1,3-butadiene by 26% and the selectivity of 1-MOD by 15%.[30,42] By using ligands **7** and **8**, which possess two or three *ortho*-MeO groups, respectively, up to 94% selectivity was obtained. Furthermore, ligand **9** with *para*-methoxy groups exhibited the best catalytic activity with a catalyst TON of 22 784. Trialkyl phosphines were also studied for this process by Carlini and co-workers.[41,42] As a general rule, the tested ligands proved to be more productive than PPh_3 at low reaction temperature (60 °C). Regarding the selectivity towards 1-MOD, linear triethylphosphine **12** and tributylphosphine **13** showed higher selectivity than PPh_3, while sterically hindered triisopropylphosphine **14** and tricyclohexylphosphine **15** preferably formed 1,3,7-octatriene as the formal dimerization product.

In order to improve catalyst stability and shorten the induction period for the formation of the active catalyst species, different palladium complexes were also investigated as catalyst precursors. Inspired by the easily prepared monophosphine–Pd(0)–(1,6-diene) catalyst reported by Pörschke,[108] several enhancements were made by some of us for the telomerization of 1,3-butadiene with methanol. For example, the reaction can proceed smoothly even at −10 °C by using a triphenylphosphine–palladium–(η^2,η^2-allylether) catalyst **16**.[40] At the same time, such catalysts, including 1,3-divinyltetramethyldisiloxane (dvds) **17**, are stable in air and easy to handle.

Van Leeuwen and collaborators studied the structure effects of bulky phosphines **18**–**20** in detail (see Fig. 4), which were used for cross-coupling reactions previously.[109,110] Ligands with a xanthene backbone exhibited superior properties, especially regarding selectivity, activity and stability. Among these phosphines, ligand **18** showed highly satisfactory results, reaching a TOF of 140 000 h^{-1} in 5 min at 100 °C with up to 84% selectivity for 1-MOD. Further, the modified electron-rich ligand **19** showed to be a more outstanding monoXantphos ligand, increasing 1,3-butadiene conversion to 95% and selectivity for 1-MOD to 93% at 90 °C. Under industrial production conditions, monoSPANphos **20** was a very active ligand at low temperature with better stability at 90 °C for this reaction. Through structural and activity analysis, the reasonable backbone design and the coordination properties of oxygen atoms were considered to be the reason for this better performance.[111]

Essentially, classical bidentate phosphine ligands with diverse structures were also studied for the Dow telomerization reaction (Fig. 4). In the case of diphosphine ligands, such as dppm, dppe, and dppp (n = 1–3), these ligands exhibited lower activity compared to PPh_3. Yet, the conversion significantly improved from DPPB **24** to DPPH **25** (n = 4 to 6) as the bite angle of the ligands increased. To allow for easier catalyst recycling, we further developed bidentate phosphines **26** and **27** with a binaphthyl backbone for the reaction of 1,3-butadiene and MeOH under organic or two-phase conditions.[112] So far, the bidentate phosphine catalysts with the highest selectivity towards 1-MOD were ligand **28** and **29** (92–96% selectivity at 70 °C).[113]

N-Heterocyclic carbenes (NHCs) are also very important ligands for catalysts applied in telomerization reactions due to their similar properties to phosphine ligands.[114–117]



[a] condition 1: 1,3-butadiene/Pd = 32000, ligand/Pd = 2, 90 °C, 2 h; [b] in terms of 1,3-butadiene; [c] 1-MOD to the mixture of 1-MOD,3-MOD, OCT, VCH; [d] 1-MOD/(1-MOD+3-MOD); [e] condition 2: 1,3-butadiene/Pd = 2000, ligand/Pd = 2, 60 °C, 0.5 h.

Fig. 3 Performance of selected monophosphine ligands used in the palladium-catalyzed telomerization reaction of 1,3-butadiene with methanol.

Hence, a series of structurally diverse NHC–Pd catalysts **30–34** were developed and investigated. In these studies, triphenylphosphine was used as a reference to compare the activities of different *N*-heterocyclic carbenes. As presented in Table 1, at a low temperature of 50 °C, triphenylphosphine did not catalyze the conversion of 1,3-butadiene (entry 3). However, in comparison, NHC **30** showed obvious activity and yielded 57% of the products (entry 7). When the reaction temperature was further increased to 70–90 °C, catalyst **30** exhibited an amazing activity for complete conversion of 1,3-butadiene with 97% linear selectivity (entries 10 and 6). To verify the activity and stability of this powerful catalytic system, even using a very small catalyst dosage (0.00033 mol%) led to complete conversion of the reaction and gave 89% yield of the desired products with high productivity (entry 8, TON = 267 000, TOF up to 100 000 h^{-1}). Further reducing the catalyst loading of **30** at 90 °C resulted in an efficiency of 1 540 000 in 97% linear selectivity.[38–40,118,119] Remarkably, the selectivity to the desired linear product stayed fixed at about 97% even at different temperatures. Most importantly, this Pd–carbene catalytic system exhibited excellent activity and stability even when using C4 crack as a

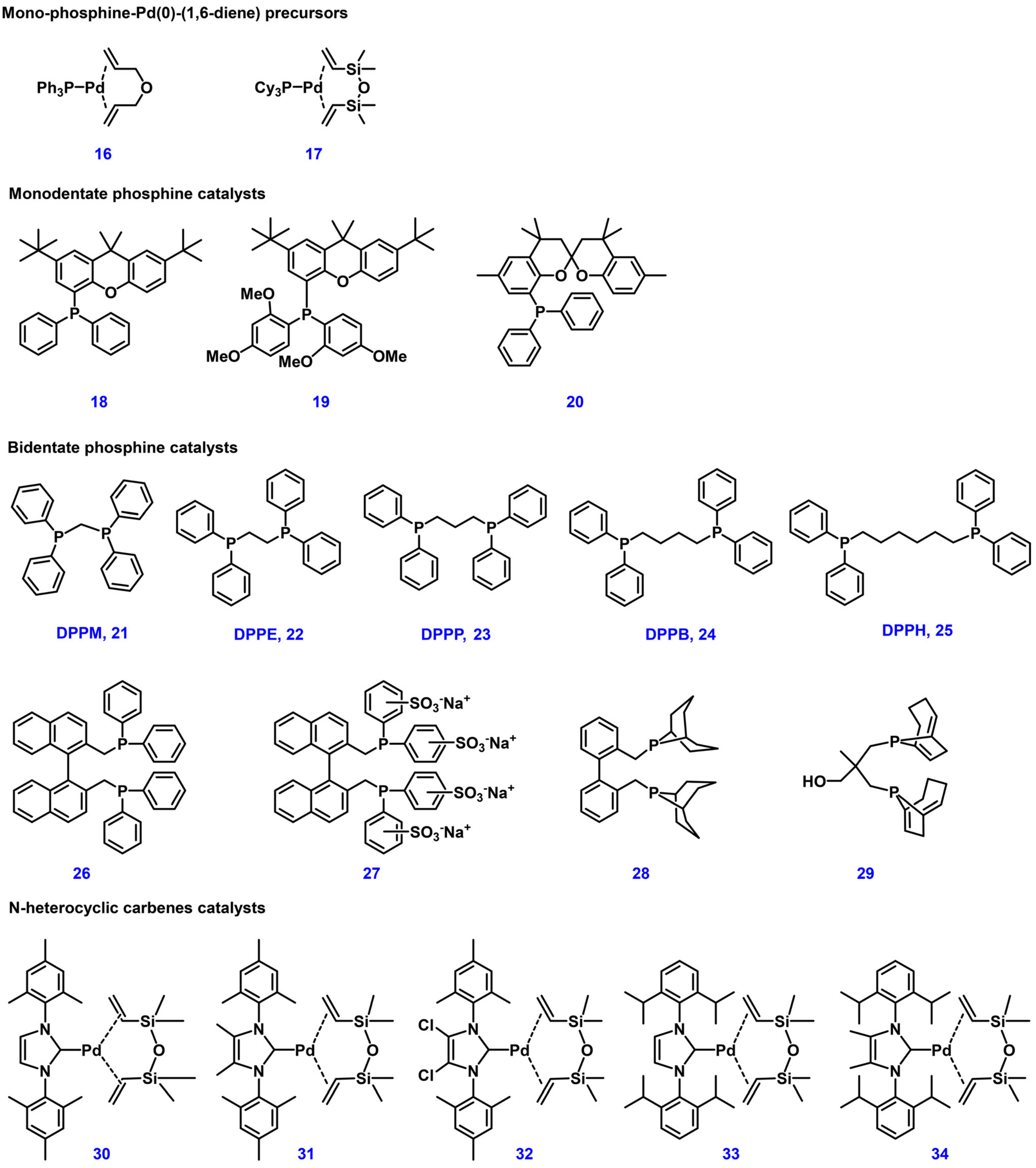


Fig. 4 Other ligand development for the palladium-catalyzed telomerization of 1,3-butadiene with methanol.

source of 1,3-butadiene (C4 crack = 42% 1,3-BD, 25% isobutene, 16% 1-butene, 5% 2-butene, 5% isobutane and 7% others). This system has been utilized by Evonik on a continuous pilot plant scale with a capacity of tons in Marl, Germany.[38,119]

In addition to the studies of conditions and catalysts, other aspects, including catalyst recovery, two-phase production systems, continuous reaction in loop reactors, ionic liquids as solvents, *etc.*, have been studied by various research groups in detail.[35,36,120] Similar to the Dow process, several major companies have also investigated the expansion of nucleophiles. For instance, Shell developed the telomerization of 1,3-butadiene with acetic acid.[121,122] Evonik reported the telomerization of 1,3-butadiene with formic acid,[123,124] giving a

Table 1 Comparison between *N*-heterocyclic carbene and phosphines for the telomerization of 1,3-BD with MeOH

Entry	Ligand	$Pd(OAc)_2$ (mol%)	*T* (°C)	MOD yield (%)	Chemoselectivity[b] (%)	Linear : branched	TON
1[a]	PPh_3	0.001	90	79	90	12 : 1	78 700
2[c]	PPh_3	0.001	70	26	87	24 : 1	26 000
3[a]	PPh_3	0.001	50	2	—	13 : 1	2000
4[a]	P^nBu_3	0.001	90	57	90	10 : 1	57 000
5[a]	17	0.001	90	60	77	10 : 1	60 000
6[a]	30	0.001	90	≥98	99	36 : 1	98 000
7[a]	30	0.001	50	57	>99	82 : 1	57 000
8[a]	30	0.00033	90	89	98	41 : 1	267 000
9[a]	30	0.00005	90	77	99	49 : 1	1 540 000
10[c]	30	0.001	70	96	>99	49 : 1	96 000
11[c]	31	0.001	70	93	99	49 : 1	93 000
12[c]	32	0.001	70	96	>99	49 : 1	96 000
13[c]	33	0.001	70	90	97	12 : 1	90 000
14[c]	34	0.001	70	2	—	10 : 1	2000

[a] Conditions: 1.0 mol% NaOH, methanol/1,3-butadiene = 2, 16 h. [b] Chemoselectivity = MOD/product mixture × 100%. [c] Conditions: Pd loading = 0.001 mol%, 16 h, 1.0 mol% NaOMe, methanol/1,3-butadiene = 2.

formate that can be used for the decarboxylation process to produce octa-1,7-diene as a 1-octene precursor.[125]

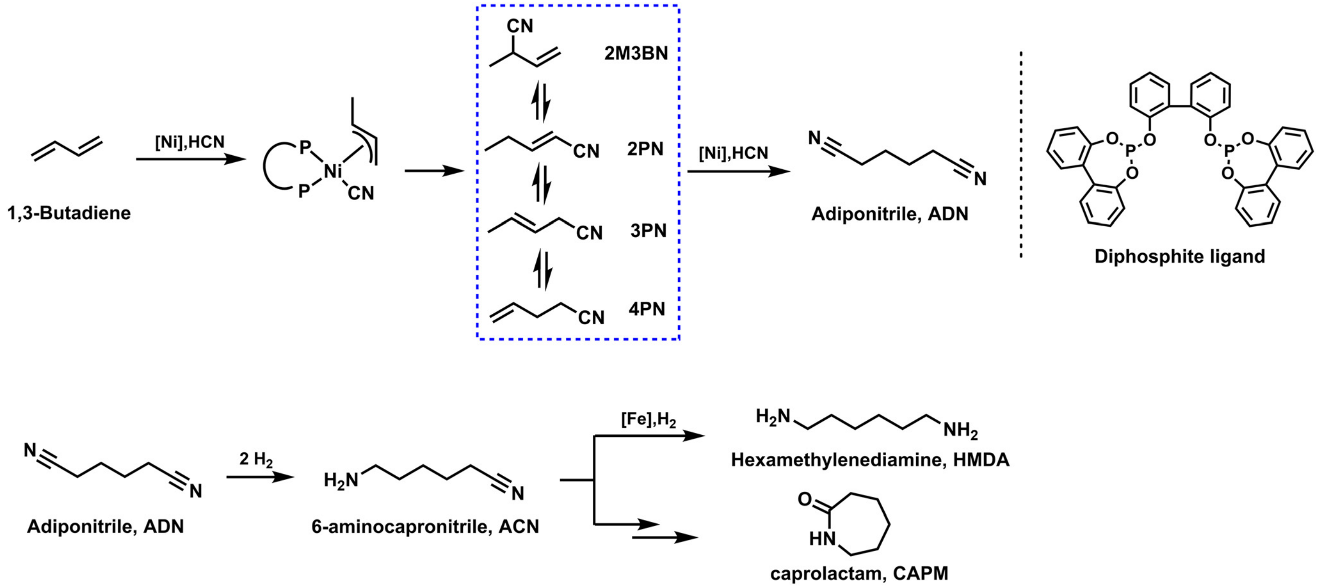
2.2 1-Octanol *via* telomerization with water (Kuraray process)

Compared with telomerization with methanol, the telomerization process with water as a nucleophile is more challenging. Nevertheless, the production of 2,7-octadien-1-ol by telomerization of 1,3-butadiene with water is also a very attractive process. Analogously to the aforementioned Dow process, 1-octanol as target chemical can be obtained from 1,3-BD *via* initial telomerization and subsequent hydrogenation of 2,7-octadien-1-ol. This specific telomerization reaction was first reported by Atkins in 1970.[126] Thereafter, the process has been studied extensively by industrial companies, such as Kuraray,[127–130] BASF,[131,132] Arkema[133] and Mitsubishi.[134,135] Representatively, Kuraray has implemented this process in production in Japan (>5000 T annually).[136] Crucial for the success of this process is the reaction of 1,3-butadiene with water in a basic (pH >7) aqueous sulfolane solution, which contains the palladium catalyst, a phosphonium salt, *e.g.* 2-(diphenylphosphino) benzenesulfonic acid sodium, as precursor of the phosphine ligand, and carbonate or bicarbonate or tertiary amines.[137]

In contrast to the telomerization of 1,3-butadiene with methanol, the one with water is positively influenced by the presence of carbon dioxide.[138,139] Surprisingly, carbon dioxide can effectively inhibit the here unwanted dimerization process of 1,3-butadiene. Even more, an effective concentration of carbon dioxide can accelerate the progress of telomerization and improve the selectivity of the linear product. Based on these observations, Kuntz and co-workers developed a reaction protocol that uses carbonate instead of carbon dioxide to avoid pressure equipment.[140,141] Finally, it is worth mentioning that Monflier and co-workers described a positive effect on related telomerization reactions using a cationic surfactant instead of organic solvent.[70,142]

2.3 Production of adiponitrile by double hydrocyanation reaction of 1,3-butadiene

Another industrially important catalytic conversion of 1,3-butadiene with an annual output of one million tons is the DuPont adiponitrile (ADN) process.[143] ADN is a central chemical intermediate not only used to manufacture polyamides[144,145] but also widely used to produce 1,6-hexanediamine (as shown in Scheme 2),[146] adipic acid, and adipamide as well as several pharmaceutical and agricultural products. Originally in industry, 1,4-dichloro-2-butene derived from the chlorination of 1,3-butadiene was used as a precursor for the synthesis of adiponitrile, which was then further reacted with cyanide salts to produce adiponitrile. Considering the strong corrosiveness of chlorine and the high waste contamination of the process, simpler processes with better atom economy were extremely desired.[147,148] In 1954, Arthur and co-workers first discovered the $Co_2(CO)_8$-catalyzed hydrocyanation of olefins with HCN as an economical source of nitriles.[149] Further, Drinkard presented a tailored $Ni((ArO)_3P)_4$ catalyst system for the hydrocyanation reaction with higher activity.[150] Researchers therefore shifted their interest to the double hydrocyanation of 1,3-butadiene, which in principle allows for 100% atom economy. The hydrocyanation of 1,3-butadiene proceeds through relatively stable π-allyl nickel cyanide intermediates. The isolation of the 16-electron complex $[Ni(P(O\text{-tolyl})_3)]$ containing a bulky monophosphite provided a rational beginning to study how various aspects of the catalytic system interact with nickel.[149] The formation and decomposition of nickel hydrides and specifically $[HNi(CN)L_3]$ in solution was investigated in detail by Tolman by ^1H and ^{31}P NMR spectroscopy.[151] It should be noted at this point that the research performed in this route has led to several important discoveries in organometallic chemistry.[149,150] At the same time, DuPont put this process into production for the first time in 1971.[151] The DuPont process can be basically described as follows: in the presence of Ni catalyst, 1,3-butadiene and HCN are quickly converted to a mixture of pentenenitriles (linear to branched isomers in a 2 : 1 ratio). It is



Scheme 2 Simplified scheme for the synthesis of adiponitrile from 1,3-butadiene.

worth noting that experiments showed that electronic effects play only a minor role compared to steric effects in determining the catalytic activity and selectivity of the Ni complexes investigated. Therefore, monodentate phosphites were replaced by bulky bidentate ligands, which create catalysts superior in terms of activity and efficiency. Subsequently, various biphenol-based diphosphate Ni^0 complexes were synthesized and applied in butadiene hydrocyanation. Such Ni catalysts, although less selective, showed a catalyst turnover at least four times higher than that of the industrially applied DuPont system [Ni(P(*O*-tolyl)$_3$)]. In order to obtain the selective product, it is important to carry out the fast isomerization of different intermediates. In this respect, the addition of Lewis acids, such as $ZnCl_2$, facilitates the isomerization of 2M3BN. The kinetic preference for the isomerization of an internal alkene to a terminal alkene contrast with the thermodynamic preference for the conjugated isomer 2PN. The isomerization of the internal alkene 3PN to the terminal alkene 4-pentenenitrile (4PN) is a decisive step in the hydrocyanation of 3PN. With the help of an additional Lewis acid, the branched by-products can be reversibly isomerized into the terminal olefin isomer. In general, through the above processes, first, the hydrocyanation reaction of 1,3-butadiene led to the desired 4-pentenenitrile with >90% selectivity.[152] Next, 4-pentenenitrile reacted at a second stage with HCN at lower temperature (about 50 °C) to produce adiponitrile, typically in 50% yield and 92% linear selectivity.[153]

3 Potential uses of 1,3-buatdiene in the future

3.1 Adipates *via* catalytic carbonylation of 1,3-butadiene

Adipates and adipic acid are core intermediates of the polymer industry. About 75% of the total adipate production is consumed by nylon manufacturing.[154] The current global annual output of adipates exceeds 5 000 000 tons with an average growth rate of 4%, whose market size is expected to exceed USD 11 billion by 2025.[155,156] A main problem in adipate manufacture is the environmental pollution by waste acid exhaust and nitrous oxide gases. For example, in 2016, the production of adipic acid alone released 20% of the 37.3 million metric tons of all gas emissions (CO_2, CH_4 and NO_2) by the chemical industry in the U.S.[157] Notably, the global warming potential of the major nitrous oxide emissions is 300 times higher than that of carbon dioxide.[158] In order to balance the growing demand for adipates and reduce the negative impact on the environment, greener and atom-economical chemical processes need to be implemented urgently.[159]

In this regard, metal-catalyzed carbonylation reactions of 1,3-butadiene to adipates are promising alternative ways for manufacturing versatile adipates, among which the linear selective dihydroformylation of 1,3-butadiene is of great interest to industry and academic laboratories.[160–162] However, this double hydroformylation reaction is extremely challenging due to slow reaction rate, regioselectivity problems, and low product stability, especially in basic or acidic media, inevitably forming a large number of unwanted by-products. Simultaneously, the aldol addition reactivity of aldehyde intermediates leads to incompatibility between this process and typical industrial distillation techniques.[163] Therefore, in 2016 Hofmann and co-workers developed an isomerizing hydroformylation process in which pentenal intermediates were converted to acetates *in situ* to avoid side products.[164] Fundamental insights into the reaction pathways of this rhodium-catalyzed dihydroformylation were obtained; the adipaldehyde selectivity was found to be strongly dependent on the bite angle and the backbone structure of the ligand used in the reaction.[165] Regarding state-of-the-art catalysts, ligand **35** provided 50% yield of adipic aldehyde from 1,3-butadiene, or 93% yield starting from 4-pentenal

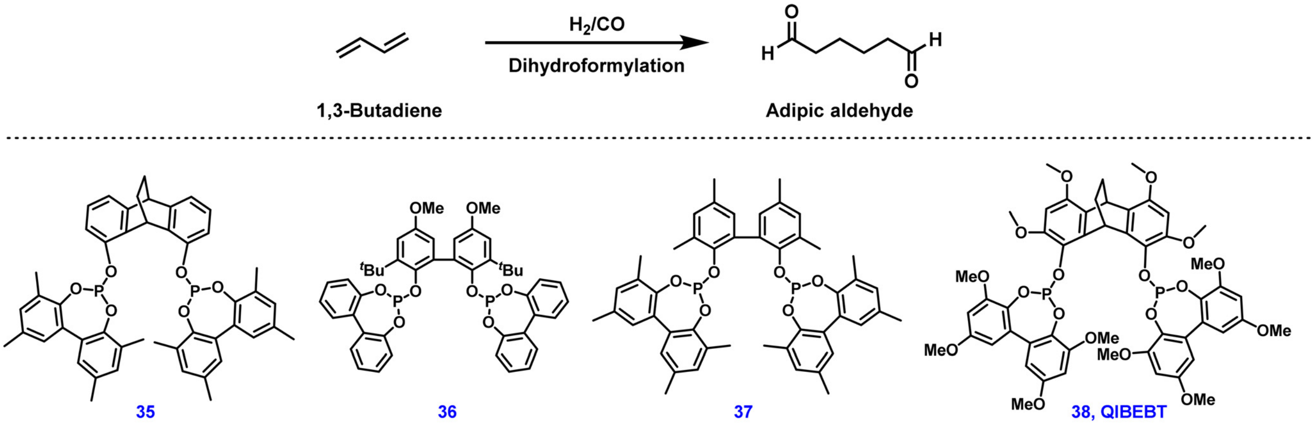


Fig. 5 Representative ligands for linear selective dihydroformylation of 1,3-butadiene.

(Fig. 5).[166] Recently, QIBEBT-phosphite **38** developed by Yang and co-workers exhibited a slightly improved yield of 54% to adipic dialdehyde from 1,3-butadiene.[167] However, unfortunately these results seem to be still insufficient for industrial applications.[168]

Besides the dihydroformylation process, carbonylation reactions of 1,3-butadiene utilizing alcohol/water as nucleophiles to synthesize adipates directly constitute also highly attractive reactions to both academia and industry. Clearly, these 100% atom-economic reactions would make the production of adipate/acid more environmentally friendly (Fig. 6). However, again such catalytic processes also face various challenges: (i) the catalyst should mediate two diverse carbonylation processes continuously, which places elevated demands on the activity and stability of the catalyst; (ii) in order to obtain a linear dicarbonylation product, the reaction intermediates must undergo a particularly thermodynamically unfavorable isomerization; and (iii) various side conversions such as telomerization, hydroalkoxylation, carboxytelomerization and (co)polymerization must be suppressed to improve the yield of adipates.[183]

Back in 2002, some of us uncovered a suitable alkoxycarbonylation of 1,3-dienes using a palladium-based catalyst in combination with the ligand DPPB **24**, resulting in 3-methyl pentanoate with a yield of 69% (Fig. 7a).[169] By 2014, it was found that under similar conditions, the yield of 3-methyl pentanoate could be increased to 85% under acid-free conditions when Xantphos was used as the ligand.[170] Afterwards, diverse site-selective monocarbonylation reactions through the regulation of ligands were described in 2015. Detailed experimental studies have shown that different catalysts induce various reaction pathways. As an example, Xantphos selectively catalyzed the production of β,γ-unsaturated esters, while 2-pyridyl-diphenylphosphine **40** preferably led to α,β-unsaturated ester products (Fig. 7b). The above-described processes realized the conversion of 1,3-butadiene to methyl-3-penetenoate in good yields. In addition, chemical procedures for the conversion of methyl-3-pentenoate to adipic acid/esters

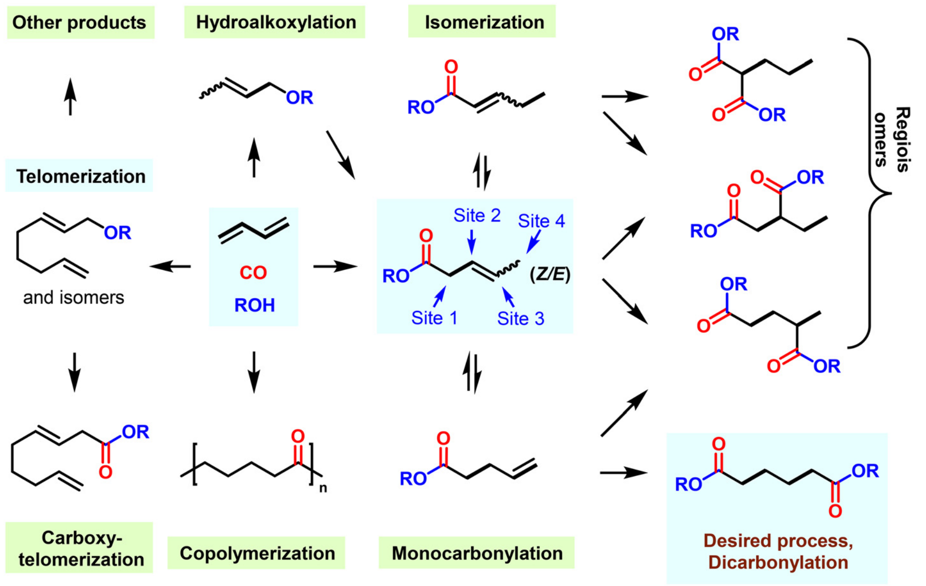


Fig. 6 The complex reaction network for the synthesis of adipates from 1,3-butadienes.

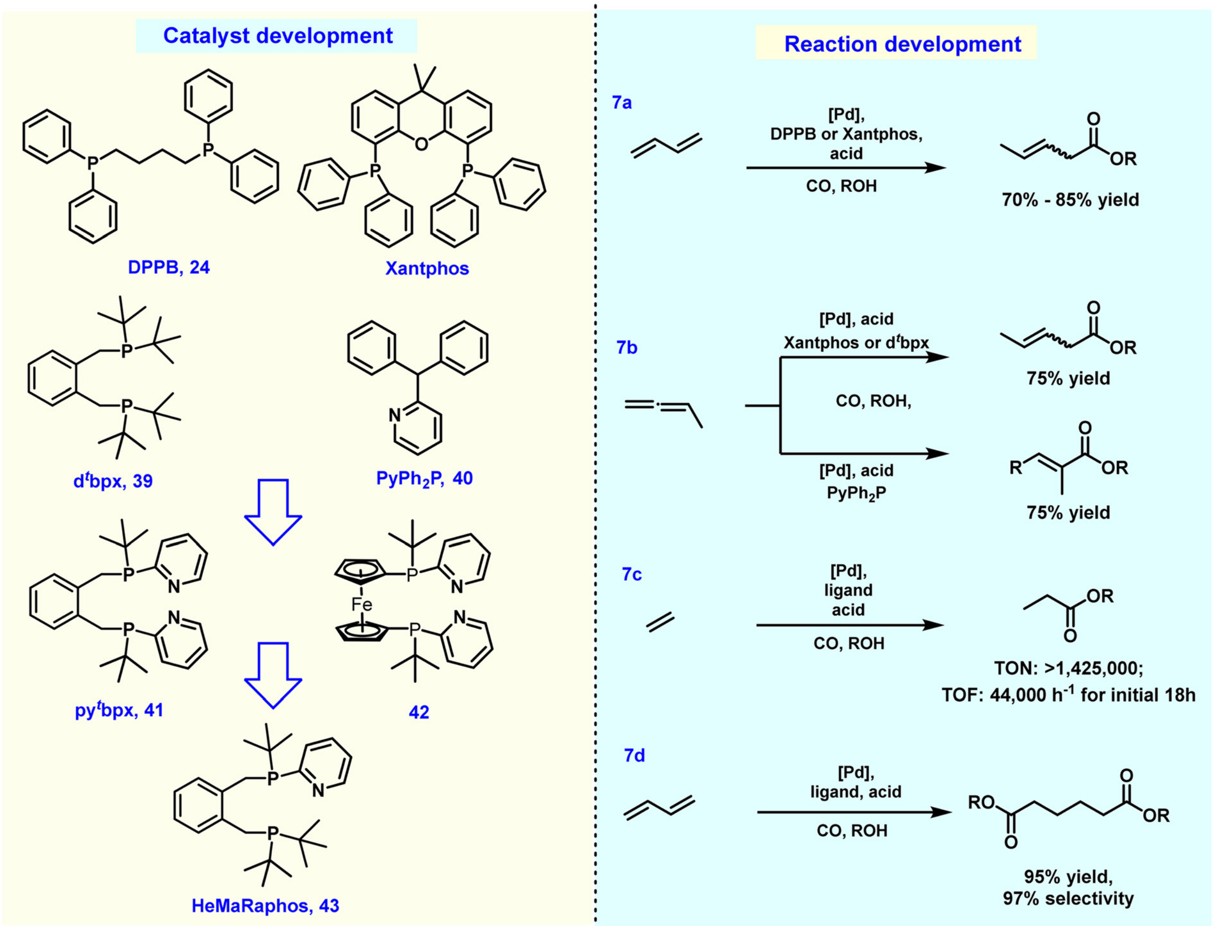


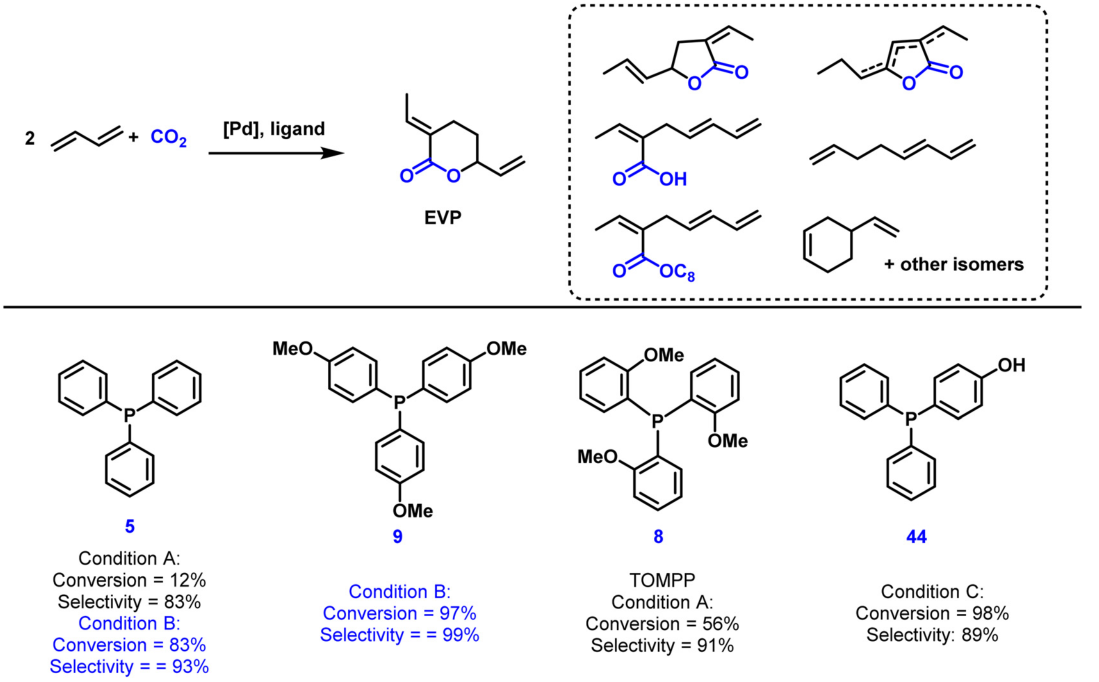
Fig. 7 Ligand advancements and reaction development for palladium-catalyzed carbonylation of 1,3-butadiene.

have also been established in >90% yield and about 80% selectivity, but the most prominent disadvantage is that the related processes are very complicated and involve multi-step processing.[171–174] Earlier in 1987, Drent and co-workers showed elegantly that the use of the ligand 2-pyridyl-diphenylphosphine **40** allows for exceptional activity in the carbonylation of propylene. It was speculated that the active catalytic species was stabilized by the hemilabile P–N coordination of the ligand.[175] Inspired by Drent's work, some of us introduced the 2-pyridyl unit into various bidentate phosphines. Among these obtained ligands, 1,2-bis((*tert*-butyl(pyridinyl)phosphanyl)methyl)benzene (py^{t}bpx, **41**) exhibited superior activity in carbonylation of ethylene (Lucite α-process). DFT calculations on the elementary steps showed that the pyridyl group is immediately protonated, which promoted the formation of the active [Pd–H] species (Fig. 7c). After the insertion of alkene and carbon monoxide, the corresponding Pd–acyl species was reversibly formed. Notably, the formed intermediate is stabilized by hemilabile coordination of the pyridyl group. Then, metal–ligand cooperation significantly increases the rate of alcoholysis of the acyl palladium complex.[176] This finding greatly improved the efficiency of the overall catalyst system, which allowed a general alkoxycarbonylation of olefins including demanding tetrasubstituted ones. As an example, the efficient carbonylation of ethylene exhibited a TON of >1 425 000 and selectivity of >99%.[177]

From 2000 to 2008, Drent and co-workers at Shell developed interesting two-step processes for the synthesis of adipic acid. Here, pentenoic acids were produced in the first step and then distilled out from the reaction system and exposed to a second carbonylation stage with a higher concentration of water as nucleophile. This second step involved an induction period of more than 5 hours. Although such a continuous process simplified the relevant steps and operations, due to the altered conditions of both steps, the overall process still has some limitations such as adjustment of reaction medium, charging/discharging of carbon monoxide gas and adding additional water.[178–181] In this respect, the direct conversion of 1,3-butadiene to adipates would be advantageous. For this purpose, the multifunctional catalyst HeMaRaphos **43** was designed, which integrated two basic backbones controlling reactivity and selectivity: the steric and electron-rich di-*tert*-butylphosphino portion could assist fast isomerization of C═C bonds, while the *tert*-butyl-2-pyridyl phosphino group enabled the generation of the active Pd–hydride complex and enhanced the key alcoholysis step. Indeed, by utilizing the Pd–HeMaRaphos catalyst, an excellent yield of 95% and linear selectivity of 97% was obtained for the synthesis of adipates by dicarbonylation of 1,3-butadiene (Fig. 7d). In addition, the catalytic system was also effective for the conversion of numerous other nucleophiles.[177,182–185] With respect to the industrial realization of such a process, it is important to note that apart from the technical success, the implementation of such a methodology will strongly depend on the development of the different feedstock prices (*e.g.* benzene *versus* 1,3-butadiene).

3.2 Telomerization of 1,3-butadiene with CO_2 to EVP

Since the beginning of the industrial revolution, the continuously increasing emissions of carbon dioxide have been a major contributor to global warming. The resulting problems urge a need to develop more sustainable technologies to realize a circular economy for human society. Clearly, reducing CO_2 releases are a core issue requiring many efforts. In this regard, using carbon dioxide as an eco-friendly and available reagent for chemical transformations provides the possibility to synthesize a variety of useful chemical products. However, due to its most oxidized state and its inertness, the utilization of carbon dioxide usually requires a large amount of energy input.[186–188] This energy input can be provided externally, *e.g.* by heating, or intrinsically by using "energy-rich" substrates. As an example for the latter case, here we present the telomerization of 1,3-butadiene with CO_2 as a straightforward route towards interesting fine chemical building blocks (*e.g.*, 3-ethyl-6-vinyltetrahydro-2*H*-pyran-2-one, EVP). This reaction was first explored by Inoue and Musco in the 1970s.[189,190] After that, to improve the reaction efficiency, a large number of palladium-based catalytic systems have been developed.[191–195] As a more recent representative, some of us presented a Pd_2-dba_3/TOMPP system requiring no complex reaction systems or expensive additives and catalyzed the formation of the desired EVP in 67% yield (Scheme 3).[191] Recently, Dong and co-workers developed the triphenylphosphine-based ligand **44** as a promoter-free telomerization system, which achieved remarkable improvements of both activity (TON up to 4540) and selectivity (EVP and δ-lactone isomers up to 97%) by simply introducing a hydroxyl group into the PPh_3 ligand.[195] Specifically, the activity depends on the position of the hydroxyl group. In contrast to the inactivity of catalysts with *o*-hydroxyl-substituted triphenylphosphine, catalysts with *p*-hydroxyl-substituted ligands manifested high activity with good selectivity towards the CO_2-incorporated δ-lactone. These results validated that embedding one weak coordination phenolic hydroxyl group into the parent PPh_3 ligand could dramatically improve the activity of the resulting Pd catalyst. In addition, Bay reported a very efficient and selective system in 2018 by using $Pd(OAc)_2$ and tris(*p*-methoxyphenyl)phosphine **9** as catalysts in the presence of *p*-hydroquinone and *N*,*N*-diisopropylethylamine as additives. A high catalyst turnover number of 4500 and



Condition A:
Conversion = 12%
Selectivity = 83%
Condition B:
Conversion = 83%
Selectivity = = 93%

Condition B:
Conversion = 97%
Selectivity = = 99%

TOMPP
Condition A:
Conversion = 56%
Selectivity = 91%

Condition C:
Conversion = 98%
Selectivity: 89%

Conversion = lactones/1,3-butadiene, selectivity = EVP/lactones. condition A: 1,3-butadiene = 50-60 mmol; $Pd(acac)_2$ (0.06 mol%), ligand (0.18 mol%), CO_2 (1.5-2.0 equiv.), MeCN as solvent. 80 °C, 20h. condition B: 1,3-butadiene = 120 mmol, $Pd(OAc)_2$=0.01 mmol%; phosphine/Pd=3/1; p-hydroquinone = 0.25 mol%; N,N-diisopropylethylamine = 0.5 mmol%; 4 mL of acetonitrile; 30 bar of CO2; 70 °C; 5h. condition C: 1,3-butadiene = 1.0 mol; $Pd_2(dba)_3$ (0.01 mol%), ligand (0.06 mol%), CO_2 (1.36 equiv.), MeCN as solvent. 80 °C, 8 h.

Scheme 3 Telomerization of 1,3-butadiene with CO_2 and representative catalytic systems.

excellent selectivity of 96% for EVP were achieved after 5 hours at 70 °C.[196] Currently, EVP is being synthesized on a mini-plant scale,[197] which indicates the potential of further upscaling to realize industrialization, especially with the current emphasis on carbon neutrality.

Since EVP has multiple functional groups, it can be transformed into a variety of interesting fine chemicals and monomers for polymers.[198,199] For example, hydrogenation to 2-ethylheptanoic acid, which is used widely not only in lubricants but also as a stabilizer for PVC, has been described.[200] In addition, the transformation to synthesize high-performance polymers using EVP as a monomer has received attention in recent years.[201–205] For example, Nozaki reported the first homopolymerization of EVP in 2014 *via* radical polymerization.[206] A novel polymer with lactone repeating units was obtained (M_n = 5.7 kg mol^{-1}, $Đ$ = 1.3), which was later used for post-polymerization modifications by hydrolysis or aminolysis to obtain multifunctional materials.

3.3 Other chemical transformations

In addition to the aforementioned processes, 1,3-butadiene undergoes numerous other interesting transformations. For example, cyclodimerization of 1,3-butadiene is highly attractive from an industrial point of view.[207] The current process makes use of a nickel(0)/phosphine catalyst system.[208] The obtained cyclooctadiene (COD) can react with ethylene *via* olefin metathesis to produce 1,5-hexadiene, which is a valuable intermediate, *e.g.* to produce suberaldehyde by hydroformylation. On the other hand, COD can undergo selective hydrogenation to produce the important chemical cyclooctene or direct hydrogenation to cyclooctane, which is further oxidized to suberic acid that is used as a nylon 6/8 precursor.[209] Similarly, vinylcyclohexene (VCH) can also be obtained by Diels–Alder reaction from two molecules of 1,3-butadiene. VCH has been further converted into ethylbenzene or styrene. Interestingly, in contrast to the synthesis of COD under Ni(0) catalysts, two molecules of 1,3-butadiene can produce also divinyl cyclobutane in significant yields when a Ti-bipyridyl catalyst is used.[210]

Epoxidation of 1,3-butadiene has been developed by Eastman Chemical as an efficient route to synthesize 3,4-epoxy-1-butene under mild conditions using a silver-based catalyst and air as oxidant.[211,212] The resulting epoxide has been directly converted to 1,4-butanediol further on, or thermally rearranged to 2,5-dihydrofuran. In addition, numerous academically interesting functionalizations of 1,3-butadiene have been reported in recent years, including hydroboration,[213–215] hydrosilylation,[216–218] hydroamination,[219–222] *etc.* The exploration of these novel methodologies might provide more possibilities of converting 1,3-butadiene into industrially relevant chemicals in the future.

4 Summary and outlook

1,3-Butadiene is a major aliphatic feedstock for the chemical industry and the most important 1,3-diene. Its efficient and selective conversion towards a variety of products continues to attract significant attention from many researchers in both the chemical industry and academia. Its specific chemical structure allows for many unique and efficient transformations, which laid the foundation for its irreplaceable chemical value. In this review, we summarize currently used catalytic transformations of 1,3-butadiene from the perspective of industrial production apart from polymerization. Specifically, we focus on the application of homogeneous catalysts and provide representative examples for the readers. For example, palladium-catalyzed telomerization of 1,3-butadiene offers versatile platform chemicals for the production of 1-octene, 1-octanol, and higher-value EVP lactones through the participation of diverse nucleophiles. Meanwhile, efficient difunctionalization of 1,3-butadiene provides a straightforward access for the synthesis of various polymer precursors, including adiponitrile, adipaldehyde, and adipic diesters. For all these chemical processes, the development of efficient catalytic systems plays a key role to enable atom-economic and selective processes. Although significant progress has been made in various conversions of 1,3-butadiene, further advancements are needed in many areas to come up with new practical applications. In this respect, artificial intelligence technologies to predict the performance of a ligand in an efficient way can help to develop improved systems more efficiently. Indeed, currently machine learning and artificial intelligence applications are receiving a boost in performance and information from both academic research and industry. Machine learning might become an outstanding tool to accelerate catalyst discovery by enabling extensive prediction of immeasurable compositions, driving exploration to quickly discover the performance optima, and quantitatively considering the structure and activity–structure–property relationships. Therefore, instead of a traditional synthesis–structure–property relationship based on sometimes a not clear image of the catalytic mechanism, data-focused mathematical models may progressively understand and facilitate property prediction, guided optimization, and fundamental understanding of catalysts. In the context of a sustainable chemical industry a key issue for the future use of 1,3-butadiene will be its origin. Cleary, at present the vast majority of 1,3-butadienes is fossil based as a by-product of naphtha cracking. However, there is increasing interest in producing this feedstock from biobased ethanol with lower environmental impact. If this will be realized, we believe that 1,3-butadiene will be even more widely employed in the chemical industry of the future to produce a variety of intermediates for daily life products.

Author contributions

J. Y. and P. W. contributed equally. J. Y. and M. B. conceived this review. M. B., H. N. and R. J. planned parts of the here described research. J. Y., P. W. and M. B. wrote the paper.

Conflicts of interest

The authors declare no conflict of interest.

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