Nucleophilic Addition

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Facile Access to Key Reactive Intermediates in the Pd/PR_3-Catalyzed Telomerization of 1,3-Butadiene**

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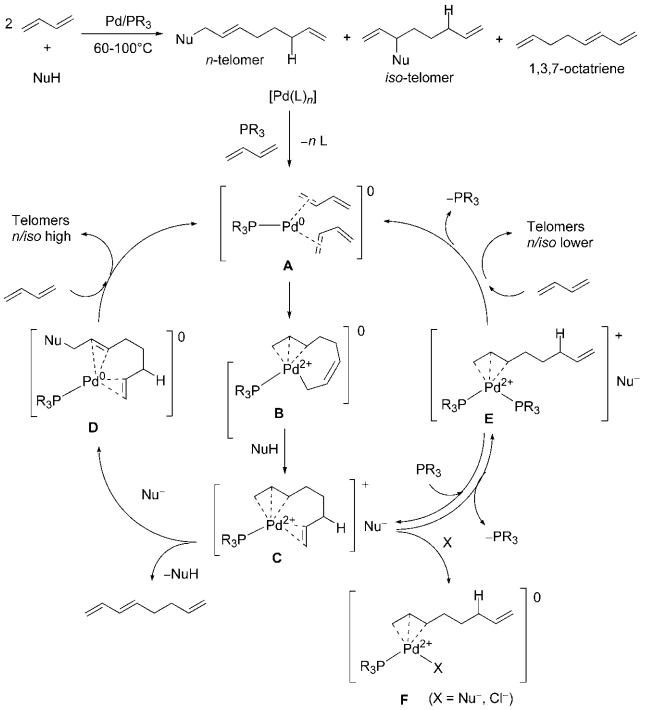
The Pd-catalyzed telomerization of 1,3-dienes is an important atom-efficient transformation, which effectively adds nucleophiles (NuH, for example, H_2O, MeOH, NH_3) over two C–C coupled dienes in a 1,6- or 3,6-fashion (see Scheme 1).[1] As such, telomerization provides an economically attractive route for the production of C8 bulk chemicals, such as 1-octanol[2] and 1-octene.[3] Pd-catalyzed telomerization is also increasingly explored as a potential route for the valorization of biomass-derived feedstock.[1a]

Although the catalytic cycle (Scheme 1) is generally regarded as well understood, only a limited number of studies have been reported that involve the preparation of reactive intermediates.[4–6] Clearly cumbersome preparative methods and the poor stability of [Pd(1,2,3,8-η^4-octadien-1,8-diyl)-(PR_3)] (**B**) are limiting further study. As a result the preparation of reactive intermediates derived from commercially relevant ligands (e.g. TPPTS; TPPTS = 3,3′,3″-phosphinidynetris(benzenesulfonic acid) trisodium salt) remains elusive.[7] **B** mainly acts as a base on NuH during catalysis and is readily converted into [Pd(1,2,3,7,8-η^5-octa-2,7-dien-1-yl)(PR_3)]$^+$ (**C**)[4–5] and its derivatives. Both from a synthetic and catalytic point of view, **C** is the key intermediate as it lies at the focal point of the catalytic cycle and leads via several mechanistic pathways to species such as **D**, **E**, and **F**.

Previously, we have reported on the catalytic activity of Pd/TOMPP (TOMPP = tris(2-methoxyphenyl)phosphine) with biomass-derived substrates such as glycerol, glycols, sugars, and sugar alcohols.[8–10] Mechanistic studies on this catalyst system resulted in a general method for the direct preparation of complexes of type **C** and could be successfully applied to a series of phosphine ligands including PPh_3, TOMPP, and TPPTS. Herein, we report a simple and efficient method for the preparation of cationic complexes of type **C** (**1b**–**5b**), a detailed description of their solid- and solution-state structures, as well as a comparison of their reactivity towards the common methoxide nucleophile.



Scheme 1. Overall reaction and catalytic cycle of the Pd/PR_3-catalyzed telomerization of 1,3-butadiene.

Complexes **1b**[5]–**4b** (Scheme 2) were prepared by a simple one-pot procedure involving the dropwise addition of [HPR_3]BF_4 salt (**1a**–**4a**; 1 equiv) to a mixture of [Pd(dba)$_2$] (1 equiv; dba = *trans*,*trans*-dibenzylideneacetone) and 2,7-octadienol (2 equiv) in CH_2Cl_2 at room temperature. Isolation by precipitation gave the air-stable solids **1b**–**4b** as pure (off)white powders in good to excellent yields (78–94%). For the preparation of TPPTS complex **5b**, a CH_2Cl_2/MeOH (1:1, v/v) solvent mixture was used to improve solubility. Precipitation from MeOH/acetone gave **5b** as the disodium salt in 85% yield.

Structural information on complexes **1b** and **3b** was obtained by means of single-crystal X-ray crystallography (Figure 1, Table 1; see the Supporting Information for **1b**). To

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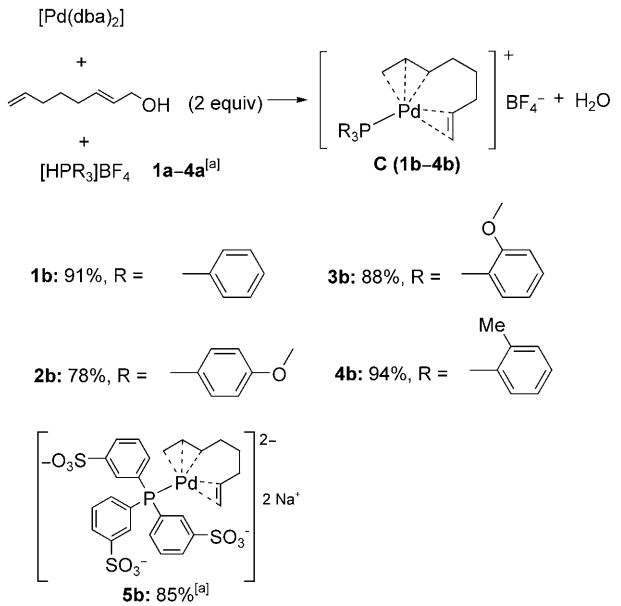


Scheme 2. Preparation of **1b–5b**. Conditions: CH_2Cl_2, 1 h, room temperature. [a] For **5b**: CH_2Cl_2/MeOH (1:1, v/v), 3 equiv HBF_4 and 1 equiv PR_3 were added separately.

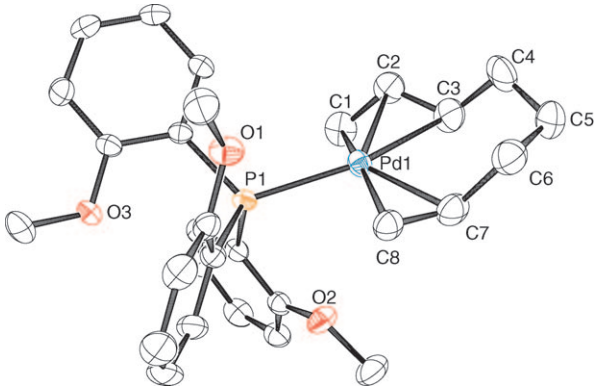


Figure 1. ORTEP diagram of the X-ray structure of **3b.** Hydrogen atoms and BF_4^- anion are omitted for clarity. Ellipsoids are drawn at 50% probability.

Table 1: Selected bond lengths [Å] of **1b** and **3b** (crystal), **1b** (calculated), and of nickel analogue **H**.

	3b M = Pd R = 2-$MeOC_6H_4$	**1b** (1) M = Pd R = Ph	**1b**[15] M = Pd R = Ph	**H**[16] M = Ni R = Ph
M1–C1	2.163(3)	2.142(7)	2.167	2.08(1)
M1–C2	2.185(3)	2.128(7)	2.219	2.02(1)
M1–C3	2.242(4)	2.256(7)	2.335	2.16(2)
M1–C7	2.300(3)	2.322(6)	2.415	2.18(2)
M1–C8	2.236(3)	2.257(5)	2.307	2.04(1)
M1–P1	2.3390(8)	2.358(2)	2.428	2.225(4)

the best of our knowledge, these are the first crystal structures of intermediate **C** of the Pd-catalyzed telomerization of 1,3-butadiene. The two structures show that the 2,7-octadien-1-yl ligand is bonded in η^5 fashion to Pd through an η^3-allylic fragment (C1, C2, C3) and a chelating η^2-olefin tail (C7, C8). Interestingly, the TOMPP ligand displays an *exo*-2 configuration (i.e. only two methoxy groups point outward from the pyramidal phosphine structure).[11] This result shows that the large steric demand of the octadienyl ligand, exemplified by a C1-Pd-C8 angle close to 180°, results in a decrease of the PR_3 cone angle from 205° (*exo*-3) for the free ligand to 176° (*exo*-2) for the complex.[12] In both complexes the olefin moiety (C7, C8) is oriented in-line with the coordination plane of palladium (i.e. defined by Pd1, C1, C3, and P1). This preference is expected for trigonal/square-planar ML_3 complexes[13] and has been observed previously for complexes of the type [M(η^3-allyl)(η^2-olefin)(L)] (M = Pt).[14] A recently calculated structure of **1b** is in fairly good agreement with the crystal structure data of **1b** (and **3b**).[15] However, allyl bonds C1–C2 and C2–C3 and metal–ligand bonds Pd1–C3, Pd1–C7, and Pd1–P1 are significantly shorter in **1b** and **3b** than in the calculated structure. The crystal structure of **1b** is isomorphous to the nickel analogue (**H**) reported earlier by Taube et al.,[16] although the larger size of palladium is clearly reflected in the metal–ligand bond lengths.

The solution structures of complexes **1b–5b** were studied by multinuclear (variable-temperature) NMR spectroscopy and by high-resolution ESI-MS (see the Supporting Information). Room temperature ^{1}H NMR spectra of all complexes show that none of the protons of the η^5-2,7-octadien-1-yl ligand are magnetically equivalent, indicating structural rigidity. Variable-temperature (VT) NMR measurements of complexes bearing phosphines with relatively small cone angles (i.e. **1b**, **2b**, and **5b**) support this conclusion, as the spectra are largely temperature-independent. Importantly, the results of ^{1}H{^{31}P} and ^{1}H-^{1}H COSY measurements confirm that the structure of the cyclic metal fragment in solution is comparable to the structure observed for **1b** and **3b** in the solid state. Notably, the NMR spectra of **3b** and **4b** are temperature-dependent. This dependency is most pronounced for complex **4b**. Both ^{1}H and ^{31}P NMR data show that **4b** is in dynamic exchange between three distinct rotamers. The dynamic behavior observed for **4b** is fairly comparable to that observed for other P(*o*-tolyl)$_3$ complexes as described by Buchwald and co-workers.[11] The NMR data of TOMPP complex **3b** shows a similar dynamic behavior; however, as a result of the lower steric demand of the *o*-methoxy substituents, rotational barriers are lowered considerably. These results show that the η^5-2,7-octadien-1-yl ligand remains rigid in noncoordinating solvents and chelates even under the influence of increased steric hindrance.

In telomerization, it has been shown that the addition of bases such as NR_3 and RO^- is beneficial[5] and particularly in case of Pd/TPPTS-catalyzed telomerization of 1,3-butadiene even required for a successful reaction, suggesting that the nucleophilic addition of Nu^- to **C** is the rate-determining step in catalysis. To investigate the role of **C** in catalysis, the stoichiometric reaction of complexes **1b–5b** with NaOMe was studied by UV/Vis spectroscopy (Figure 2 and Scheme 3).

GC–MS analysis identified 1-methoxy-2,7-octadiene (*n*-telomer) and 3-methoxy-1,7-octadiene (*iso*-telomer) as main reaction products in all cases. From the obtained data, initial rates ($\Delta(\Delta\varepsilon)/\Delta t$) were extrapolated and are reported relative to **1b** (Table 2). Surprisingly, *p*-methoxy complex **2b** exhibits

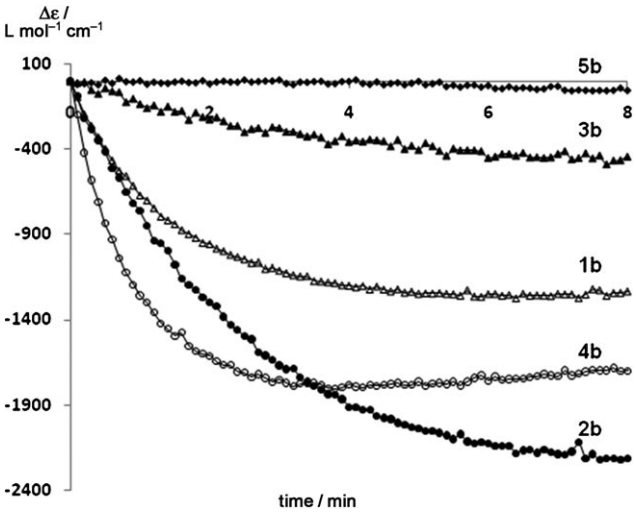
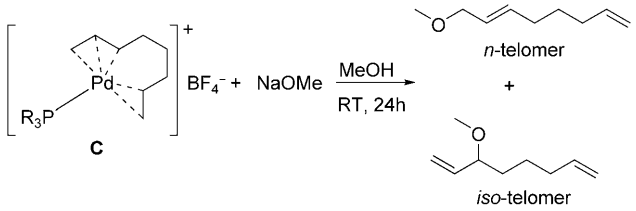


Figure 2. Time-resolved UV/Vis spectroscopic changes Δε ($L mol^{-1} cm^{-1}$) ($\lambda = 310$–315 nm) for the nucleophilic addition of NaOMe to **1b** (△, $\lambda = 309$ nm), **2b** (●, $\lambda = 316$ nm), **3b** (▲, $\lambda = 314$ nm), **4b** (○, $\lambda = 311$ nm), and **5b** (◆, $\lambda = 310$ nm). Conditions: MeOH, room temperature, 10 min.



C

Scheme 3. Stoichiometric nucleophilic addition of NaOMe to **1b**–**5b**. Conditions: MeOH, room temperature, overnight.

Table 2: Relative initial rates of the nucleophilic addition of NaOMe to **1b**–**5b**, TON of Pd/PR_3-catalyzed telomerization of glycerol with 1,3-butadiene,[8a] cone angles θ [°] of coordinated PR_3 ligands, and ν_{CO} [cm^{-1}] of $[Ni(CO)_3(PR_3)]$ complexes.

	Rel. rate	TON	Cone angle θ [°]	ν_{CO} [cm^{-1}]
1b (R = Ph)	1.00	–	145[17]	2068.9[17]
2b (R = 4-$MeOC_6H_4$)	1.07	18	145[17]	2066.1[17]
3b (R = 2-$MeOC_6H_4$)	0.16	1520	176[12]	2058.3[17]
4b (R = 2-MeC_6H_4)	2.37	51	194[17]	2066.6[17]
5b (R = 3-$SO_3C_6H_4$)	0.02	–	152–166[18]	2070[18]

a similar rate as **1b**, whereas *o*-methoxy complex **3b** is approximately six times slower than **1b**. In contrast, *o*-methyl complex **4b** is more than twice as fast as **1b**, and TPPTS complex **5b** is the slowest of the series and reacts 50 times slower than **1b**. These significant rate differences clearly illustrate that properties of the supporting phosphine strongly influence the reactivity of complex **C**.

When the rates are compared to previously reported catalytic data,[8a] it is clear that the addition of the nucleophile to **C** is not always the rate-limiting step in catalysis. For example, the results of Pd/TPMPP (**2b**; TPMPP = tris(4-methoxyphenyl)phosphine) and Pd/TOMPP (**3b**) illustrate this fact, as a much higher turnover number (TON) can be achieved with glycerol in a shorter time period (**3b**: 1520, 0.5 h, **2b**: 18, 5 h) even though the reaction rate of **3b** with methoxide is six times slower than that of **2b.** For TPPTS complex **5b**, however, the sluggish reaction rate is well in line with previous observations[5] and demonstrates that because of the proximity of the anionic sulfonate groups, the approach of the methoxide anion to **5b** is unfavorable. In addition, the attractive electrostatic interaction of the sulfonated ligand with the cationic metal causes complex **5b** to be additionally stabilized despite of its relatively low electron donation (based on the value of ν_{CO} of the corresponding $[Ni(CO)_3(PR_3)]$ complexes, see Table 2). The stability of **5b** is exemplified by the observation that it degrades much slower to palladium black in solution than **1b**, **2b**, or **4b**. The striking difference in reactivity and stability between regioisomers **2b** and **3b** can essentially be attributed to a similar influence now exerted by the *o*-methoxy substituents in **3b**. The proximity of these electronegative substituents to the cationic metal center (Pd1–O2: 3.211(6) Å) considerably increases the stability of **3b** by additional electrostatic attraction (i.e. **3b** degrades much more slowly to palladium black in solution than **1b**, **2b**, and **4b**). Conversely, the increased reaction rate of **4b** with respect to **1b** also clearly shows that the strong (repulsive) interaction of the *o*-methyl groups ($\theta = 194°$) with the Pd(1,2,3,7,8-η^5-2,7-octadien-1-yl) fragment destabilizes the complex and enhances its reactivity. Nevertheless, the catalytic results of Pd/TTP (TTP = tris(*o*-tolyl)phosphine) show that increased reactivity of **4b** is not necessarily productive, as it does not lead to increased telomerization activity. For **3b** a similar steric effect ($\theta = 176°$) could be expected, but the NMR data clearly show that the steric influence of the *o*-methoxy groups is much less pronounced. In addition to this steric, destabilizing effect the TOMPP ligand also stabilizes complex **C** by both electron donation through phosphorus ($\nu_{CO} = 2058.3\ cm^{-1}$) and electrostatic interaction with the *o*-methoxy substituents. The influence of these substituents in the other steps of the cycle may therefore also be considered. The same properties that destabilize saturated palladium(0) species by promoting ligand exchange (steps **D** to **A**, and **E** to **A**) at the same time stabilize unsaturated species by hemilabile coordination of the *o*-methoxy groups. Furthermore, the oxidative coupling of **A** to **B** is promoted by strong electron donation, whereas complex **B** is also stabilized by the electrostatic interactions considered for complex **C**. It thus appears that *o*-methoxy groups possess the most favorable combination of steric and electronic properties for each intermediate in the catalytic cycle.

In summary, a simple and efficient one-pot procedure for the preparation of stable cationic complexes **C** (**1b**–**5b**), which represent the key reactive intermediate in the Pd/PR_3-catalyzed telomerization of 1,3-butadiene, is presented. The employed method not only avoids the use of 1,3-butadiene as reactant, but more importantly enables detailed mechanistic studies for a large variety of Pd/PR_3-based catalyst systems. Furthermore, the solid-state structures of **1b** and **3b** constitute the first crystallographic evidence for intermediate **C**. Solution-state NMR spectroscopic and reactivity studies show that both the steric and electronic properties of the phosphine

ligand impart a strong influence on the complex. The combination of electron donation, electrostatic interaction, and steric repulsion is particularly important for controlling the reactivity of complex **C**. These insights have important implications for rational catalyst design for telomerization and other Pd-mediated reactions.

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