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Development of a Highly Selective and Efficient Catalyst for 1,3-Butadiene Dimerization

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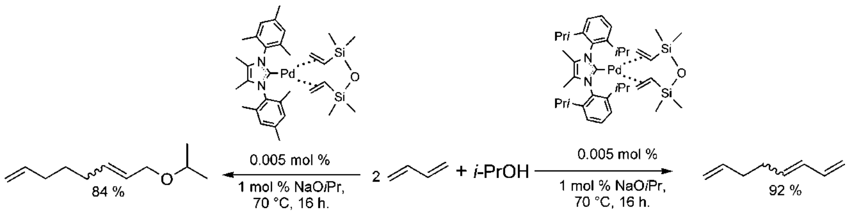
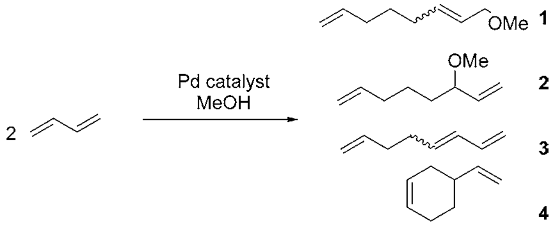
ABSTRACT



A selective dimerization reaction of 1,3-butadiene in the presence of 2-propanol to give 1,3,7-octatriene has been developed. By modification of palladium carbene catalysts an unexpected selectivity switch from the telomerization to the dimerization product occurred. In applying the 1,3-bis(2,6-diisopropylphenyl)-4,5-dimethyl-3*H*-imidazolidenylpalladium(0) complex 9, unprecedented catalyst efficiency (TON > 80 000 and TOF > 5000 h^{-1}) has been obtained for this transformation.

Functionalization and refinement reactions of 1,3-butadiene to provide more valuable organic building blocks and polymers are of significant interest to industrial chemistry and catalysis. With respect to this area, in the past we have been interested in the understanding and practical application of palladium-catalyzed telomerization reactions of 1,3-butadiene and methanol. In general, telomerization reactions are defined as dimerization of two molecules of a 1,3-diene in the presence of an appropriate nucleophile HX, for example, methanol (Scheme 1).[1] The main product of this 100% atom-efficient reaction is the linear 1-methoxy-2,7-octadiene **1**. Major byproducts include the branched 3-methoxy-1,7-octadiene **2**, 1,3,7-octatriene **3**, and 4-vinylcyclohexene **4**. Recently, we have shown that monocarbenepalladium-(0)-olefin complexes are highly active and productive catalysts for the telomerization of 1,3-butadiene with various alcohols.[2] While studying the telomerization reaction in the presence of 2-propanol, we observed a dramatic selectivity switch to give 1,3,7-octatriene **3** as the major product. Here, we report the outcome of this study which presents the most efficient process for **3** known to date.

Scheme 1. Telomerization of 1,3-Butadiene with Methanol



Octatrienes have been reported to be useful intermediates for the manufacturing of butylene oligomers with molecular weights of 350−500,[3] 1,5- and 1,6-octadienes,[4] of different polymers,[5] and for the synthesis of bicyclic alcohols.[6]

In the past, palladium−phosphine complexes such as $Pd(PPh_3)_4$ (TON = 1834)[7] or palladium−phosphonite com-

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plexes (TON = 3482)[8] have been reported to catalyze the linear dimerization of 1,3-butadiene to 1,3,7-octatriene **3**. Interestingly, the catalyst activity and selectivity is influenced by the presence of CO_2.[9] Recently, the reaction of 1,3-butadiene with water under suitable conditions (0.2 mol % $Pd(OAc)_2$, 0.6 mol %, PPh_3, 90 °C) provided **3** in moderate to good yield.[10] In addition, it is known that the linear dimerization of 1,3-butadiene can be carried out using cobalt-,[11] iron-,[12] and rhodium-based[13] catalyst systems to form 5-methyl-1,3,6-heptatriene, 1,3,6-octatriene, and 2,4,6-octatriene while dimerization with nickel catalysts usually gives 1,5-cyclooctadiene.[14] Basically, all procedures known to date for the dimerization of 1,3-butadiene suffer from low catalyst turnover numbers (TON < 3500) and/or low catalyst activity (TOF < 450).

As a starting point of our investigation, we tested different (carbene)palladium(0)−dvds (dvds = 1,3-dimethyldivinylsiloxane) complexes[15] **5**−**9** (Figure 1) for the dimerization of 1,3-butadiene in 2-propanol as solvent and compared their performance to standard palladium catalysts. The applied palladium(0) catalysts are stable for months and can be easily handled even under air.[16]

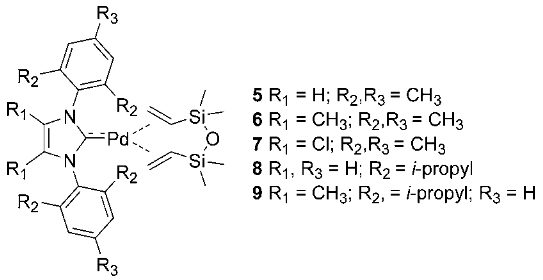

Figure 1. Monocarbenepalladium(0) dvds complexes.

As shown in Table 1 (entries 1−2), $Pd(dba)_2$ and $Pd(OAc)_2$ did not result in any reaction (entries 1−2), while the known system $Pd(OAc)_2/PPh_3$ gave 16% of 1,3,7-octatriene **3** (entry 3). Applying monocarbenepalladium(0)−olefin complexes **5**−**7**, which have a mesityl group attached to the carbene nitrogen atoms, significantly higher activity is obtained (100% conversion). Unfortunately, the selectivity for the desired product **3** is low (17−31% of 1,3,7-octatriene). Instead, mainly the octadienyl ethers **1** and **2** (Table 1, entries 4−6) are produced. However, by applying complex **8**, which resembles **5** except for the 2,6-diisopropylphenyl group attached to the carbene nitrogen, the yield of **3** is increased

Table 1. Dimerization of 1,3-Butadiene in 2-Propanol with Different Catalysts[a]

entry	catalyst	yield[b] (%)	chemoselectivity[c] (%)	TON	TOF[d] (h^{-1})
1	$Pd(dba)_2$	0			
2	$Pd(OAc)_2$	0			
3	$Pd(OAc)_2$/3 PPh_3	16	84	3200	200
4	**5**	17	17	3400	212
5	**6**	16	16	3200	200
6	**7**	31	31	6200	387
7	**8**	62	62	12 400	775
8	**9**	92	95	18 400	1150
9	$Pd(OAc)_2$/4 L	83	93	16 600	1037

[a] General conditions: Pd = 0.005 mol %, 16 h, 70 °C, 1.0 mol % NaOR, ROH/1,3-butadiene = 2:1, 3 mL of THF, diglyme as internal standard. [b] Yield of 1,3,7-octatriene. [c] Chemoselectivity = (yield of octatriene)/(yield of telomer + octatriene + 4-vinylcyclohexene) × 100. [d] Calculated with respect to 1,3,7-octatriene. L = 1,3-bis(2,6-diisopropylphenyl)-4,5-dimethyl-3*H*-imidazol-1-ium bromide.

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(14) An exception is the linear dimerization in alcoholic media with low-valent nickel complexes: (a) Müller, H.; Wittenberg, D.; Seibt, H.; Scharf, E. *Angew. Chem.* **1965**, *77*, 318. (b) Feldman, J.; Saffer, B. A.; Frampton, O. D. U.S. Pat. 3284529, 1966; *Chem. Abstr.* **1967**, *66*, 28373.

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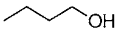
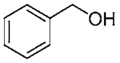
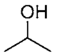
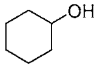
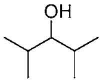
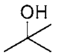
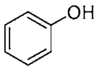
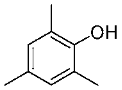
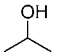
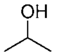
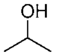
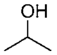
(16) Similar palladium-carbene catalysts are commercially available from STREM.

to 62% (Table 1, entry 7). Surprisingly, using complex **9**, which has two extra methyl groups on the C-4 and C-5 position of the imidazole ring, provided excellent yield (92%) of **3** with 95% selectivity and a turnover number TON = 18 400. Interestingly, the in situ prepared catalyst **9** gave similar results (Table 1, entry 9). It is important to note that in general 1,3,7-octatriene **3** is obtained as a mixture of two isomers (cis and trans) in a ratio of 1:1.7. Spectroscopic studies (NMR, UV) rule out any formation of the corresponding conjugated triene.

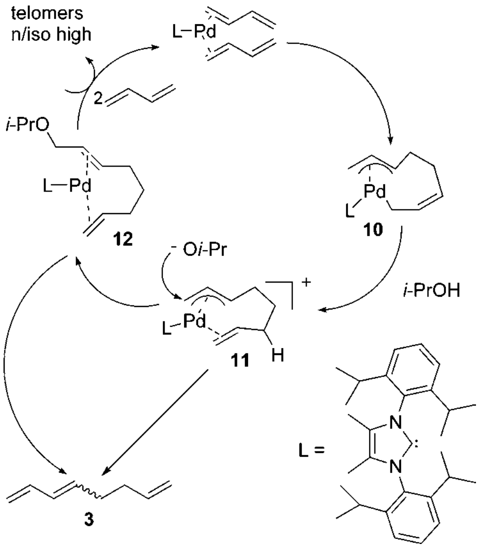
Next, we were interested in the effect of different alcohols on the selectivity of the dimerization process. Table 2 shows a summary of the results obtained in the presence of catalyst **9**. Using aprotic solvents such as toluene and THF led to no conversion (Table 2, entries 1−2). In the presence of primary alcohols, predominantly octadienyl ethers were obtained (Table 2, entries 3−5) due to the easier attack of the alcohol on the intermediate palladium allyl complex (see also Scheme 2). As expected, in the presence of the secondary alcohol cyclohexanol **3** is obtained in good yield (83%) (Table 2, entry 7). However, by using more hindered alcohols such as 2,4-dimethyl-3-pentanol and *t*-BuOH very low conversion is seen (Table 2, entries 8 and 9). This is also true for phenols.

Table 2. Dimerization of 1,3-Butadiene with Different Alcohols and Phenols[a]

Entry	ROH / ArOH	Yield **3** [%]	Chemoselectivity. [%][b]	TON	TOF [h^{-1}][c]
1[d]	-	-	-	-	-
2[e]	-	-	-	-	-
3[f]	MeOH	2	47	1,750	109
4[f]		44	56	44,000	2,750
5		7	14	1,400	87
6		92	95	18,400	1,150
7[g]		83	95	16,600	1,037
8		2	99	400	25
9		2	>99	400	25
10		<1	6	100	6
11		0	-	-	-
12[h]		84	92	16,800	1,050
13[f]		81	94	81,000	5,062
14[i]		2	-	400	25
15[f,j]		69	95	69,000	4,312

[a] General conditions: 16 h, 0.005 mol % of catalyst **9**, 1.0 mol % of NaOR, ROH/1,3-butadiene = 2:1, 3 mL of THF, 70 °C, diglyme as internal standard. [b] Chemoselectivity = (yield of **1**)/(yield of **1** + **2** + **3** + vinylcyclohexene) × 100. [c] Calculated with respect to 1,3,7-octatriene. [d] Toluene instead of ROH. [e] THF instead of ROH. [f] Catalyst = 0.001 mol %. [g] NaOR = NaO^{t}Bu. [h] Temperature 50 °C. [i] 0.25 equiv of ROH with respect to 1,3-butadiene. [j] Pd/L = 1:10, L = 1,3-bis(2,6-diisopropylphenyl)-4,5-dimethyl-3*H*-imidazol-1-ium bromide.

Scheme 2. Proposed Mechanism for the Dimerization/Telomerization of 1,3-Butadiene with Alcohols



By optimizing the catalyst efficiency of **9** in the presence of 2-propanol (Table 2, entries 12−15) turnover numbers >80 000 and catalyst activity >5000 h^{-1} are observed at 70 °C. To the best of our knowledge, this is the highest catalyst productivity and activity reported for any 1,3-diene dimerization reaction. Interestingly, even at lower temperature (50 °C) 1,3-butadiene is smoothly dimerized in 84% yield (Table 2, entry 12).

With regard to the mechanism of the reaction the basic question is whether **3** is formed directly from the [Pd(carbene)(η^1,η^2-C_8H_{13})] species **11** or via **12** with subsequent elimination. The generally accepted mechanism of the telomerization reaction is shown in Scheme 2. Important mechanistic studies of the telomerization of alcohols and 1,3-butadiene in the presence of a palladium phosphine catalyst have been performed by Jolly and co-workers.[17] More recently, we also proposed a possible mechanism for this reaction.[18]

Earlier, Smutny had shown that, under suitable conditions, 1-phenoxy-2,7-octadiene can be converted to 1,3,7-octatriene

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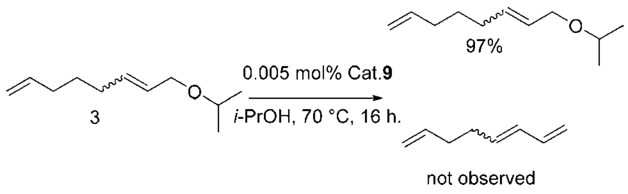
3 in good yield and conversion;[19] in addition, Keim and coworkers proposed a similar mechanism for the formation of **3**.[20] However, this mechanistic proposal is not supported by the results shown in Table 2.

Hence, we performed catalytic reactions of 1-isopropoxy-2,7-octadiene in the presence of 0.005 mol % of complex **9** in 2-propanol under typical reaction conditions (70 °C, 16 h).

As shown in Scheme 3, 97% of the used 1-isopropoxy-2,7-octadiene was reisolated after the reaction. Obviously, formation of 1,3,7-octatriene formation via **12** is ruled out. Thus, as shown in Scheme 2, we believe that the isopropoxide ion instead of adding to the allylic terminus of C1 or C3, abstracts preferentially a proton on C4 in the presence of **9** to give 1,3,7-octatriene via β-hydrogen elimination.

Scheme 3. Formation of 3 via 1 and 2



In summary, we have developed a highly productive and active catalyst system **9** for the dimerization of 1,3-butadiene to 1,3,7-octatriene. For the first time, this catalyst seems to fulfill the criteria required for industrial application of this reaction.

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Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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