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A Highly Efficient Catalyst for the Telomerization of 1,3-Dienes with Alcohols: First Synthesis of a Monocarbenepalladium(0)–Olefin Complex[**]

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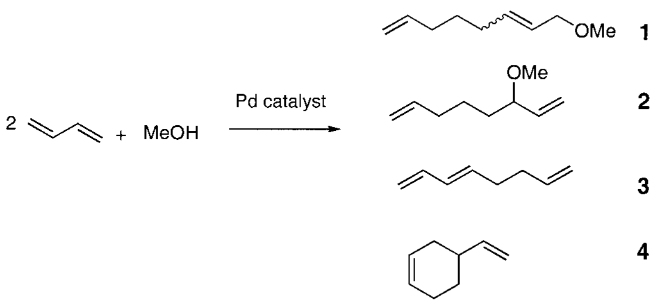
Dedicated to Professor Bernhard Lücke
on the occasion of his 65th birthday

Some time ago we started a program to develop atom-efficient homogeneous catalytic reactions, which are of interest for the chemical industry, especially the fine chemical industry.[1] We recently became interested in palladium-catalyzed telomerizations, since these reactions assemble simple starting materials in a 100% atom-efficient manner.[2] In general, the telomerization reaction is the dimerization of two molecules of an 1,3-diene in the presence of an appropriate nucleophile HX, for example, an alcohol,[3] to give substituted octadienes (1-substituted 2,7-octadiene, 3-substituted 1,7-octadiene). The resulting compounds are useful as intermediates in the total synthesis of several natural products[4] as well as in industry, as precursors for plasticizer alcohols,[5] monomers, solvents, corrosion inhibitors, and nonvolatile herbicides.[6]

Because of their ready availability and their exceedingly low price,[7] 1,3-butadiene and methanol are the most attractive starting materials for the telomerization reaction (Scheme 1), and yield mainly the 1-substituted 2,7-octadiene **1**. As previous studies have shown, the major by-products include the 3-substituted octa-1,7-diene (**2**; branched product), 1,3,7-octatriene (**3**; formed by the linear dimerization of butadiene), and 4-vinylcyclohexene (**4**; formed by the Diels–Alder reaction of two molecules of butadiene).



Scheme 1. Products of the telomerization of butadiene with methanol.

As a result of elegant studies from Jolly[8] and recent investigations from our side[9] the mechanism of the palladium-catalyzed telomerization reaction is well-understood. From the catalytic cycle of the reaction it is apparent that one strongly bound and sterically hindered ligand on the palladium center is sufficient to generate a productive and highly selective catalyst system. In fact, in the presence of only one strongly coordinated ligand the activity of the catalyst should be high, because free coordination sites for catalysis are readily available at the metal center.

Therefore, we had the idea that monophosphanepalladium complexes with basic phosphanes should lead to improved catalysts for telomerization reactions. Unfortunately, the tested monophosphanepalladium-1,6-diene[10] complexes proved not to be superior to the standard palladium/triphenylphosphane catalyst.[11] Next, we thought that monocarbenepalladium(0) complexes might be more suitable catalysts for our purpose. In the last five years palladium–carbene complexes have become increasingly important as catalysts for Heck-, Suzuki-, and Sonogashira reactions, copolymerizations, and aminations of aryl halides.[12] However, they have not been reported as catalysts for telomerization reactions.[13] Despite the increasing interest in this class of complexes, there are only few examples of characterized palladium(0)–carbene complexes known.[14] To our knowledge there has been no monocarbenepalladium(0) complex without additional phosphane ligands synthesized and characterized. Nevertheless, the synthesis of a monocarbenepalladium(0)–diolefin complex was achieved smoothly by treating the palladium(0)diall-

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yl ether complex $[Pd_2(dae)_3]$[15] (dae = diallylether) with 1,3-dimesitylimidazol-2-ylidene carbene (dmi)[16] in 1,1,3,3-tetramethyl-1,3-divinyl-disiloxane (dvds) at −30 °C.[17a] Crystals of the product 1,3-dimesitylimidazol-2-ylidene-palladium(0) η^2,η^2-1,1,3,3-tetramethyl-1,3-divinyl-disiloxane ($[(dmi)Pd^0(dvds)]$; **5**) suitable for X-ray crystallography (Figure 1)[17b] were obtained by crystallization from pentane at −70 °C.

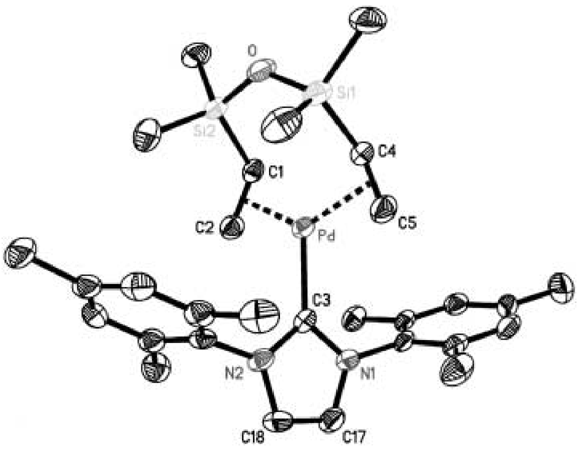

Figure 1. Molecular structure of **5**. The thermal ellipsoids are set at 30 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C3−N1 1.373(5), C3−N2 1.369(6), C17−C18 1.320(6), C1−C2 1.408(6), C4−C5 1.388(6), Pd−C3 2.076(5), Pd−C1 2.156(5), Pd−C2 2.137(5), Pd−C4 2.190(5), Pd−C5 2.141(6), N1−C3−N2 102.0(4), N2−C18−C17 106.7(5), N2−C3−Pd 129.3(3), CE1−Pd−CE2 130.3, C3−Pd−CE1 115.3, C3−Pd−CE2 114.3 (CE = mid-points of the coordinated C=C bonds).

The central palladium atom is coordinated by $H_2C{=}CHSiMe_2OSiMe_2HC{=}CH_2$ and the carbene ligand (trigonal-planar coordination, Figure 1). The plane of the carbene heterocycle and the coordination plane form an angle of 64.7°. The distance between the palladium center and the carbene atom is 2.076(5) Å, which is in the range found for other palladium–carbene complexes.[18]

We tested the telomerization of 1,3-butadiene with methanol in the presence of **5**. To be of relevance for practical applications we used comparably small amounts of catalyst (1,3-butadiene:catalyst = 100 000:1–300 000:1). Using our previously optimized reaction conditions (90 °C, methanol:butadiene = 2:1, 1 mol % NaOH) the former best catalyst system ($Pd(OAc)_2/3\,PPh_3$; **7**) gives a product yield of 79 %, a chemoselectivity of 90 %, and a linear:branched (l:b) ratio of 12:1 (Table 1, entry 1). At 50 °C the catalyst is barely active. Using $PnBu_3$ as the ligand instead of PPh_3 product yield (57 %), and l:b-ratio (10:1) are lower and chemoselectivity is the same (Table 1, entry 4).

The monophosphanepalladium(0)–dvds complex **6**[10] with a sterically hindered basic phosphane as ligand (PCy_3) is relatively active but comparably low chemoselectivity and l:b ratio are obtained (Table 1, entry 5). In contrast, the monocarbenepalladium(0) complex shows improved catalyst productivity and extremely high selectivity (chemoselectivity = 99 %; l:b = 36:1) giving the desired product in 98 % yield! (Table 1, entry 6). At 50 °C there is hardly any other product detected (≤1 %) apart from the desired diene **1**. Even with a substrate:catalyst ratio of 300 000:1 nearly full conversion is obtained (Table 1, entry 8; catalyst turnover number TON = 267 000). With a further lowering of the catalyst concentration the conversion becomes incomplete. Nevertheless, this is the highest catalyst productivity reported for any telomerization reaction.

Having demonstrated the superiority of **5** in the industrially most important telomerization reaction, we were interested in the coupling of 1,3-butadiene with different alcohols. In general, other alcohols react in the presence of known catalyst systems much less efficiently than methanol and ethanol. In all the reactions the standard conditions as described above were used. The results are summarized in Table 2.

Using aliphatic alcohols the monocarbenepalladium complex **5** is significantly more active and selective than the standard catalyst ($Pd(OAc)_2/3\,PPh_3$). For example using *n*-hexanol and *iso*-propanol in the presence of 0.001 and 0.005 mol % of **5**, respectively, the telomerization products are obtained in 92 and 73 % yield, respectively (Table 2, entries 5 and 7). Applying the same catalyst concentration with the standard catalyst only 1 and 5 % of the corresponding octadienylethers are obtained (Table 2, entry 6 and 8). Also in the presence of phenol as the alcohol the new catalyst proved to be more productive, however, the l:b ratio is lower with **5**, a result which is not understood so far.

In summary, we have synthesized and characterized the first monocarbenepalladium(0)olefin complex. This catalyst shows remarkable productivities and selectivities for a number of telomerization reactions. It is believed that this class of catalysts will be also of use for other palladium-catalyzed coupling reactions. Further studies in this direction, as well as the synthesis of other monocarbenepalladium(0) complexes are in progress.

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

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

[a] General conditions: 16 h, 90 °C, 1 mol % NaOH, MeOH:Butadiene = 2:1, Pd:L = 1:3. [b] Yield of **1** + **2**. [c] Chemoselectivity = (**1** + **2**)/(**1** + **2** + **3** + **4**) × 100.

Table 2. Telomerization of 1,3-butadiene with different alcohols.[a]

Entry	Pd cat.	ROH	Pd [mol %]	Yield [%][b]	Chemoselectivity [%][c]	l:b	TON
1	**5**	$CH_3OC_2H_4OH$[d]	0.001	97	97	39:1	97000
2	**7**	$CH_3OC_2H_4OH$[d]	0.001	35	47	16:1	35000
3	**5**	n-C_4H_9OH[e]	0.001	91	96	52:1	91000
4	**7**	n-C_4H_9OH[e]	0.001	17	35	16:1	17000
5	**5**	n-$C_6H_{13}OH$[f]	0.001	92	93	37:1	92000
6	**7**	n-$C_6H_{13}OH$[f]	0.001	≤ 1	–	–	–
7	**5**	i-C_3H_7OH[e]	0.005	73	73	4:1	14600
8	**7**	i-C_3H_7OH[e]	0.005	5	11	1:1	1000
9	**5**	C_6H_5OH[g]	0.005	56	98	8:1	12000
10	**7**	C_6H_5OH[g]	0.005	38	97	19:1	7600

[a] General conditions: 16 h, 90 °C, 1 mol % Base, ROH:1,3-Butadiene = 2:1, **7** = $Pd(OAc)_2/3\,PPh_3$. [b] Yield of l + b. [c] Chemoselectivity = (l + b)/(l + b + **3** + **4**) × 100. [d] Base: $CH_3OC_2H_4ONa$. [e] Base: NaOH. [f] Base: n-$C_6H_{13}ONa$. [g] Base: C_6H_5ONa, C_6H_5OH (46 %) in THF.

Experimental Section

General procedure for the telomerization: [(dmi)Pd^0(dvds)](**5**; 1.6 mg, 2.77×10^{-6} mol) was dissolved in methanol (17.8 g, 0.555 mol) under argon (or $Pd(OAc)_2$ (0.62 mg, 2.77×10^{-6} mol) and PPh_3 (2.2 mg, 8.33×10^{-6} mol) in the other cases). Then NaOH (111 mg, 2.77×10^{-3} mol) was added and the mixture transferred under argon into a secured stainless steel Parr autoclave (100 mL). Then the autoclave was cooled with dry ice. 1,3-butadiene (15 g, 2.77×10^{-1} mol) was condensed in a separate pressure cylinder (75 mL, mass control) and this defined amount of 1,3-butadiene was then condensed into the cooled autoclave and the vessel heated to reaction temperature. After the reaction was finished the autoclave was cooled to room temperature and the remaining 1,3-butadiene condensed. *iso*-octane (5 mL) was added as an internal standard. The yield of telomerization products was determined by gas chromatography (GC) by using an HP6869A gas chromatograph. To isolate the different octadienyl ethers the reaction mixture was distilled in vacuo.

cis/*trans*-**1**: ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.49$ (q, $J = 8.0$ Hz, 2H), 2.68–2.76 (m, 4H), 3.31 (s, 3H), 3.86 (dd, $J = 6$ Hz, $J = 2$ Hz, 2H), 4.95–4.99 (m, 2H), 5.49–5.61 (m, 1H), 5.64–5.87 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 27.0$, 28.3, 28.7, 31.7, 33.2, 57.6, 57.9, 68.1, 73.2, 114.5, 126.3, 126.4, 133.2, 134.4, 138.5, 138.6.

2: ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.34$–1.68 (m, 4H), 2.01–2.10 (m, 2H), 3.26 (s, 3H), 3.46–3.54 (m, 1H), 4.90–5.20 (m, 2H), 5.14–5.22 (m, 1H), 5.58–5.87 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 24.6$, 33.7, 34.8, 56.1, 82.9, 114.5, 117.0, 138.7, 138.8.

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[17] $[Pd_2(dae)_3]$ (405 mg, 0.8 mmol) were suspended in 1,1,3,3-tetramethyl-1,3-divinyl-disiloxane (5 mL). The mixture was immediately cooled to −30 °C and 1,3-dimesitylimidazol-2-ylidene (340 mg, 1.1 mmol) was added. After warming up to room temperature the solution was stirred for 1 h at this temperature. Then the white complex formed was collected by filtration, washed with pentane (2 × 5 mL), and dried in vacuo. X-ray structural analysis of **5**: STOE-IPDS diffractometer, graphite monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, structure solved by direct methods (SHELXS-86: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467) and refined with the full-matrix least-squares method against F^2 (SHELXL-93: G. M. Sheldrick, Göttingen, Germany, **1993**), structural representation: XP (Siemens), 0.4 × 0.3 × 0.2 mm, yellow prism, space group $P2_1/n$, monoclinic, $a = 13.100(3)$, $b = 18.235(4)$, $c = 13.467(3)$ Å, $\beta = 105.07(3)°$, $V = 3106.3(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.277$ g cm^{-3}, 6157 measured reflections, 3279 were independent of symmetry, of which 2412 were observed ($I > 2\sigma(I)$), $R = 0.033$, $wR2$ (all data) = 0.076, 316 parameters. CCDC-171440 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Simple Synthesis of Oligosilyl-α,ω-dipotassium Compounds[**]

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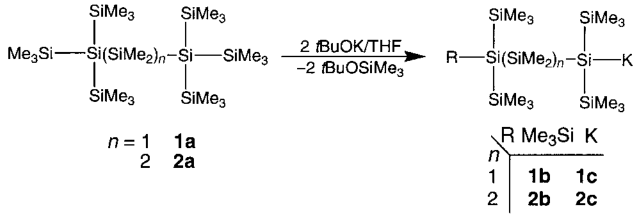
The chemistry of electrophilic silicon compounds is a well established and intensively studied area, whereas their nucleophilic counterparts, the so-called silyl anions, enjoyed much less attention for a long time. This is quite astonishing, considering the high popularity of the tris(trimethylsilyl)silyl group, which is mainly introduced through the respective silyl anion, in main group and organometallic chemistry. However, over the last few years this situation has changed and anionic silyl compounds are now the subject of increased investigations.[1] Recently, in this context, we have reported the synthesis of oligosilyl anions by cleavage of trimethylsilyl groups with potassium *tert*-butoxide.[2] This reaction can be regarded as a variation of the method developed by Gilman et al. for the synthesis of oligosilyllithium compounds by cleavage of trimethylsilyl groups with methyllithium.[3] An advantage of using potassium alkoxides instead of alkyllithium compounds becomes evident in the reaction with higher oligosilanes. In cases where there are additional Si–Si bonds besides the ones between the central silicon atom and the peripheral trimethylsilyl groups, these 'inner' bonds are cleaved exclusively by methyllithium,[3] whereas potassium *tert*-butoxide selectively removes a trimethylsilyl group.[2, 4] The access to these higher silyl anions opened the possibility of studying the prospects for the synthesis of multiply metalated oligosilanes.[4, 5]

Therefore, we treated bis[tris(trimethylsilyl)silyl] compounds, bridged with one (**1a**)[2, 6] or two (**2a**)[7] dimethylsilylene units with potassium *tert*-butoxide in THF at elevated temperatures (Scheme 1). Following a fast first metalation step,[2, 5, 8] the subsequent formation of the dianion takes place more easily when the negative charges are further apart. Whereas the reaction of **2a** to the dianion, occurs at a very low rate, even at room temperature, the conversion of **1a** requires prolonged heating to 60 °C.



Scheme 1. Synthesis of mono- and dipotassium compounds.

Concerning their reactivity **1c** and especially **2c** behave almost like isolated silyl anions. Derivatization reactions like hydrolysis (→**4**), alkylation with dimethyl sulfate (→**3**)[9] and the formation of homo- and heterocyclic rings by the reactions with dimethylsilyl (→**5**),[10] dimethyltin (→**6**),[11] and metallocene dihalides (→**7**, **8**) proceed very cleanly (Scheme 2). In contrast to what is found for lithium silanides,[12] the THF molecules of **1b,c** and **2b,c** are not bound very firmly. They can be removed in part in vacuum; therefore, depending on the conditions of isolation a different content of donor molecules can be observed for these compounds.

Control of conversion and characterization of the silyl anions can be achieved most easily by ^{29}Si NMR spectroscopy. The formal exchange of one trimethylsilyl group for a potassium atom results in a shift of the resonance signal of the affected silicon atom of $\Delta\delta \approx 60$ to lower frequencies. At the same time the trimethylsilyl groups in β-position experience a shift of $\Delta\delta \approx 4-5$ in the opposite direction. The second metalation step from **2b** to **2c** effects an additional slight shift of the ^{29}Si resonance signal of the metalated nucleus to lower frequency ($\delta = -192$), which is in accordance with previous observations with alkylidene-bridged dianions.[5] In contrast to this **1c** exhibits an NMR signal for the metalated silicon

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