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Development of Palladium–Carbene Catalysts for Telomerization and Dimerization of 1,3-Dienes: From Basic Research to Industrial Applications

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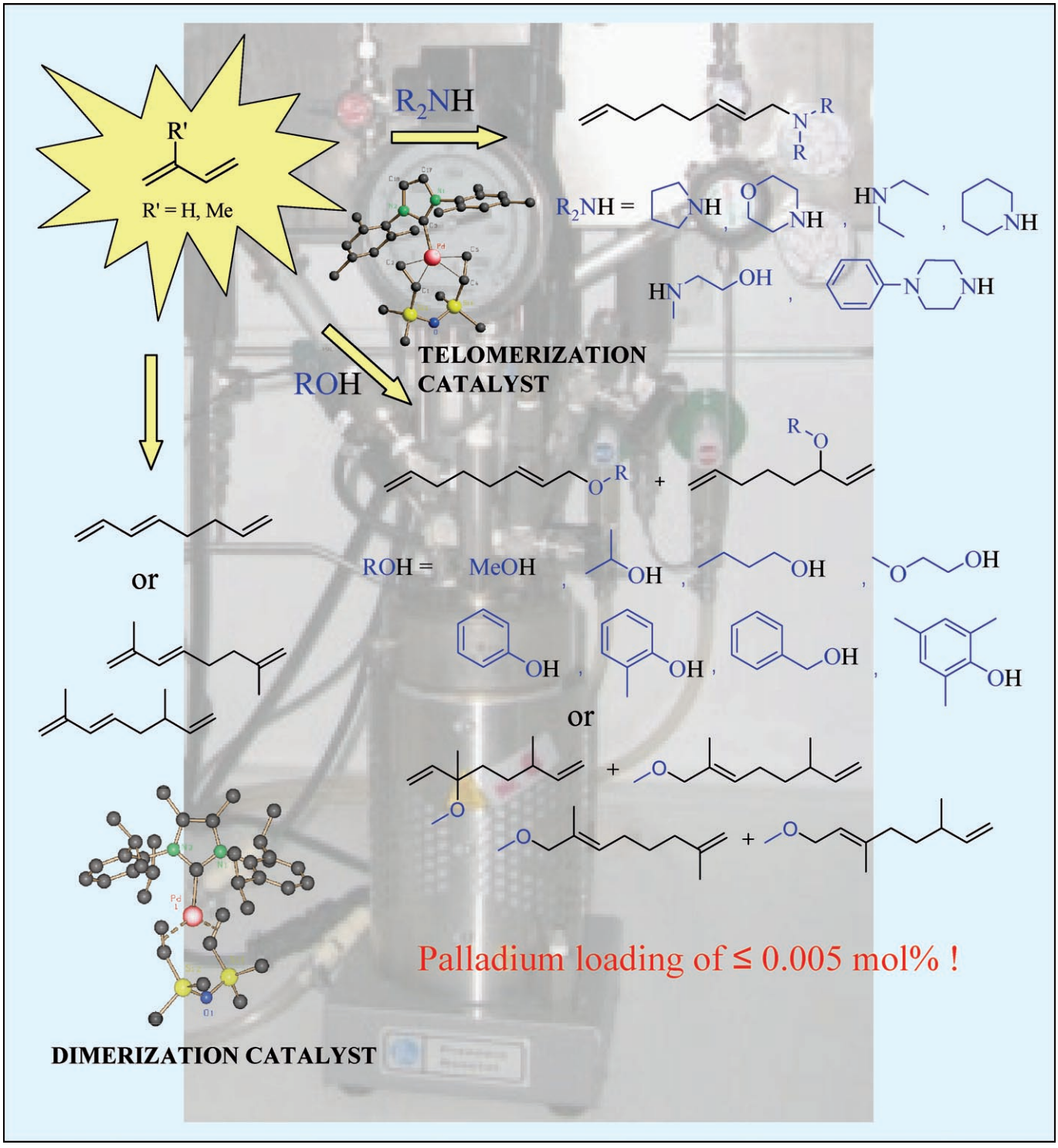
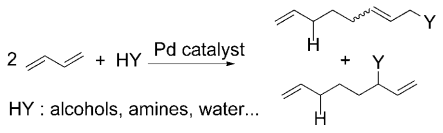


Abstract: The following account summarises recent developments in the area of palladium-catalysed telomerisation and dimerisation reactions of 1,3-dienes. The most active types of catalyst, palladium–carbene complexes, were tested in pilot plant and proved to be industrially viable.

Keywords: dimerization · green chemistry · N-heterocyclic carbenes · palladium · telomerization

Introduction

The development of new and improved processes that allow efficient access to important chemical products from cheap and available starting materials represents a major challenge for chemists in industry and academic institutions. In this respect the concept of green and sustainable chemistry has become as important as economical considerations. It is generally agreed that state-of-the-art processes should have an optimal atom efficiency, easily available starting materials, minimum amount of reaction steps, and thus minimisation of workup procedures, solvents, energy and so forth. Clearly, the production of hazardous products and toxic or dangerous waste has to be avoided. Undeniably, catalysis represents one of the most powerful tools to conciliate both economical and "green" requirements.[1] For example, it is well established that the use of catalytic amount of palladium complexes permits the efficient creation of C–C bonds in coupling reactions.[2] Amongst the different palladium-catalysed coupling reactions studied in our group, the so-called telomerisation reaction constitutes an interesting dimerisation of 1,3-dienes in the presence of an appropriate nucleophile, which furnishes substituted oligomers. Due to its low price and availability the most important starting material for telomerisation reactions is 1,3-butadiene. In this case a variety of octyl derivatives can be easily obtained with 100% atom efficiency (Scheme 1).[3] In addition, reactions



Scheme 1. Telomerisation of 1,3-butadiene with nucleophiles.

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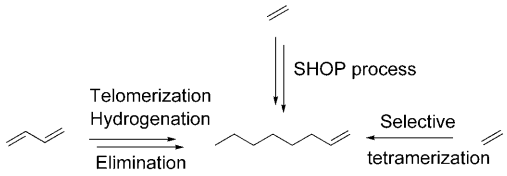
of isoprene have gained some importance due to the connection to natural terpenes.

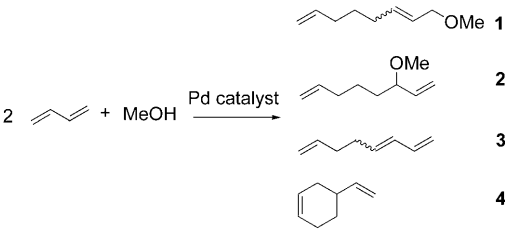
In the last decade, an enormous interest exists towards the development of novel cost-efficient synthesis of 1-octene.[4] This concern is mainly based on the increasing industrial use of 1-octene as co-monomer for polyethylene.[5] In this respect also significant attention is attributed to the selective dimerisation of 1,3-butadiene with methanol as part of a potential route to 1-octene (Scheme 2 and in more detail see Scheme 14 later).



Scheme 2. Potential industrial routes to 1-octene.

The main advantages of this reaction are the low price and the availability of methanol and 1,3-butadiene, which makes it preferable to the ethylene route with respect to raw material costs.[6]

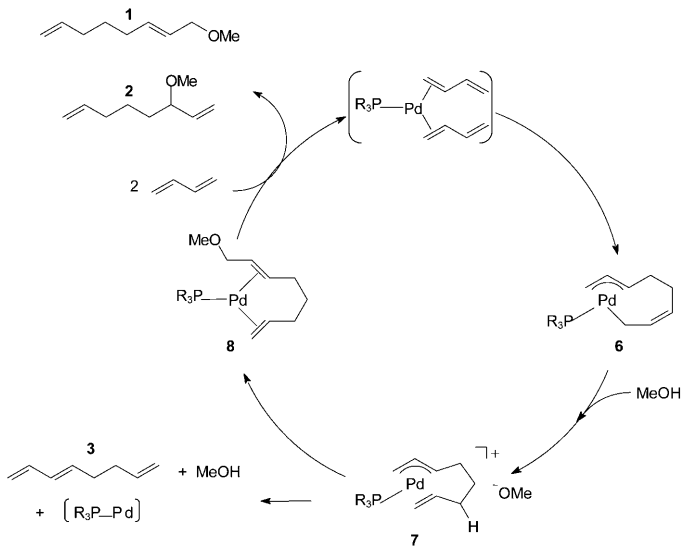
As shown in Scheme 3 the major product of the telomerisation of 1,3-butadiene and methanol is 1-methoxyocta-2,7-diene (**1**), which might be in addition a useful precursor in



Scheme 3. Telomerisation of 1,3-butadiene with methanol.

industry as intermediate for plasticiser alcohols,[7] solvents, and corrosion inhibitors.[8] The by-products, mainly the 3-substituted methoxyocta-1,7-diene(**2**), 1,3,7-octatriene (**3**; formed by the linear dimerisation of butadiene) and 4-vinylcyclohexene (**4**; formed by the Diels–Alder reaction of two molecules of butadiene) are also of some commercial interest. Hence, it is not surprising that telomerisation of 1,3-butadiene with MeOH has been the subject of intensive research in both academic and industrial laboratories.[9] Based on elegant experimental studies performed by Jolly and coworkers, different catalytic intermediates of the telomerisation of 1,3-butadiene with methanol were identified and characterised. The catalytic cycle for this reaction is commonly accepted and shown in Scheme 4.[10]

Initially, oxidative coupling of two molecules of 1,3-butadiene at a low-coordinated Pd^0 centre produces the Pd^{II}–



Scheme 4. Proposed catalytic cycle for the telomerisation of 1,3-butadiene with methanol.

($^1\eta$-$^3\eta$-octadiendiyl) complex **6**. Protonation by methanol at the C6 atom of the C_8 chain affords the methoxy–Pd^{II}–(η^2-η^3-octadienediyl) species **7**. Subsequent addition of the methoxy group to the allylic C1 position forms the 1-substituted product **1** via **8**. On the other hand, nucleophilic addition at the C3 position leads to the 3-substituted product **2**. If nucleophilic attack does not take place on the η^2-η^3-intermediate **7**, then 1,3,7-octatriene (**3**) is produced by β-H abstraction at the C4 position.

Table 1. Telomerisation of 1,3-butadiene and methanol: influence of phosphane ligands on the catalyst productivity.[a]

	Catalyst	Pd cat. [mol%]	Butadiene conv. [%]	Yield [%] 1	2	3	TON 1+2+3
1	$Pd(OAc)_2$	2×10^{-3}	4	0.6	0	0.5	550
2	$Pd(OAc)_2$/3 PPh_3	1.8×10^{-3}	58	47	2.5	5.4	30500
3	$Pd(OAc)_2$/3 PCy_3	2×10^{-3}	22	16	1.5	4.5	11000
4	$Pd(OAc)_2$/3 P(*o*-tTol)$_3$	2×10^{-3}	9	7	0.3	1.7	4500
5	$Pd(OAc)_2$/3 H-TTPTS[b]	2×10^{-3}	5	2.5	0	0.4	1450
6	$Pd(OAc)_2$/5 dppb[c]	2×10^{-3}	7	0.5	0	6	3250
7	$Pd(OAc)_2$/3 dppdmo[d]	2×10^{-3}	0.5	< 0.1	0	< 0.1	< 100

[a] Reaction conditions: 1.0 mol butadiene, 2.2 mol methanol, 2.0 mmol NEt_3, 90 °C, 2.5 h. [b] TTPTS: triphenylphosphane trisulfonate. [c] dppb: 1,4-bis(diphenylphosphino)butane. [d] dppdmo: 2-(2-diphenyl-phosphinophenyl)-4,4-dimethyl-4,5-dihydrooxazole.

The Development Of More Efficient Palladium–Phosphane Catalysts

About 10 years ago, one of us (M.B.) started to investigate the telomerisation reactions. At that time a collaboration between our research group and Jochen Krause from Aventis Research and Technology (former Central Research part of Hoechst AG) was started in order to find more commercially viable catalysts for the telomerisation of 1,3-butadiene with water. This reaction is used by Kuraray for the production of 1-octanol on several thousand ton scale. To run this process on a larger scale, we were interested to improve the catalyst productivity and to understand catalyst deactivation processes. As a model reaction Frank Vollmüller (at that time a PhD student in the group of M.B.) studied the telomerisation with methanol at low catalyst loadings (10^{-2}–10^{-3} mol%). The effect of the type of phosphane used as ancillary ligand, but also the ratio Pd/PR_3, the temperature, concentration and the effect of added base was investigated. Selected results of this initial studies are shown in Tables 1 and 2.[9g]

It became clear that the reaction is considerably influenced by the nature of the phosphane ligand. The catalyst based on $Pd(OAc)_2$/3 PPh_3 was found to be the most active in this reaction, affording a high yield of the telomeric products (Table 1, entry 2). Before our work, it had been reported that the addition of reducing agents and bases like triethylamine often improves the reaction rate and/or the selectivity of the Pd-catalysed telomerisation reaction.[11] However, in our hands the addition of 100 equivalents of triethylamine had only a positive influence on the catalyst performance at short reaction time (Table 2; entries 1, 2, 5, 6, 11, 12, 15, 16). This observation, confirmed by calorimetric experiments,[9g] indicated that the addition of triethylamine only facilitates the reduction of the Pd^{II} complex producing the catalytically active Pd^0 species more rapidly.

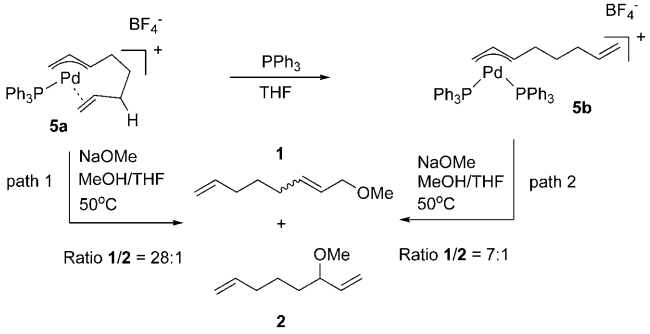
In general, increasing the Pd/PPh_3 ratio (at low Pd concentration!) and the temperature led to a significant increase in the catalyst productivity. For example an increase from 3 to 50 in the Pd/PPh_3 ratio produced an increase of turnover number (TON) from 21500 to 28000 at 50 °C, these values reaching 55000 and 70000, respectively, at 90 °C (Table 2; entries 3 and 9, 13 and 19). After 60 h a total catalyst TON of 97000 was reached with a Pd/PPh_3 ratio of 50 (Table 2, entry 20). At that time, it was the highest catalyst productivity reported for a palladium–phosphane catalyst in telomerisation reactions. It is worth noting that the chemoselectivity is significantly decreased with increasing temperature (due to the formation of **3** and **4** at 90 °C), whereas the regioselectivity (ratio **1**/**2**) usually drops with increased phosphane concentration (Table 2, entries 1–10 and 11–20).

To explain this decrease in regioselectivity with increasing phosphane concentration, mechanistic investigations on the decisive nucleophilic addition of the methoxy group, which governs the ratio **1**/**2** of the reaction, were performed by Wolfgang Mägerlein for his diploma thesis (Scheme 5).[12] Addition of an excess of sodium methoxide to the isolated

Table 2. Telomerisation of 1,3-butadiene and methanol: Catalyst productivity (TON) and activity (TOF).[a]

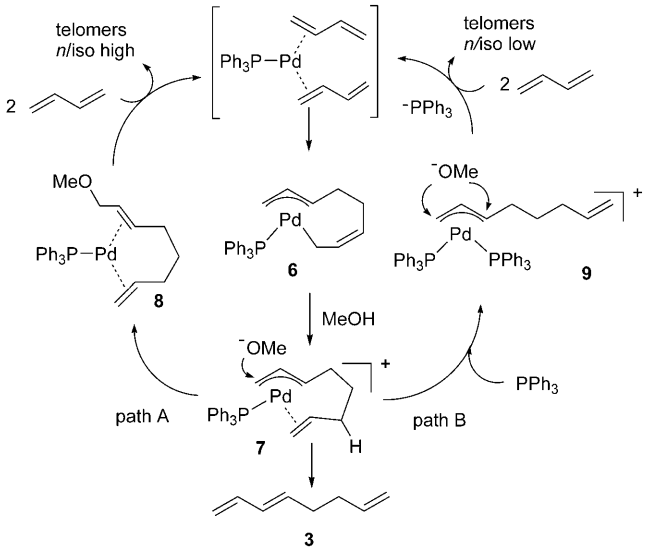
	Pd/PPh_3	Reaction conditions	TON **1+2+3**	TOF [h^{-1}]	Chemoselectivity[c] [%]	*n*/iso
1	1:3	50°C/2 h	4500	2250	97	8:1
2	1:3	50°C/2 h; 100 equiv NEt_3	6200	3100	98	8:1
3	1:3	50°C/16 h	21500	1350[b]	96	9:1
4	1:3	50°C/16 h; 100 equiv NEt_3	19000	1200[b]	95.5	9:1
5	1:10	50°C/2 h	2900	1450	98	7:1
6	1:10	50°C/2 h; 100 equiv NEt_3	3700	1850	98.5	8:1
7	1:10	50°C/16 h	17000	1050[b]	96	7:1
8	1:10	50°C/16 h; 100 equiv NEt_3	15200	950[b]	97	7:1
9	1:50	50°C/16 h	28000	1750[b]	99	7:1
10	1:50	50°C/60 h	87000	1450[b]	98	7:1
11	1:3	90°C/0.5 h	8900	17800	79	13:1
12	1:3	90°C/0.5 h; 100 equiv NEt_3	12500	25000	86	15:1
13	1:3	90°C/16 h	55000	3500[b]	66	15:1
14	1:3	90°C/16 h; 100 equiv NEt_3	59000	3700[b]	61	14:1
15	1:10	90°C/0.5 h	5500	11000	85	8:1
16	1:10	90°C/0.5 h; 100 equiv NEt_3	6000	12000	88.5	7:1
17	1:10	90°C/16 h	71000	4400[b]	66	13:1
18	1:10	90°C/16 h; 100 equiv NEt_3	75000	4700[b]	67	13:1
19	1:50	90°C/16 h	70000	4400[b]	75	7:1
20	1:50	90°C/60 h	97000	1600[b]	67[d]	7:1

[a] All experiments were carried out with a substrate ratio 1,3-butadiene/methanol = 2:1; Pd source = $Pd(OAc)_2$. [b] Average number over 16 h/60 h reaction time. [c] Chemoselectivity: $(\mathbf{1+2}/\mathbf{1+2+3+4})\times 100$. [d] 11% 4-vinylcyclohexene **4**.



Scheme 5. Selectivity studies of the addition of $^-$OMe to **5a** and **5b**.

monophosphane complex **5a** resulted in the production of a high amount of the linear telomer **1** (ratio **1**/**2** = 28:1), as a result of nucleophilic addition of the methoxy group essentially at the terminal allylic C1 (Scheme 5, path 1). In contrast, the same experiment performed with the isolated bisphosphane complex **5b** (directly obtained from **5a** by addition of one equivalent of PPh_3) led to the formation of a higher amount of the branched telomer **2** (ratio **1**/**2** = 7:1) resulting from increased reactions at the allylic C3 (Scheme 5, path 2). These different experiments gave some mechanistic hints of the effect of excess phosphane ligands on the regioselectivity of the reaction. Hence, an extended version of Jolly's catalytic cycle for the telomerisation of 1,3-butadiene with methanol, which accounts for the observed regioselectivity of the reaction, was proposed in 2000 (Scheme 6).[12]



Scheme 6. Extended mechanism for the Pd-catalysed telomerisation of 1,3-butadiene with methanol.

Following the Jolly-mechanism, oxidative coupling of two molecules of coordinated 1,3-butadiene at a low-coordinated Pd^0 centre leads to the Pd^{II} complex **6**. Subsequent protonation by the alcohol produces the Pd^{II}–methoxy complex **7**, the evolution of which will depend on the reaction conditions. When the reaction is carried out without excess PPh_3, the catalytic cycle can be described by path A (Scheme 6). Driven by the formation of the thermodynamically more stable Pd^0–(1,6-diene) complex **8**, the nucleophilic addition of the methoxy group occurs mainly at the C1-allylic terminus giving high yield of the linear telomer **1** (Scheme 5, path 1). However, in the presence of an excess PPh_3, as described in path B (Scheme 6), the coordination of a second phosphane to **7** results in the loss of the double bond coordination at the Pd centre, thereby producing **9**. The addition of the methoxy group on the allyl moiety is no longer driven by the formation of the thermodynamically stable chelating complex **8**, but is dependent on electronic and steric parameters of **9**. Hence, a higher proportion of branched telomer **2** is produced (Scheme 5, path 2).

From Phosphane-Based to N-Heterocyclic-Carbene-Based Catalysts

We have demonstrated that the use of an excess of triphenylphosphane leads to a lower regioselectivity in telomerisation. Furthermore, from the proposed catalytic cycle (Schemes 4 and 6) it is apparent that only one phosphane

ligand bonded to the metal is sufficient during the whole catalytic cycle to ensure a productive and selective catalyst. Therefore, Mario Gomez Andreu started in 2000 to synthesise and test well-defined monophosphane–Pd^0–olefin complexes (Figure 1) in different palladium-catalysed coupling

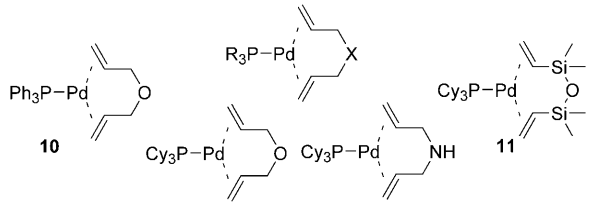
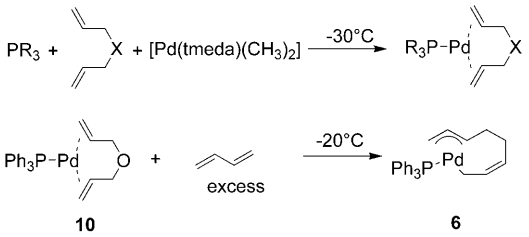


Figure 1. Selected examples of monophosphane–Pd^0–(1,6-diene) complexes.

reactions. Based on the elegant work of Pörschke et al.,[13] who developed a highly effective route for the synthesis of Pd^0–1,6-diene complexes, we synthesised various monophosphane Pd^0 species in quantitative yield upon stirring at low temperature a solution of $[Pd(CH_3)_2(tmeda)]$ with the phosphane and the 1,6-diene (Scheme 7). Once isolated, the

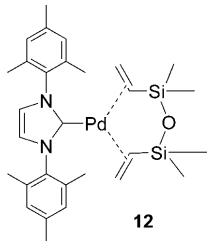


Scheme 7. Synthesis of monophosphane–Pd^0–(1,6-diene) complexes and **6**.

complexes have shown good activities in different palladium-catalysed coupling reactions of aryl halides.[14]

With respect to telomerisation it is worth noting that complex **10** has been shown to react even at low temperature with 1,3-butadiene to give the catalytic intermediate **6**, thus demonstrating the ease of formation of the active catalyst from **10** (Scheme 7). Nevertheless, this type of Pd^0–monophosphane complexes gave similar catalyst productivity compared to the classical Pd-$(OAc)_2$/PPh_3 system.[12]

Around 2000, we started to discuss the possibility to use the telomerisation of methanol and 1,3-butadiene as part of a process for 1-octene together with Dirk Röttger and Franz Nierlich of Oxeno Olefinchemie GmbH (now Evonik–Degussa).[15] Due to the strong patent position of Dow[16] with phosphane-based palladium catalysts and our experience, we looked for other type of ligands that could satisfy our objectives better. Hence, a joint project aiming at palladium–carbene complexes for telomerisation was started and Ralf Jackstell became the project leader for this topic in our institute.



During the last decade, N-heterocyclic carbenes (NHC) have proved to be extremely useful alternatives to basic phosphane ligands in numerous transition-metal-catalysed reactions.[17,18] In general, they are better σ-donor ligands and present quite distinctive steric parameters from phosphane ligands.[19] Hence, we synthesised and tested $[Pd^0(dvds)(IMes)]$ (**12**; dvds = 1,1,3,3-tetramethyl-1,3-divinyl-disiloxane; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) in the telomerisation of 1,3-butadiene with methanol. Some of the initially obtained results are summarised in Table 3.[20]

To our delight the reaction was efficiently catalysed by **12**. For example at 50 °C, the classical triphenylphosphane-based palladium catalyst does not promote the reaction, whereas in the presence of **12**, 57 % of telomers are obtained with excellent regio- and chemoselectivity (Table 3, entries 2 and 7). At 90 °C, we were pleased to see that complex **12** gave the telomeric products in almost quantitative yield and with excellent selectivity (Table 3, entry 6). Comparatively, catalytic systems with PPh_3 or $P(nBu)_3$ gave poorer results (Table 3, entries 1 and 4). Impressively, 89 % of telomers are obtained with high selectivity for **1** in the presence of only 0.00033 mol % of **12**, giving once more the highest catalyst productivity (TON = 267 000) reported for a telomerisation reaction at that time (Table 3, entry 8). Notably, these results constituted the first example of a telomerisation reaction catalysed by a palladium–NHC complex.

In 2001 Benno Bildstein from Innsbruck visited our institute and reported on the synthesis of ferrocenyl-based carbene ligands.[21] Thus, a small cooperation between our groups was started and we tested his ligands (**13**–**20**; see also

Table 3. Comparing palladium–phosphane and –carbene catalysts for telomerisation of 1,3-butadiene with methanol.[a]

	Catalyst	Pd [mol %]	*T* [°C]	Yield **1**+**2** [%]	Chemoselectivity[b] [%]	*n*/iso	TON
1	$Pd(OAc)_2$/3 PPh_3	0.001	90	79	90	12:1	78 700
2	$Pd(OAc)_2$/3 PPh_3	0.001	50	2	–	13:1	2000
3	$Pd(OAc)_2$/3 PPh_3	0.00033	90	75	88	13:1	225 000
4	$Pd(OAc)_2$/3 $PnBu_3$	0.001	90	57	90	10:1	57 000
5	**11**	0.001	90	60	77	10:1	60 000
6	**12**	0.001	90	≥ 98	99	36:1	98 000
7	**12**	0.001	50	57	> 99	82:1	57 000
8	**12**	0.00033	90	89	98	41:1	267 000

[a] Conditions: 16 h, 1.0 mol % NaOH, MeOH/butadiene = 2:1. [b] Chemoselectivity = (**1**+**2**)/(**1**+**2**+**3**+**4**) × 100.

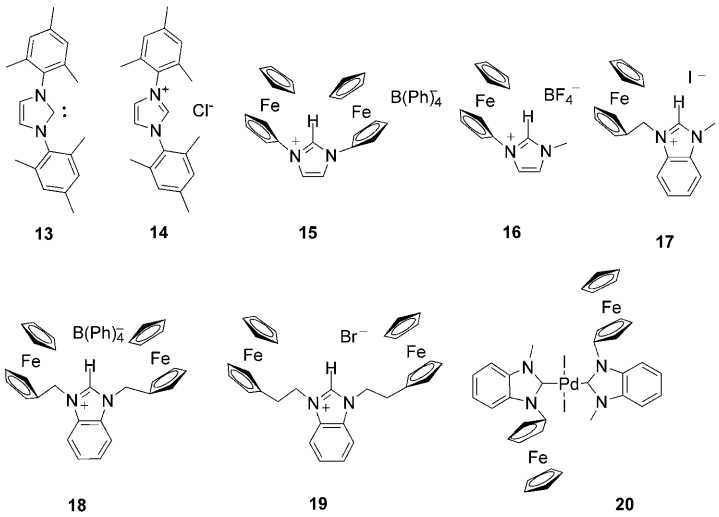


Table 4) in the telomerisation of butadiene and different alcohols.[22] From a practical standpoint, and from industrial interest, catalysts generated in-situ from simple and stable palladium sources and imidazolium salts, as N-heterocyclic carbene precursors are more conveniently tested compared to the corresponding isolated metal complexes.

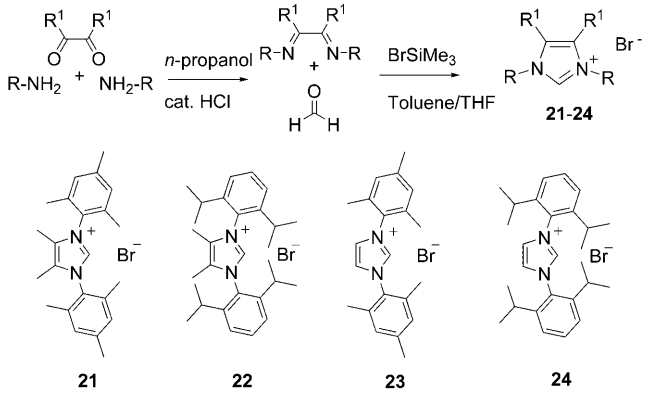
Table 4. Telomerisation of 1,3-butadiene with methanol.[a]

	Pd catalyst	Pd [mol%]	Ligand	Pd/L	Yield **1+2** [%]	Chemoselectivity[b] [%]	*n*/iso	TON
1	$[Pd(dba)_2]$	0.001	PPh_3	1:2	86	92	14:1	86000
2	$[Pd(dba)_2]$	0.0003	PPh_3	1:2	69	92	14:1	230000
3	$[Pd(dba)_2]$	0.001	**13**	1:2	92	98	35:1	92000
4	$Pd(OAc)_2$	0.001	**13**	1:2	93	98	35:1	93000
5	$[Pd(dba)_2]$	0.001	**14**	1:2	95	98	35:1	95000
6	$Pd(OAc)_2$	0.001	**14**	1:2	87	98	36:1	87000
7	$[Pd(dba)_2]$	0.0003	**13**	1:2	83	97	39:1	278000
8	$[Pd(dba)_2]$	0.0003	**13**	1:4	89	98	39:1	296000
9	$[Pd(dba)_2]$	0.0003	**14**	1:4	92	98	39:1	308000
10	$Pd(OAc)_2$	0.0003	**14**	1:4	94	98	39:1	314000
11	$[Pd(dba)_2]$	0.001	**15**	1:2	0	–	–	–
12	$[Pd(dba)_2]$	0.001	**16**	1:2	73	96	61:1	73000
13	$[Pd(dba)_2]$	0.001	**17**	1:2	8	75	99:1	8000
14	$[Pd(dba)_2]$	0.001	**18**	1:2	88	97	42:1	88000
15	$[Pd(dba)_2]$	0.0003	**18**	1:4	41	94	25:1	137000
16	$[Pd(dba)_2]$	0.001	**19**	1:2	82	97	36:1	82000
17	**20**	0.001	–	–	48	94	61:1	48000

[a] Reaction conditions: 16 h, 90 °C, 1.0 mol% NaOH, MeOH/butadiene = 2:1. [b] Chemoselectivity: **(1+2/1+2+3+4)** ×100.

As shown in Table 4 (entries 5 and 6, 9 and 10) the use of imidazolium salt **14** with either $Pd(OAc)_2$ or $[Pd(dba)_2]$, afforded under the same reaction conditions, similar results to those obtained with the well-defined complex **12** (Table 3, entries 6 and 8). Furthermore, performing the catalytic reactions with the free carbene **13** instead of **14** gave identical results, thus suggesting fast generation of the carbene ligand from the imidazolium salt **14** during the catalytic reaction. Due to their different structure employing the imidazolium salts **15**–**19** or the complex **20** gave worse results (Table 4, entries 11–17).

Having demonstrated the beneficial use of 1,3-diaryl-substituted N-heterocyclic carbene ligands, a broader range of carbene ligands was synthesised in our group and their catalytic performance evaluated. In addition, we evaluated some carbene ligands from the groups of Kingsley Cavell (Cardiff University) and Steve Nolan (now ICIQ, Tarragona).[23] However, none of the imidazolium salts employed showed significantly better results compared to the IMes ligand. Encouraged by theoretical calculations realised by Haijun Jiao in our institute,[23] the effect of different substituents on the backbone (4- or 5-position) of the carbene ligand became of interest to us. Unfortunately, the different synthetic routes to imidazolium salts described in the literature did not permit efficient access to carbene precursors bearing alkyl groups in the 4- and 5-positions.[24] The final ring-closing step from the diimine was problematic using the traditional HX/paraformaldehyde mixture. However, Ralf Jackstell and Surendra Harkal discovered that the use of trialkylhalosilanes[25] instead of classic Broenstedt acids (HX; X = Cl, Br) was the decisive additive for the cyclisation of such 4,5-dialkyl-substituted imidazolium salts. Reaction of the diimine with paraformaldehyde followed by addition of trimethylbromosilane produced the imidazolium salts **21**–**24** in good yields (**21**, 56%, **22**, 80%, **23**, 60%, **24**, 76%, Scheme 8).[26]



Scheme 8. A novel synthesis of imidazolium salts.

Using these imidazolium salts, the corresponding $[Pd^0$-(dvds)(NHC)] complexes were synthesised to gain structural information on the binding of the carbene ligands to a Pd^0–(1,6-diene) core, which would mimic some of the catalytic intermediates of the telomerisation reaction. Interestingly, the different complexes **12** and **25**–**28**, which were obtained by addition of the free carbene to a solution of Pd^0/dvds (8–12 mol% Pd) in THF, are stable for months and can even be handled in air. The corresponding X-ray crystal structures of the different NHC complexes are presented in Figure 2.

To our surprise, the X-ray structure analysis revealed that replacing hydrogen by methyl or chloro substituents in the

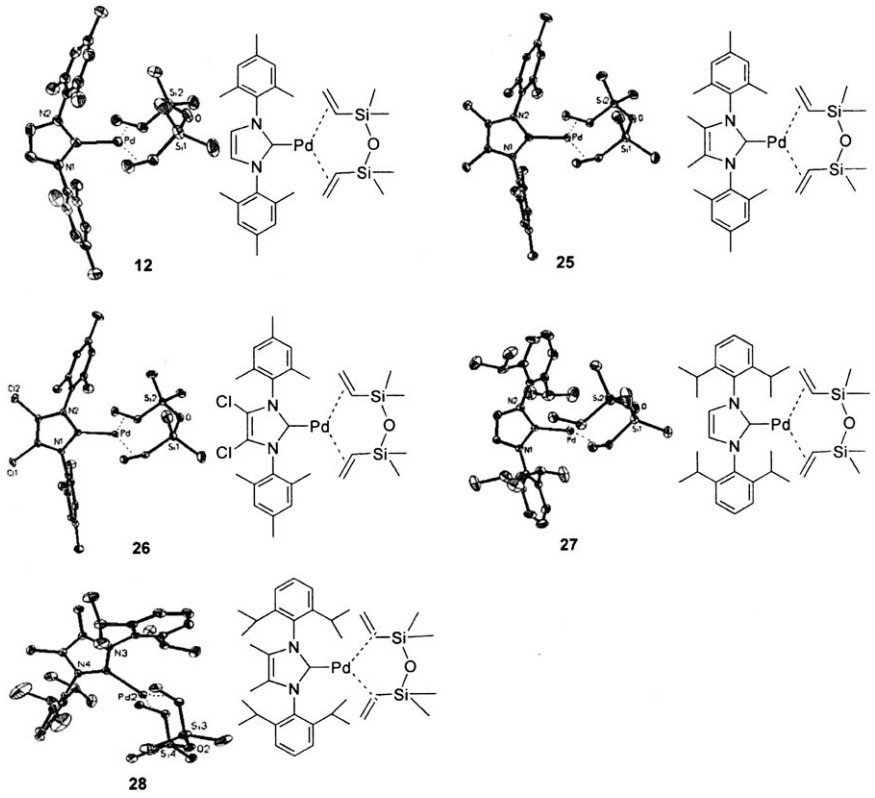


Figure 2. ORTEP representation of [Pd^0(dvds)(mono-NHC)] complexes **12** and **25**–**28**. Hydrogen atoms as well as one of the two molecules of the asymmetric unit of complex **28** are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Crystallographic data as well as selected bond lengths and angles can be found elsewhere.[23]

4- or 5-position of the carbene ligand bearing the *N*-mesityl substituents does not significantly influence the Pd–NHC bond length (Pd–NHC bond length: **12** = 2.076(5), **25** = 2.093(3), **26** = 2.080(3) Å). However, if the carbene ligand bears sterically more hindered *N*-2,6-diisopropylphenyl substituents, a relatively longer Pd–NHC bond length is observed when methyl groups instead of hydrogen atoms are present on the backbone of the NHC ligand (Pd–NHC bond length: **27** = 2.084(3), **28** = 2.114(3) Å). The increased steric congestion is the likely reason for the long Pd–NHC bond in **28**. Evidently, all complexes synthesised were tested in the reaction of 1,3-butadiene with methanol. Some selected results are presented in Table 5.

Apart from complex **28**, all other NHC-based palladium catalysts showed improved catalyst performance compared to $Pd(OAc)_2/PPh_3$ at 70 °C (Table 5). With the *N*-mesityl-substituted carbene ligand, variation at the 4- and 5-position of the imidazole ring had no effect on the catalytic performance of the palladium(0)–mono-NHC complex (Table 5, entries 1–3). Similarly, the telomers were obtained nearly quantitatively with excellent chemo- and regioselectivities when the reaction was carried out in presence of the well-defined [Pd^{II}(allyl)Cl(IMes)] complex (**29**). However, catalysts with *N*-2,6-diisopropylphenyl-substituted carbene ligands gave comparatively lower regioselectivity with ratio *n*/iso = 10–12:1 (Table 5, entries 27, 28, 30). A lower yield was also observed with the [Pd^{II}(allyl)(IDipp)]Cl (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) complex (**30**), whereas complex **28** yielded nearly no telomers (vide infra dimerisation reaction). On the other hand, monitoring the activity of the complexes with time put in light a significant effect of the different carbene substituents on the reaction rate (Figure 3).

For example, the presence of chloride substituents instead of hydrogen atoms in the backbone of the *N*-mesityl-substituted carbene ligand increased the initial rate of the reaction (complex **12** versus **26**), whereas the presence of methyl groups decreased it (complex **12** versus **25**). The *N*-2,6-diisopropylphenyl-substituted carbene complex **27** is also significantly slower than the *N*-mesityl-substituted complex **12**.

Due to the high activity and productivity of palladium–carbene catalysts in the reaction of butadiene with methanol we became interested to apply these complexes in telomerisation reactions using further nucleophiles (telogens) and isoprene as taxogen. Hence, the telomerisation of 1,3-butadiene with different alcohols was studied in more detail (Scheme 9).[23]

Table 5. Telomerisation of 1,3-butadiene and methanol in the presence of different palladium–carbene catalysts.[a]

	Palladium catalyst	Yield **1**+**2** [%]	Chemoselectivity[b] [%]	*n*/iso	TON	TOF [h^{-1}]
1	**12**	96	> 99	49:1	96000	6000
2	**25**	93	99	49:1	93000	5813
3	**26**	96	> 99	49:1	96000	6000
4	**27**	90	97	12:1	90000	5625
5	**28**	2	-	10:1	2000	125
6[c]	**29**	94	99	49:1	94000	5875
7[d]	**30**	46	96	12:1	46000	2875
8	$Pd(OAc)_2/3\,PPh_3$	26	87	24:1	26000	1625
9	$Pd(OAc)_2/4$ IMesHCl	94	> 99	49:1	94000	5875

[a] Conditions: Pd = 0.001 mol%, 16 h, 70 °C, 1.0 mol% NaOMe, MeOH/butadiene = 2:1. [b] Chemoselectivity: $(\mathbf{1}+\mathbf{2}/\mathbf{1}+\mathbf{2}+\mathbf{3}+\mathbf{4})\times 100$. [c] Complex **29**: (allyl)chloro[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]palladium. [d] Complex **30**: (allyl)chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]palladium.

Again, the Pd–NHC-based catalytic system proved to be far more efficient under standard reaction conditions than

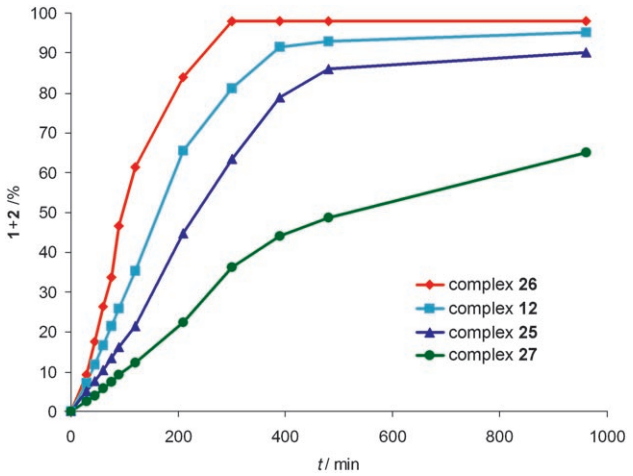
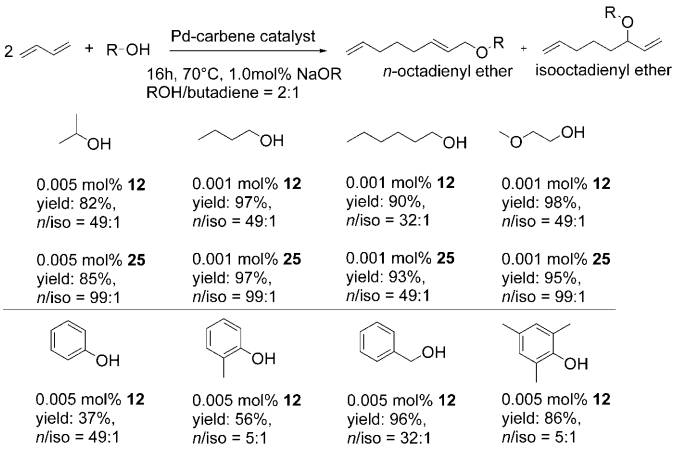


Figure 3. Activity of palladium complexes **12** and **25**–**27** at 70 °C.

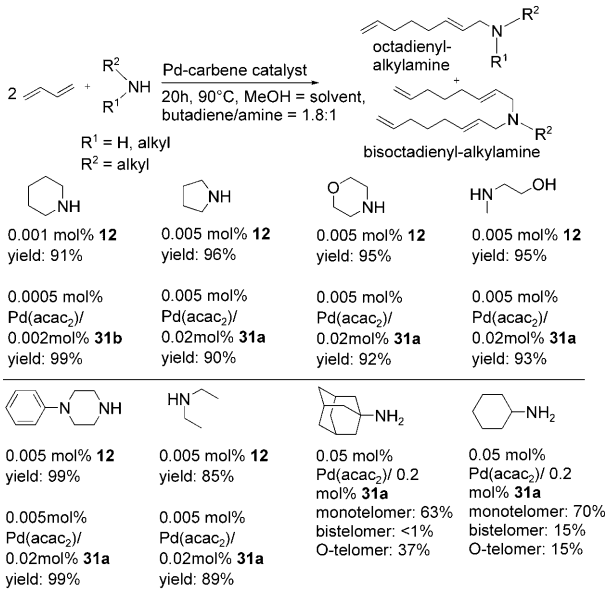


Scheme 9. Telomerisation of different alcohols.

the triphenylphosphane-based palladium catalyst. For example, the catalyst system $Pd(OAc)_2/3\,PPh_3$ reacted with *n*-butanol to form only 36% telomers with an *n*/iso-ratio of 19:1 (Pd: 0.001 mol%). Complexes **12** and **25** were the most effective catalysts for the telomerisation of 1,3-butadiene with both primary and secondary aliphatic alcohols giving high yields and good selectivity to the linear telomers. However, somewhat lower results were obtained using aromatic alcohols.

In 2003, Nolan and co-workers reported on the telomerisation with amines using a catalytic mixture of complex **30** and $NaPF_6$ in THF.[27] Compared to the telomerisation with alcohols relatively high catalyst loadings (>0.1 mol%) were required, which makes these reactions less attractive for the preparation of bulk and fine chemicals.

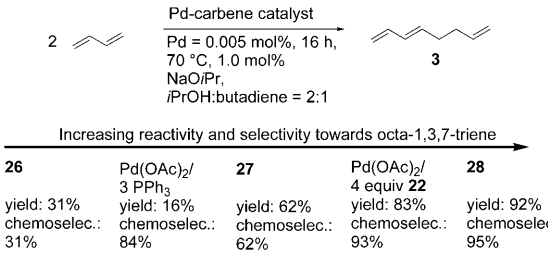
However more recently, Anne Grotevendt (a Ph.D. student in Rostock) found that this reaction proceeded in high yield at low catalyst loading by using different catalyst precursors and MeOH as solvent (Scheme 10).[28] The maximum TONs are achieved using $Pd(acac)_2$ with 1,3-dimesitylimidazolium carboxylate **31b** as in situ system for the telomerisation of 1,3-butadiene with piperidine. In general, both complex **12** and the catalytic mixture $Pd(acac)_2$ with 1,3-dimesitylimidazolium mesylate **31a** perform equally well in these reactions. Again, these TONs are the best reported for such reactions. It is important to note that even if MeOH is a competing nucleophile the telomerisation with secondary amines proceeds selectively to the N-telomer and not to the O-telomer!



Scheme 10. Telomerisation of 1,3-butadiene with secondary and primary amines.

During the course of our study to find an optimised catalyst for the reaction of 1,3-butadiene with methanol, complex **28** showed an activity very different from other palladium–NHC complexes (Table 5). Due to the steric bulk this particular catalyst did not allow for an attack of the nucleophile; instead β-hydride elimination is promoted. Hence, applying sterically hindered nucleophiles, for example, isopropanol, selective dimerisation of 1,3-butadiene occurred (Scheme 11).[29]

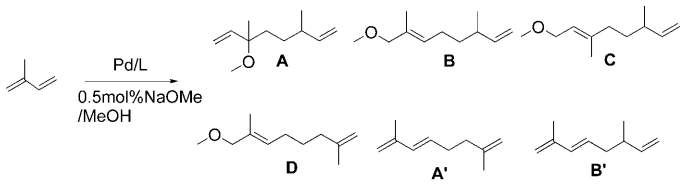
While in presence of complex **28** or the corresponding in situ generated catalyst 1,3,7-octatriene is obtained in very good yield and excellent chemoselectivity, other catalytic systems tested produced only low to moderate amount of **3** with a lower chemoselectivity. In addition to the structure of



Scheme 11. Dimerisation of 1,3-butadiene in isopropanol with different catalysts.

the ligand, the nature of the solvent is crucial for this selective dimerisation. When the reaction was carried out in THF, toluene, methanol or phenol, almost no 1,3,7-octatriene was produced.[29] After reaction optimisation a TON of 81 000 and a TOF of 5000 h^{-1} were obtained (Scheme 11). This is the top catalyst productivity and activity reported for any 1,3-diene dimerisation reaction.

Palladium–carbene catalysts also proved to be efficient for the telomerisation of isoprene. Due to the lower reactivity of isoprene and the different nature of the double bonds, these reactions led to a more complex product mixture. In addition to twelve different telomers (regioisomers), dimers and trimers can be formed.[30] Using the previously optimised reaction conditions we found that only four regioisomers **A**–**D** were formed together with the two dimers **A′** and **B′** and to a lesser extent unidentified trimers (Scheme 12, Table 6).



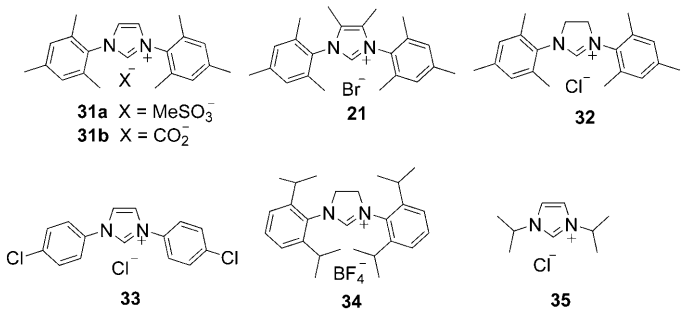
Scheme 12. Telomerisation of isoprene with methanol.

Table 6. Palladium-catalysed telomerisation of isoprene with different ligands.[a]

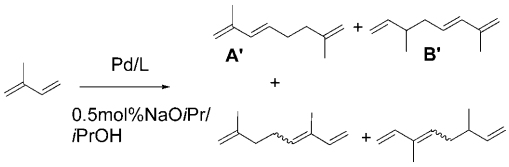
	Ligand	Yield[b] [%]	Selectivity[c] [%]				Yield[d] [%]		Yield[e] [%]
			A	**B**	**C**	**D**	**A′**	**B′**	
1	**31a**	51	7	17	75	1	6	4	9
2[f]	**31a**	66	7	20	72	1	6	4	17
3	**21**	10	9	15	76	<1	2	2	<1
4	**32**	51	10	16	74	<1	7	5	10
5	**33**	3	4	20	74	2	<1	<1	<1
6	**34**	17	38	17	45	<1	15	11	10
7	**35**	19	3	24	71	2	1	2	<1
8[f]	PPh_3	54	<1	49	6	45	<1	<1	3
9[f]	PCy_3	23	3	83	9	5	<1	<1	1

[a] General conditions: $Pd(acac)_2$ = 0.002 mol%, Pd/Ligand = 1:4, 70 °C, pN_2 = 25 bar, 20 h, 0.5 mol% NaOMe/MeOH (12 mL), isoprene (15 mL). [b] Yield of different telomers **A**–**D**. [c] Selectivity of different telomers. [d] Yield of different dimers. [e] Yield of different trimers. [f] Pd/ligand = 1:10.

Of all imidazolium salts tested (**21**, **31**–**35**), the catalytic systems with the imidazolium salts **31a** and **32** gave the best catalyst productivity with 51% yield of telomers (Table 6, entries 1 and 4). The catalyst that contains **31a** was also found to be more productive than catalysts containing PPh_3 or PCy_3 (Table 6, entries 2, 8 and 9) with a TON of 33 000 being reached when ten equivalents of imidazolium salt **31a** per palladium are employed. To the best of our knowledge this is the maximum TON reported of any telomerisation of isoprene.

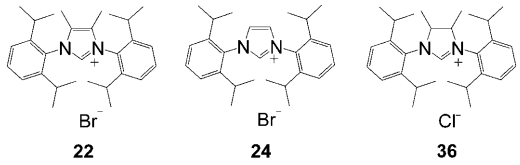


In terms of regioselectivity, the ligand has a strong influence on the product distribution. Whereas most NHC ligands gave mainly the head-to-head isomer **C** with regioselectivity up to 76%, the catalytic system with PPh_3 gave **B** and **D** with regioselectivities of 49% and 45%, respectively, while in the presence of PCy_3 mainly **B** is obtained with 83% regioselectivity. Similar to 1,3-butadiene, the dimerisation of isoprene in isopropanol proceeded also smoothly (Scheme 13).[30]



Scheme 13. Dimerisation of isoprene in isopropanol.

The tail-to-tail product **A′** and the tail-to-head product **B′** were identified as the main products. Selected results of the dimerisation of isoprene with mixtures of $Pd(acac)_2$ with different imidazolium salts (**22**, **24**, and **36**) and phosphanes are presented in Table 7. Once again NHC-based catalysts were found to be significantly more productive than palladium phosphane catalysts.



From Laboratory to Industrial Pilot Plant

The telomerisation of 1,3-butadiene and water to 2,7-octadienol and the preferential refinement to 1-octanol in the 1980s by Kuraray was probably the first industrial realisation of this methodology on multithousand ton scale. However, the Kuraray process is relatively complicated, especially the workup and catalyst recycling.[31] As mentioned above in the last decade the reaction of 1,3-butadiene with methanol gained more industrial interest due to the increased im-

Table 7. Dimerisation of isoprene in isopropanol with different catalysts.[a]

	Ligand	Pd [mol%]	T [°C]	Yield[b] [%]	Selectivity[c] [%] A′	B′	others
1	**PCy_3**	0.02	90	14	84	<1	15
2	**PPh_3**	0.02	90	3	16	<1	83
3	**31a**	0.02	90	87	70	22	8
4	**34**	0.02	90	84	81	11	8
5	**22**	0.02	90	72	58	26	16
6	**24**	0.02	90	62	71	16	13
7[d]	**36**	0.02	90	98	75	16	9
8	**31a**	0.01	70	68	47	37	16
9[e]	**31a**	0.01	70	68	45	38	17
10	**34**	0.01	70	82	74	16	10
11	**34**	0.005	70	76	71	15	14
12	**36**	0.01	70	93	72	17	11
13	**36**	0.005	70	35	67	17	16

[a] General conditions: $Pd(acac)_2$, Pd/L = 1:10, t = 24 h, pN_2 = 30 bar, 0.5 mol% Na*i*PrO/*i*PrOH (15 mL), isoprene (10 mL). [b] Yield of different dimers. [c] Selectivity of different dimers. [d] 0.5 mol% NaO*i*Pr/*i*PrOH (20 mL), isoprene (5 mL). [e] pN_2 = 50 bar.

portance of 1-octene as co-monomer for polyethylene. To be applied for this purpose, clearly a continuous operation mode is preferable and catalyst efficiency has to be significantly improved up to a range of TON $>10^6$. Thus, we spent more than three years investigating in detail the effects of base, concentration, additives, temperature and catalyst precursors at low catalyst loadings (0.5–10 ppm Pd) in the telomerisation of 1,3-butadiene with methanol. Ralf Jackstell, Surendra Harkal, and Ilona Stahr were mainly involved in this optimisation process. Selected results of more than 500 experiments are presented in Table 8 and Figures 4 and 5.

Table 8. Telomerisation of 1,3-butadiene with MeOH: optimisation of catalyst productivity.[a]

	Pd catalyst	Pd [mol%]	Ligand[b] [mol%]	Yield **1+2** [%]	Chemoselectivity[c] [%]	*n*/iso	TON	TOF [h^{-1}]
1	–	0	0.004	0	0	–	0	0
2	**12**	0.0001	–	20	89	49:1	200000	12500
3	**29**[d]	0.0001	–	19	90	49:1	190000	11875
4	**12**	0.0001	0.0002	17	88	49:1	170000	10625
5	**12**	0.0001	0.0004	40	95	49:1	400000	25000
6	**12**	0.0001	0.001	69	97	49:1	690000	43125
7	**12**	0.0001	0.002	87	98	49:1	870000	54375
8	**12**	0.0001	0.004	91	99	49:1	910000	56875
9	**29**[d]	0.0001	0.004	89	98	49:1	890000	55625
10	**12**	0.00005	0.004	77	99	49:1	1540000	96250

[a] Reaction conditions: 16 h, 90 °C, 1.0 mol% NaOMe, MeOH/butadiene = 2:1. [b] L = 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride. [c] Chemoselectivity: (**1+2**/**1+2+3+4**) × 100. [d] Complex **29**: (allyl)chloro[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]palladium.

To prevent precipitation of unwanted side-products during the continuous process, the solubility behaviour of the base is an important parameter. Hence, various bases have been studied with respect to catalyst activity and lifetime.

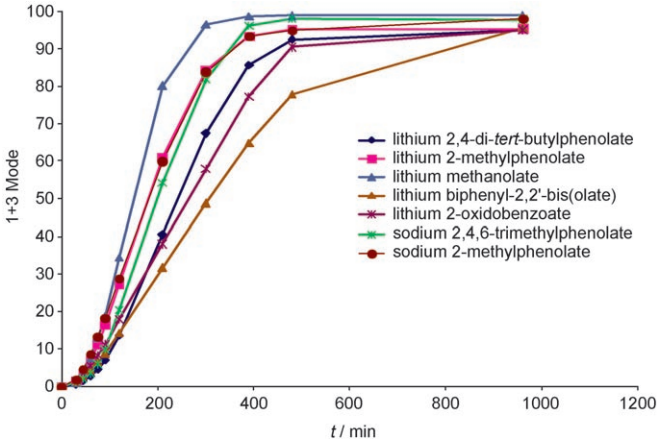


Figure 4. Activity studies in the presence of different bases (80 °C, 25 mL THF, 5 mL isooctane, 15 g 1,3-butadiene, 25 mL MeOH, 0.5 mol% MOR, 0.001 mol% $Pd(acac)_2$, Pd/L = 1:10, L = **31a**).

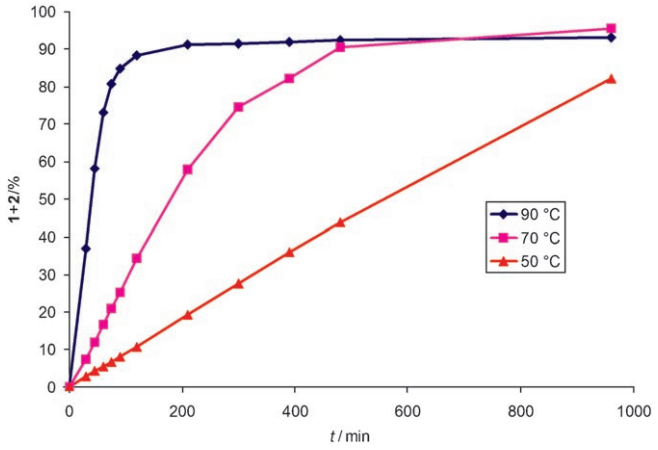


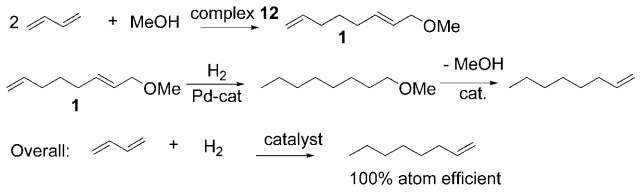
Figure 5. Activity studies at different temperature (15 g 1,3-butadiene, 25 mL MeOH, 0.5 mol% NaOMe, 25 mL THF, 10 mL isooctane, 0.001 mol% complex **12**).

It turned out that phenolates showed improved solubility compared to methanolate; however they reduced the catalyst activity to some extent. In Figure 4 the activity of some bases under standard conditions is shown. Not surprisingly, the influence of the temperature on the reaction is large (Figure 5). At 90 °C the catalyst system turned out to be extremely fast (up to 100000 h^{-1}) and is stable for weeks if enough ligand is present in the reaction system. Some optimisation experiments are revealed in Table 8.

No telomers are obtained when the reaction is carried out in absence of the palladium–NHC catalyst (Table 8, entry 1). When the reaction was performed in the presence of 1 ppm (0.0001 mol%) of catalyst **12** or **29**, about 20% of octadienyl ethers are obtained with good chemo- and regioselectivity (TON = 200000). Notably, addition of excess imidazolium salt to **12** or **29** had a profound effect on the yield of the reaction. For example, increasing the ratio imidazolium salt/complex **12** from 2 to 40 resulted in a progressive increase

of the yield of telomers from 17 to 91% and associated with an excellent chemo- and regioselectivity (Table 8, entries 4–8). By further decreasing the catalyst loading of **12** to 0.5 ppm of Pd in the presence of 40 ppm of imidazolium salt, an excellent TON of 1540000 is obtained with very high selectivity (Table 8, entry 10). This catalyst turnover number is still the top productivity reported for any telomerisation reaction until to date. It is also important to remark that even if the reaction was conducted in presence of a large excess of ligand per palladium, the regioselectivity stays excellent. These results are in contradiction with the original results observed for the system $Pd(OAc)_2/PPh_3$. It seems to indicate that, even in presence of large excess of imidazolium salts, only one NHC ligand stays on the palladium centre.

For the industrial realisation of this reaction it is important to note that the use of so-called crack C4 as feedstock (crack C4 = 42% 1,3-butadiene; 25% isobutene; 16% 1-butene; 5% isobutane; 5% 2-butene; 7% other) is advantageous.[32] While crack C4 represents a cheaper source for 1,3-butadiene, its also adds more requirements for the catalyst, since it needs to react with high selectivity toward 1,3-butadiene and the catalyst should not be deactivated by the present other olefins and alkynes. However, the palladium–carbene catalyst system proved to perform similarly well, giving high productivity and selectivity for the linear telomer even when using alkyne-free crack C4 as a source of 1,3-butadiene. Thus, the system has been used by Evonik–Oxeno in Marl (Germany) on a continuous pilot plant scale and several thousand kg of telomers were produced according to Scheme 14.



Scheme 14. Pilot plant process for 1-octene by a telomerisation reaction.

The overall process is composed of palladium-catalysed telomerisation, subsequent hydrogenation and a final base-catalysed elimination. The telomerisation of 1,3-butadiene with methanol constitutes the first step, producing linear methoxyocta-2,7-diene (**1**) with excellent selectivity (>98.2%). Heterogeneous hydrogenation of **1** gives 1-methoxyoctane, from which methanol is eliminated in the presence of a basic zeolite to produce 1-octene. To the best of our knowledge this constitutes the first example of the use of a palladium–NHC catalyst in industry. The overall process is in theory 100% atom efficient and it is undeniable that this synthesis fulfils the requirements of a green and sustainable process. It should be noted that Dow Chemicals recently announced the production of 1-octene by a similar process.[33]

Conclusion and Outlook

In the last decade N-heterocyclic carbene based palladium catalysts have stimulated significant interest in organometallic chemistry and organic synthesis. While most work has been focused on the popular palladium-catalysed coupling reactions of aryl halides,[17,18,34] these catalysts also offer exciting possibilities for other catalytic transformations. In this respect, industrially important telomerisation and dimerisation reactions are of special interest. Here, we have shown in recent years that the use of palladium–carbene catalysts allowed us to reach the best catalyst productivities and activities ever reported for such reactions. For the first time the telomerisation of 1,3-butadiene and methanol has been applied on an industrial multiton scale. It is expected that more telomerisation and dimerisation reactions will become of industrial interest due to the high efficiency of the now-available catalysts. Due to the price advantage of 1,3-butadiene, octyl-derived products can be accessed more economically compared to other feedstocks. In addition, the various functionalisations of the resulting octadienyl products allows for the synthesis of numerous interesting fine chemicals. We believe that the present study also demonstrates nicely that starting from very basic mechanistic studies new catalysts can be developed, which allow even for industrial applications.

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