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Journal of Organometallic Chemistry 692 (2007) 4737–4744
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Telomerization and dimerization of isoprene by *in situ* generated palladium–carbene catalysts

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Received 5 April 2007; received in revised form 31 May 2007; accepted 7 June 2007
Available online 29 June 2007

Dedicated to Prof. Dr. Gerhard Erker on the occasion of his 60th birthday.

Abstract

The palladium-catalyzed telomerization of isoprene with methanol and dimerization of isoprene have been studied in presence of *in situ* generated palladium–carbene catalysts. Unprecedented catalyst productivity has been observed for these two reactions. A selectivity switch from the telomer to the dimer product occurred by using different substituted carbene ligands. Among the imidazolium salts tested 1,3-dimesitylimidazolium mesylate (**1**), 1,3-dimesityl-4,5-dihydroimidazolium chloride (**3**) gave the best yields for telomerization reaction whereas 1,3-bis-(2,6-diisopropylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (**5**) and 1,3-bis-(2,6-diisopropylphenyl)-4,5-dimethyl-4,5-dihydroimidazolium chloride (**9**) form dimers in high yield and good selectivity.

Keywords: Carbenes; Dimerization; Homogeneous catalysis; Isoprene; Palladium; Telomerization

1. Introduction

N-Heterocyclic carbene ligands have become in the last decade increasingly important as ligands for various catalytic transformations [1]. For example they found widespread use in palladium-catalyzed coupling reactions [2] such as the Heck–Suzuki-, and Sonogashira reactions, copolymerizations and aminations of aryl halides. In general, carbene ligands offer improved stability and higher catalytic activity compared to phosphines. Due to the stronger nucleophilic behaviour the resulting metal-ligand bonds are more stable and reversible dissociation does not occur to a significant extent [3].

Some time ago we have synthesized the first monocarbene palladium(0) complexes and demonstrated their catalytic potential in the telomerization of 1,3-butadiene with alcohols (Scheme 1) [4]. Such telomerizations of 1,3-dienes with nucleophiles constitute an interesting synthetic methodology, that combines simple starting materials in a 100% atom efficient manner to give functionalized octa-2,7-dienes [5–7].

Apart from 1,3-butadiene, comparatively few studies are known for the telomerization of other 1,3-dienes. More recently, we became interested in the use of isoprene because dimerization and telomerizations of isoprene offer attractive routes to various terpene derivatives [8]. Unfortunately, the regioselectivity of the known palladium–phosphine catalysts for these reactions are low and in most cases the non-natural coupling product is observed [9]. Here, we report for the first time the telomerization and dimerization of isoprene in the presence of palladium–carbene systems, which show improved catalyst productivity and different selectivity.

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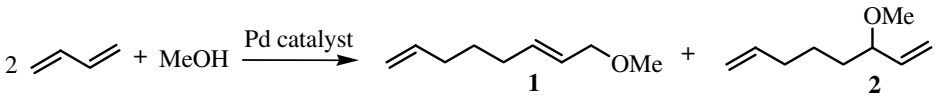
doi:10.1016/j.jorganchem.2007.06.039

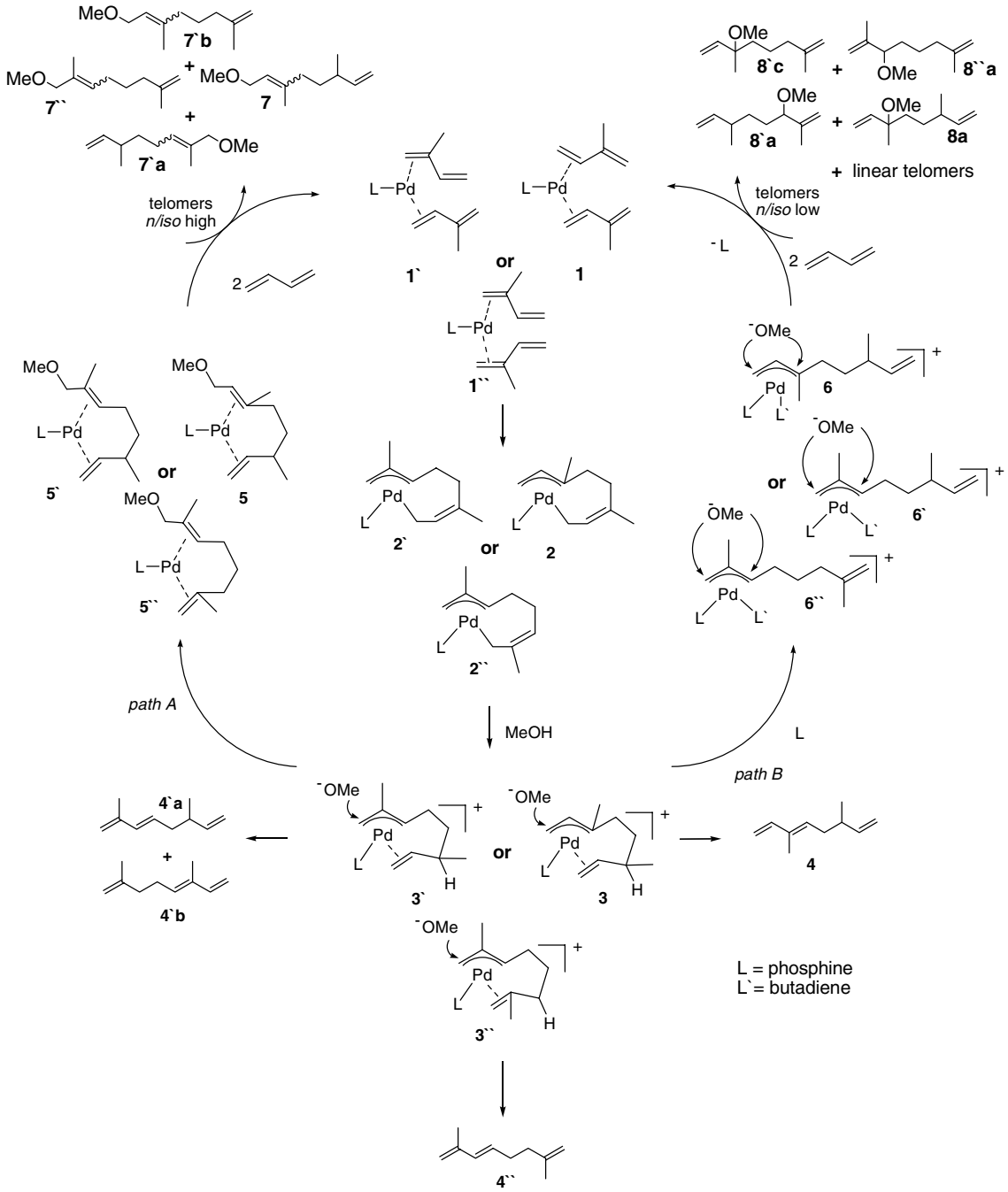


Scheme 1. Telomerization of 1,3-butadiene with methanol.

2. Results and discussion

2.1. Telomerization of isoprene

Notably, the telomerization of isoprene is significantly more difficult compared to similar reactions of 1,3-butadiene. On the one hand the reactivity of the diene is lower, on the other hand in addition to dimers and trimers 12 different telomerization products (regioisomers) can be formed. Important mechanistic studies of telomerization reaction of butadiene with methanol were done by Jolly [7] and extended by our working group [7]. Scheme 2 shows a pro-



Scheme 2. Proposed mechanism for the telomerization of isoprene with methanol.

posed catalytic cycle of isoprene telomerization. Two molecules of isoprene couple to form the ligand-Pd-(η^1,η^3-dimethyloctadiendiyl)-complex. The C–C bond formation can proceed *via* head-to-head coupling **2**, head-to-tail coupling **2′** or tail-to-tail coupling **2″**.

Furthermore the methoxide ion adds to either the allylic terminus C-1 or C-3 of the C_8-chain resulting in the formation of the telomers while dimers occur by β-hydrogen elimination from C4 in **3**.

Based on our studies of the telomerization of 1,3-butadiene with methanol, we applied 1,3-dimesitylimidazolium mesylate/Pd(acac)$_2$ as the initial catalyst system and studied the influence of different reaction parameters (temperature, catalyst concentration, metal-ligand ratio). The resulting telomerization products were isolated and their structure and stereochemistry were confirmed mainly by one- and two-dimensional NMR spectroscopy. As an example the two-dimensional NOESY spectrum of compound **D** shows correlations between the protons H-6 with H-8, H-9 with H-5, H-9 with OMe, and H-4 with H-10, respectively, indicating the *E* configuration given in Fig. 1.

As shown in Table 1 mainly three regioisomers are formed in all catalytic experiments. The dominating head-to-head isomer, **C**, is formed in 71–80% selectivity. This is in contrast to previous investigations with palladium/phosphine catalysts [8]. While, the yield of the isoprene dimer (9%) is constant and independent of the chosen temperature and reaction time, the amount of trimers parallels the telomerization products.

In all experiments product **D** is formed in traces, while compound **A** is obtained in 7–8% independent of the reaction conditions. A change in selectivity is found for **B** and **C**. By increasing the temperature from 50 °C to 70 °C we observed a decrease of product **C** from 80% to 71%, while product **B** increases from 12% to 20%. Notably is the catalyst productivity in these reactions. At a Pd loading of 0.002 mol% a catalyst turnover number (TON) of 33.000 is obtained. To the best of our knowledge this the highest catalyst productivity reported for any telomerization of isoprene. A ligand to palladium ratio of at least 4 to 1 is necessary for the catalyst productivity (Table 1, entries 1–4). The best results are achieved at 50–70 °C. At higher temperature (Table 1, entry 5) a slightly reduced conversion is observed despite the donation of a larger amount of ligand, probably due to a faster decomposition of the active species.

In Table 2, the results of a ligand screening are summarized. Different imidazolium salts as well as phosphine ligands were tested in the presence of 0.002 mol% Pd at 70 °C. In addition to the four telomerization products, we were also able to characterize and identify the isomeric dimers which are formed as by-products (see Scheme 3).

The structure of the used imidazolium salts is given in Fig. 2. High conversion is achieved in the presence of catalysts that contain **1**, **3** or triphenylphosphine. The regioselectivity of the reaction is strongly dependent on the used ligand. Triphenylphosphine caused the formation of **B** and **D** in a 1:1 ratio, whereas tricyclohexylphosphine formed predominantly **B** (83% selectivity). On the other hand triphenylphosphine showed a higher activity compared to tricyclohexylphosphine. Most N-heterocyclic carbenes (NHCs) gave predominantly the head-to-head isomer **C** with regioselectivity up to 76%. The more active NHCs led also to an increased formation of dimers and trimers. The most bulky ligand in this series **5**, which contains 2,6-diisopropylphenyl groups in C-1 and C-3 position of the imidazolium ring instead of mesityl groups, gave in larger amount **A** in comparison with the other carbenes tested. The sterically less hindered ligands **4** and **6** showed only poor activity in telomerization and dimerization reactions (see Fig. 3).

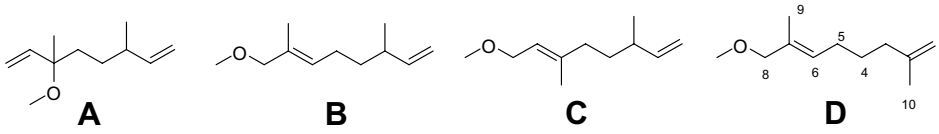


Fig. 1. Structure of formed telomers.

Table 1
Telomerization of isoprene with methanol

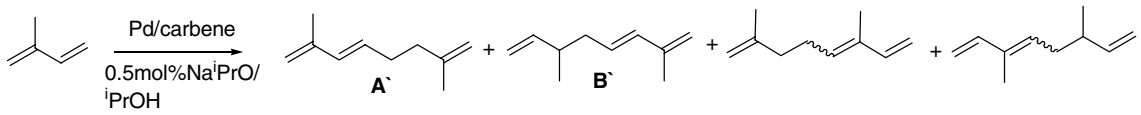
Entry	Pd (mol%)	*T* (°C)	*t* (h)	L/Pd	Yield[a] (%)	Selectivity[b] (%)				Yield[c] (%)	Yield[d] (%)
						A	**B**	**C**	**D**		
1	0.004	50	24	4/1	69	7	12	80	1	8	17
2	0.002	70	20	4/1	51	7	17	75	1	10	9
3	0.004	50	24	10/1	52	8	12	79	1	9	9
4	0.002	70	20	10/1	66	7	20	72	1	10	17
5	0.002	90	16	10/1	61	8	21	71	<1	9	15
6	0.002	70	20	20/1	65	8	20	71	1	10	16

General conditions: Pd(acac)$_2$, L = 1,3-dimesitylimidazolium mesylate, 12 ml 0.5 mol% NaOMe/MeOH, pN_2 = 25 bar, 15 ml isoprene.
[a] Yield of different telomers.
[b] Selectivity of different telomers.
[c] Yield of different dimers.
[d] Yield of different trimers.

Table 2
Palladium-catalyzed telomerization of isoprene with different ligands

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

General conditions: Pd = 0.002 mol%, 70 °C, 20 h, 12 ml 0.5 mol% NaOMe/MeOH, 15 ml isoprene, Pd/ligand = 1/4.
[a] Yield of different telomers.
[b] Selectivity of different telomers.
[c] Yield of different dimers.
[d] Yield of different trimers.
[e] Pd/ligand = 1/10.



Scheme 3. Palladium-catalyzed dimerization of isoprene.

2.2. Dimerization of isoprene

The results of the telomerization reaction in the presence of **5** indicated the possibility to form dimers to a significant extent (Table 2, entry 5). In order to minimize telomer formation less reactive isopropanol instead of methanol was used as solvent. The presence of an alcohol as solvent is important to obtain conversion that we learned from dimerization of butadiene [4d]. Indeed, by using sterically more demanding carbenes a complete switch from the telomer to the dimer products occurred. The resulting decatrienes are produced by hydride abstraction of the intermediate decadienylpalladium complex.

Among the different regioisomers (Scheme 3), we were able to isolate and identify the major products **A′** (tail-to-tail product) and **B′** (head-to-tail product) by NMR spectroscopy. The *E* configuration of the central double bond is confirmed by the coupling constants ($^3J = 15.5$ Hz) indicating the *trans* orientation of the olefinic protons in both compounds.

In Table 3 selected results of the dimerization reaction in the presence of $Pd(acac)_2$/1,3-diisopropylphenyl-4,5-dimethyl-imidazolium bromide and 0.5 mol% Na^{i}PrO/^{i}PrOH are shown. The regioselectivity towards different dimers is dependent on the temperature. For acceptable conversion a reaction temperature of at least 70 °C is required.

At this temperature a 1 to 1 mixture of **A′** and **B′** is obtained. Increasing the temperature increased the formation of the tail-to-tail coupling product (up to 65%). By

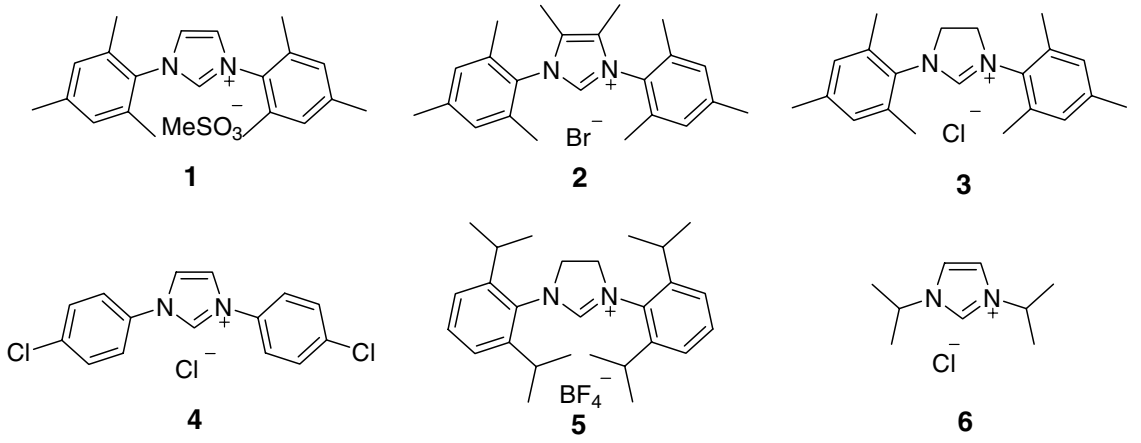
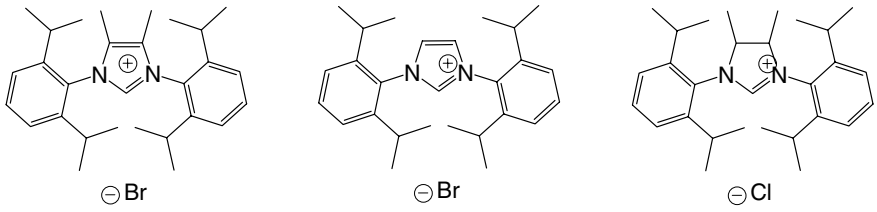


Fig. 2. Structure of tested imidazolium salts in telomerization reaction.



7 **8** **9**

Fig. 3. Imidazolium salts for the catalytic dimerization of isoprene.

Table 3
Catalytic dimerization of isoprene under different conditions

Entry	Pd (mol%)	T (°C)	t (h)	Yield[a] (%)	Selectivity[b] (%)		
					A′	**B′**	Others
1	0.01	70	48	69	41	37	22
2	0.02	70	24	63	42	38	20
3	0.01	90	48	86	57	26	17
4	0.02	90	24	72	58	26	16
5[c]	0.02	90	24	98	60	25	15
6	0.01	110	24	70	65	18	17
7	0.01	130	24	69	55	11	34

General conditions: $Pd(acac)_2$, L = 1,3-diisopropylphenyl-4,5-dimethylimidazolium bromide (**7**), Pd/L = 1/10, 15 ml 0.5 mol% Na^{i}PrO/^{i}PrOH, 10 ml isoprene, $pN_2 = 30$ bar.
[a] Yield of different dimers.
[b] Selectivity of different dimers.
[c] $pN_2 = 50$ bar.

ascending the Nitrogen pressure from 30 bar to 50 bar (Table 3, entry 4 vs. entry 5) full conversion is reachable. At 90 °C and a pressure of 30 bar the isoprene molecules are distributed into the liquid and vapor phase, exchange is feasible by diffusion. At 90 °C and a pressure of 50 bar the isoprene molecules are forced into the liquid phase which facilitates full conversion without diffusion control. However, applying temperatures above 90 °C gave rise to polymerization of isoprene and to formation of vinylcyclohexene derivatives as by-products. Therefore, further catalytic experiments were carried out at 70–90 °C. In Tables 4 and 5 the influence of various ligands is presented.

Table 4
Catalytic dimerization of isoprene with different ligands at 90 °C

Entry	Ligand	Pd (mol%)	Yield[a] (%)	Selectivity[b] (%)		
				A′	**B′**	Others
1	**PCy$_3$**	0.02	14	84	<1	15
2	**PPh$_3$**	0.02	3	16	<1	83
3	**1**	0.02	87	70	22	8
4	**5**	0.02	84	81	11	8
5	**7**	0.02	72	58	26	16
6	**8**	0.02	62	71	16	13
7[c]	**9**	0.02	98	75	16	9

General conditions: $Pd(acac)_2$, Pd/L = 1/10, $t = 24$ h, $pN_2 = 30$ bar, $T = 90$ °C, 15 ml 0.5 mol% Na^{i}PrO/^{i}PrOH, 10 ml isoprene.
[a] Yield of different dimers.
[b] Selectivity of different dimers.
[c] 20 ml 0.5 mol% Na^{i}PrO/^{i}PrOH, 5 ml isoprene.

Table 5
Catalytic dimerization of isoprene with different ligands at 70 °C

Entry	Ligand	pN_2 (bar)	Pd (mol%)	Yield[a] (%)	Selectivity[b] (%)		
					A′	**B′**	Others
1	**1**	30	0.01	68	47	37	16
2	**1**	50	0.01	68	45	38	17
3	**5**	30	0.01	82	74	16	10
4	**5**	30	0.005	76	71	15	14
5	**9**	30	0.01	93	72	17	11
6	**9**	30	0.005	35	67	17	16

General conditions: $Pd(acac)_2$, Pd/L = 1/10, $t = 24$ h, $T = 70$ °C, 15 ml 0.5 mol% Na^{i}PrO/^{i}PrOH, 10 ml isoprene.
[a] Yield of different dimers.
[b] Selectivity of different dimers.

Catalysts containing phosphine ligands showed only low catalyst activity (Table 4, entries 1–2). Both triphenylphosphine and tricyclohexylphosphine gave the tail-to-tail product. NHCs showed in all cases a much higher activity.

In general, no telomers are observed except for **1** which formed telomers in traces. As major by-products oligomerization products and in small extent vinylcyclohexene derivatives are observed.

3. Conclusions

Here, we reported the first telomerizations and dimerizations of isoprene in the presence of palladium–carbene catalysts. A switch of the telomerization to the dimerization products occurred depending on the nature of the imidazolium salts. *N*-Heterocyclic carbenes showed unprecedented catalyst productivity for both reactions. Furthermore the use of Pd/carbene catalysts for other telomerization reactions is currently under way in our laboratories.

4. Experimental

All manipulations were carried out under argon or nitrogen atmosphere. Isoprene was dried and distilled prior to application. Palladium acetylacetonate was received by Strem Chemicals and used without further purification. Imidazolium salts were prepared by published methods. Methanol and isopropanol were dried and distilled before addition of sodium to form a 0.5 mol% NaOR/ROH solution. ^{1}H and ^{13}C spectra were recorded on a Bruker Spectrometer AVANCE 500 (^{1}H: 500.13 MHz; ^{13}C:

125.8 MHz). The calibration of ^{1}H and ^{13}C spectra was carried out on solvent signals (δ ($CDCl_3$) = 7.25 and 77.0). The NMR signals were assigned by DEPT and two-dimensional spectra (^{1}H,^{1}H COSY; NOESY; ^{1}H,^{13}C HSQC; and ^{1}H,^{13}C HMBC). Elemental analyses were run on a Leco CHNS-932.

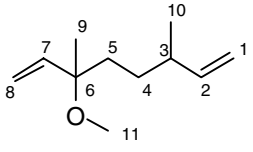
4.1. General procedure for catalytic telomerizations

0.92 mg (3.0×10^{-6} mol) of palladium acetylacetonate and 12 mg (3.0×10^{-5} mol) of **1** was added in a dried and secured vessel under argon. Afterwards 12 ml of a 0.5 mol% sodium methoxide in methanol solution and 10 ml isoprene (1×10^{-1} mol) were added. The mixture was transferred under argon into a secured 100 mL stainless steel Parr autoclave. At 25 bar nitrogen pressure the autoclave was heated to the desired reaction temperature. After 20 h the autoclave was cooled to room temperature and 5 mL of isooctane as internal standard was added. In general, the yield of telomers was determined by GC using HP 6869A gas chromatograph. The main products were isolated from the reaction mixture *via* distillation.

4.2. General procedure for catalytic dimerizations

3.5 mg (1.11×10^{-5} mol) of palladium acetylacetonate and 45.9 mg (1.11×10^{-4} mol) of **1** was added in a dried and secured vessel under argon. Afterwards 15 ml of a 0.5 mol% sodium isopropoxide in isopropanol solution and 10 ml isoprene (1×10^{-1} mol) were added. The mixture was transferred under argon into a secured 100 mL stainless steel Parr autoclave. At 30 bar nitrogen pressure the autoclave was heated to the desired reaction temperature. After 24 h the autoclave was cooled to room temperature and 5 mL of isooctane as internal standard was added. In general, the yield of dimers was determined by GC using HP 6869 A gas chromatograph. The main products were isolated from reaction mixture *via* distillation.

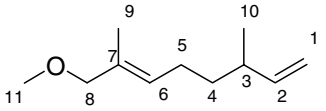
4.2.1. 3-Methoxyocta-3,6-dimethyl-2,7-diene (*A*)



^{1}H NMR ($CDCl_3$, 500.13 MHz): δ = 5.70–5.57 (m, 2H, H-2,7); 5.11–5.03 (m, 2H, H-8); 4.90–4.83 (m, 2H, H-1); 3.07 (s, 3H, $OMe_{(11)}$); 2.00 (m, 1H, H-3); 1.44 (m, 2H, H-4); 1.24 (m, 2H, H-5); 1.15 (s, 3H, $Me_{(9)}$); 0.93 (d, 3H, $^{3}J_{3,10}$ = 6.0 Hz, $Me_{(10)}$).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 144.3 (C-2); 142.8 (C-7); 114.3 (C-8); 112.5 (C-1); 77.1 (C-6); 49.7 ($OMe_{(11)}$); 38.1 (C-3); 37.1 (C-4); 30.3 (C-5); 21.3 ($Me_{(10)}$); 21.2 ($Me_{(9)}$).

4.2.2. 1-Methoxyocta-2,6-dimethyl-2,7-diene (*B*)

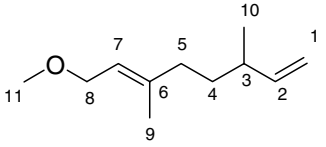


^{1}H NMR ($CDCl_3$, 500.13 MHz): δ = 5.67 (ddd, 1H, $^{3}J_{1(trans),2}$ = 17.5 Hz, $^{3}J_{1(cis),2}$ = 10.5 Hz, $^{3}J_{2,3}$ = 7.5 Hz, H-2); 5.37 (m, 1H, H-6); 4.96–4.89 (m, 2H, H-1); 3.77 (s, 2H, H-8); 3.25 (s, 3H, $OMe_{(11)}$); 2.08 (m, 1H, H-3); 1.98 (m, 2H, H-5); 1.61 (s, 3H, $Me_{(9)}$); 1.34 (m, 2H, H-4); 0.97 (d, 3H, $^{3}J_{3,10}$ = 6.0 Hz, $Me_{(10)}$).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 144.5 (C-2); 131.9 (C-7); 128.3 (C-6); 112.7 (C-1); 78.7 (C-8); 57.3 ($OMe_{(11)}$); 37.4 (C-3); 36.3 (C-4); 25.4 (C-5); 20.1 ($Me_{(10)}$); 13.7 ($Me_{(9)}$).

MS (EI): 168 [M] (2), 153 (3), 136 (19), 121 (30), 111 (42), 85 (100), 67 (67), 55 (76).

4.2.3. 1-Methoxyocta-3,6-dimethyl-2,7-diene (*C*)

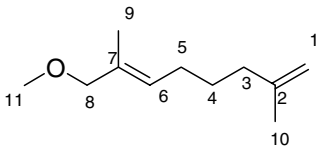


^{1}H NMR ($CDCl_3$, 500.13 MHz): δ = 5.66 (ddd, 1H, $^{3}J_{1(trans),2}$ = 17.3 Hz, $^{3}J_{1(cis),2}$ = 10.5 Hz, $^{3}J_{2,3}$ = 7.5 Hz, H-2); 5.32 (m, 1H, H-7); 4.96–4.89 (m, 2H, H-1); 3.91 (br d, 2H, $^{3}J_{7,8}$ = 7.0 Hz, H-8); 3.30 (s, 3H, $OMe_{(11)}$); 2.08 (m, 1H, H-3); 1.99 (m, 2H, H-5); 1.64 (br s, 3H, $Me_{(9)}$); 1.40 (dt, 2H, $^{3}J_{3,4}$ = 8.5 Hz, $^{3}J_{4,5}$ = 7.0 Hz, H-4); 0.98 (d, 3H, $^{3}J_{3,10}$ = 6.0 Hz, $Me_{(10)}$).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 144.5 (C-2); 140.6 (C-6); 120.6 (C-7); 112.7 (C-1); 68.9 (C-8); 57.7 ($OMe_{(11)}$); 37.4 (C-3); 37.1 (C-5); 34.6 (C-4); 20.1 ($Me_{(10)}$); 16.4 ($Me_{(9)}$).

MS (EI): 168 [M] (0.2), 136 (5), 121 (17), 111 (19), 96 (27), 85 (100), 68 (34), 55 (44), 41 (38).

4.2.4. 1-Methoxyocta-2,7-dimethyl-2,7-diene (*D*)



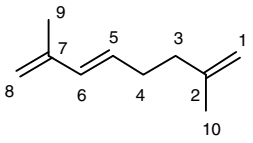
^{1}H NMR ($CDCl_3$, 500.13 MHz): δ = 5.39 (m, 1H, H-6); 4.67 (dm, 2H, H-1); 3.77 (br s, 2H, H-8); 3.26 (s, 3H, $OMe_{(11)}$); 2.05–1.96 (m, 4H, H-4,5); 1.69 (s, 3H, $Me_{(10)}$); 1.61 (s, 3H, $Me_{(9)}$); 1.49 (m, 1H, H-3). ^{13}C NMR ($CDCl_3$,

125.8 MHz): $\delta = 145.8$ (C-2); 132.2 (C-7); 128.1 (C-6); 109.8 (C-1); 78.7 (C-8); 57.3 ($OMe_{(11)}$); 37.3 (C-4); 27.4 (C-3); 27.2 (C-5); 22.3 ($Me_{(10)}$); 13.7 ($Me_{(9)}$).

Elemental analyses of a telomeric product mixture

Anal. Calc. for $C_{11}H_{20}O$: C, 78.51; H, 11.98; O, 9.51. Found: C, 78.5; H, 11.8%.

4.2.5. 2,7-Dimethylocta-1,3,7-triene (*A′*)

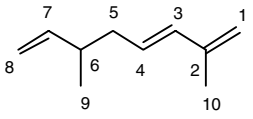


^{1}H NMR ($CDCl_3$, 500.13 MHz): $\delta = 6.16$ (br d, 1H, $^3J_{5,6} = 15.5$ Hz, H-6); 5.66 (dt, 1H, $^3J_{5,6} = 15.5$ Hz, $^3J_{4,5} = 7.0$ Hz, H-5); 4.87 (s, 2H, H-8); 4.71 (dm, 2H, H-1); 2.25 (m, 2H, H-3); 2.11 (dt, 2H, $^3J_{3,4} = 8.2$ Hz, $^3J_{4,5} = 7.0$ Hz, H-4); 1.83 (s, 3H, $Me_{(9)}$); 1.73 (s, 3H, $Me_{(10)}$).

^{13}C NMR ($CDCl_3$, 125.8 MHz): $\delta = 145.3$ (C-2); 142.1 (C-7); 133.0 (C-6); 130.2 (C-5); 114.3 (C-8); 110.1 (C-1); 37.6 (C-3); 31.0 (C-4); 22.5 ($Me_{(10)}$); 18.7 ($Me_{(9)}$).

MS (EI): 136 [M] (3), 121 (36), 107 (23), 93 (19), 81 (100), 79 (77), 53 (32), 41 (25).

4.2.6. 2,6-Dimethylocta-1,3,7-triene (*B′*)



^{1}H NMR ($CDCl_3$, 500.13 MHz): $\delta = 6.14$ (br d, 1H, $^3J_{3,4} = 15.5$ Hz, H-3); 5.76 (ddd, 1H, $^3J_{7,8(trans)} = 17.3$ Hz, $^3J_{7,8(cis)} = 10.5$ Hz, $^3J_{6,7} = 7.0$ Hz, H-7); 5.62 (dt, 1H, $^3J_{3,4} = 15.5$ Hz, $^3J_{4,5} = 7.3$ Hz, H-4); 5.00–4.92 (m, 2H, H-8); 4.86 (s, 2H, H-1); 2.27-2.05 (m, 3H, H-5,6); 1.83 (s, 3H, $Me_{(10)}$); 1.00 (s, 3H, $Me_{(9)}$). ^{13}C NMR ($CDCl_3$, 125.8 MHz): $\delta = 144.1$ (C-7); 142.1 (C-2); 134.2 (C-3); 128.9 (C-4); 114.4 (C-1); 112.6 (C-8); 39.9 (C-5); 37.8 (C-6); 19.5 ($Me_{(9)}$); 18.7 ($Me_{(10)}$).

MS (EI): 136 [M] (2), 121 (21), 107 (16), 81 (100), 55 (25), 41 (18).

Elemental analyses of a dimeric product mixture

Anal. Calc. for $C_{10}H_{16}$: C, 88.16; H, 11.84; Found: C, 88.2; H, 11.7%.

Acknowledgements

This work was supported by the state of Mecklenburg-Vorpommern, the Federal Ministry BMBF, and the Deutsche Forschungsgemeinschaft (Leibniz-price). Excellent analytic service was provided by Dr. C. Fischer and Dr. W. Baumann (both LIKAT). We thank Dr. F. Nierlich and Dr. T. Maschmeyer (Degussa AG; Oxeno Olefinchemie GmbH) for general discussions.

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