ChemPubSoc Europe

DOI: 10.1002/chem.202000251

CHEMISTRY A European Journal Full Paper

Reaction Mechanisms

Tandem Acid/Pd-Catalyzed Reductive Rearrangement of Glycol Derivatives

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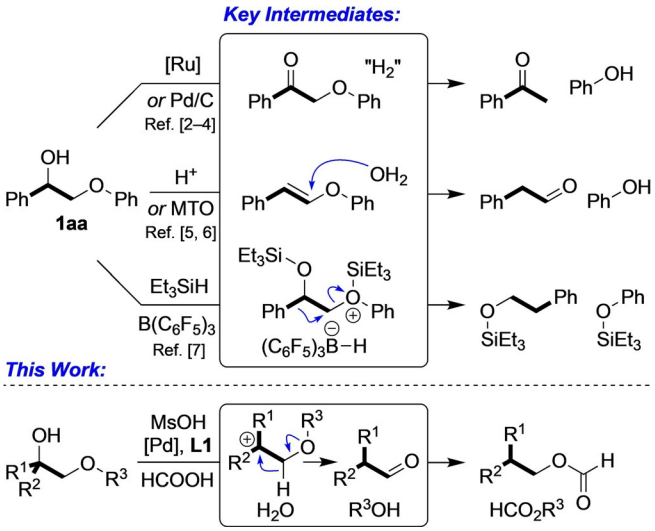
Abstract: Herein, we describe the acid/Pd-tandem-catalyzed transformation of glycol derivatives into terminal formic esters. Mechanistic investigations show that the substrate undergoes rearrangement to an aldehyde under [1,2] hydrogen migration and cleavage of an oxygen-based leaving group. The leaving group is trapped as its formic ester, and the aldehyde is reduced and subsequently esterified to a formate. Whereas the rearrangement to the aldehyde is catalyzed by sulfonic acids, the reduction step requires a unique catalyst system comprising a Pd^{II} or Pd^{0} precursor in loadings as low as 0.75 mol% and α,α′-bis(di-*tert*-butylphosphino)-*o*-xylene as ligand. The reduction step makes use of formic acid as an easy-to-handle transfer reductant. The substrate scope of the transformation encompasses both aromatic and aliphatic substrates and a variety of leaving groups.

Introduction

The conversion of oxygen-rich compounds is a valuable instrument in the hands of organic chemists and plays a key role in the utilization of lignin biopolymers as renewable feedstock.[1] For the development of such methods, model compounds like **1 aa** are often used. Compound **1 aa** is particularly suitable for studying the cleavage of ether bonds (Scheme 1). Several catalyst systems have been developed for this purpose. For example, a Ru complex was shown to catalyze the degradation of **1 aa** into acetophenone and phenol in a redox-neutral process through oxidation of the benzylic OH group followed by hydrogenolysis of the ether function.[2] A similar mechanism was found with Pd/C as catalyst[3] and under photocatalytic conditions.[4] Another redox-neutral transformation provides phenylacetaldehyde under catalysis by a Brønsted acid[5] or methyltrioxorhenium (MTO)[6] in ionic liquids. For both catalysts, a mechanism via an enol ether was proposed. An alternative pathway via a semi-pinacol rearrangement was found for the organocatalytic reduction with Et_3SiH.[7] This work was expanded to a general selective transformation of 1,2-diols,[8] but no semi-pinacol rearrangement was observed when testing the former protocol on lignin.[9]



Scheme 1. Reported mechanisms of redox-neutral and reductive transformations of lignin model compound **1 aa**.

When we aimed to expand the substrate scope of the homogeneous Pd-catalyzed transfer hydrogenolysis of benzylic alcohols developed in our group[10] to the lignin model compound **1 aa**, we observed the formation of phenethyl formate (**2 a**) beside phenol. Curious if this transformation would take place via one of the reported reaction mechanisms, we decided to study it in detail. To our surprise, the investigations revealed the occurrence of an unprecedented tandem [1,2]-rearrangement–reduction sequence via an aldehyde. The transfor-

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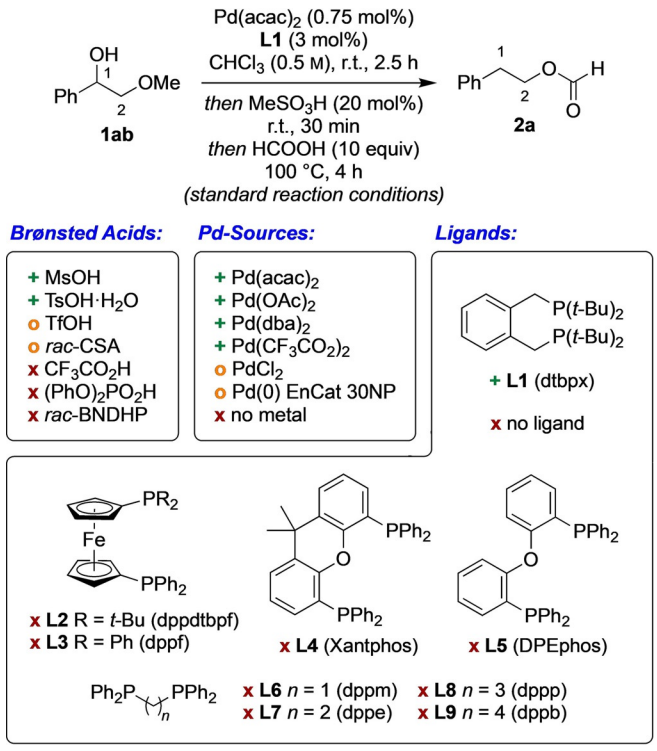
mation is promoted by a dual catalyst system based on a combination of Brønsted acid and a unique metal catalyst comprising a Pd source and the bidentate ligand α,α′-bis(di-*tert*-butylphosphino)-*o*-xylene (dtbpx, **L1**).[11] Pd/**L1** systems exhibit an exceptional selectivity in olefin carbonylation reactions due to the electron-richness and steric properties of the ligand[12] and are hence of great industrial interest.[13] Furthermore, carbonylation can be preceded by isomerization making the transformation potentially valuable for the valorization of other renewable feedstocks like cashew nut shell liquid[14] and plant oils.[15] Herein, we add an item to the list of Pd-catalyzed transformations that are specific to the dtbpx ligand.[10,16]

Results and Discussion

Starting with the screening of the reaction conditions, the 2-methoxy alcohol **1ab** was chosen as model substrate (Scheme 2). The thorough optimization was accompanied by experiments exploring the nature of the active Pd catalyst (see the Supporting Information). During this process, a crucial role of the Pd/**L1**/acid ratio was found. Best results were obtained with Pd/**L1** = 1:4 and a Pd loading of 0.75 mol% in the presence of 20 mol% methanesulfonic acid (MSA or MsOH). At 100 °C, a reaction time of 4 h showed to be sufficient. Interestingly, the sequence of the addition of the Pd source, the ligand, and the Brønsted acid had a dramatic effect on the outcome of the reaction. Upon addition of MSA to a solution of preformed Pd(**L1**)(acac)$_2$, [Pd(**L1**)(η^2-MsO)](MsO)[17] was generated. Only when starting from the latter complex, **2a** was obtained in high yields after the addition of formic acid and subsequent heating. Although various soluble Pd^{II} and Pd^0 precursors including Pd(acac)$_2$, Pd(OAc)$_2$, and Pd(dba)$_2$ (dba = dibenzylideneacetone) provided high yields, of the nine tested diphosphine ligands **L1**–**L9**, only **L1** furnished more than trace amounts of **2a**. The use of sulfonic acids, such as MSA and *p*-toluenesulfonic acid as Brønsted acid catalyst provided highest yields. From control experiments it became apparent that the rearrangement step is promoted by the Brønsted acid, whereas the reduction is Pd-catalyzed with formic acid acting as transfer reductant.

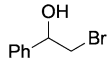
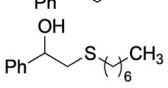


Scheme 2. Optimization of the reaction conditions. Yields were determined by quantitative GC analysis: + = > 80%, o = 20–80%, x = < 20%. CSA: camphor-10-sulfonic acid, BNDHP: 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate.

With the optimized reaction conditions in hand, exploration of the substrate scope was performed. In order to find alternative substrate classes to 2-methoxy alcohols, several compounds bearing various oxygen substituents were tested in the catalytic reaction. Replacement of the *O*-methyl group in the model substrate by a longer alkyl chain (ethyl, 1-decyl) resulted in similarly high yields of **2a** (Table 1, entries 1–3). Beside **2a** (94%), 1-decyl formate (98%) and 1-decanol (< 1%) were observed as only decane-derived byproducts in the reaction of *O*-decyl substrate **1ad**.

Phenyloxy substitution appeared to slow down the catalytic transformation compared to the reaction of substrates with an alkoxy group (Table 1, entry 4). After 4 h, **2a** was formed in 39% yield, and the reaction mixture still contained significant amounts of substrate with a formylated benzylic hydroxy group. Prolongation of the reaction time to 18 h achieved

Table 1. Scope of oxygen substituents.

Entry[a]	Educt	R^1	R^2	Yield[b] [%]
1	**1ab**	H	Me	92 (71)
2	**1ac**	H	Et	95
3	**1ad**	H	$(CH_2)_9CH_3$	94
4	**1aa**	H	Ph	39/45[c]
5	**1ae**	H	2-MeO-C_6H_4	27
6	**1af**	H	Ac	31/31[c]
7	**1ag**	H	H	58/60[c]
8	**1ah**	C(O)H	Me	90
9	**1ai**	C(O)H	$(CH_2)_9CH_3$	95
10	**1aj**	C(O)H	C(O)H	18
11	**1ak**	Ac	Me	80
12	**1al**	Ac	Ac	5
13	**1am**	Me	Me	8
14	**1an**			9
15	**1ao**			< 1

[a] General reaction conditions: Pd(acac)$_2$ (2.28 mg, 750 μmol, 0.75 mol%), **L1** (11.8 mg, 30.0 μmol, 3 mol%), **1aa**–**1ao** (1.00 mmol, 1 equiv), $CHCl_3$ (2 mL), RT, 2.5 h, then MSA (12.9 μL, 200 μmol, 20 mol%), RT, 30 min, then formic acid (377 μL, 10.0 mmol, 10 equiv), 100 °C, 4 h. [b] Determined by quantitative GC analysis, yields of isolated products are given in parentheses. [c] After 18 h.

indeed the disappearance of the formylated substrate but it only led to a slight rise in the yield. However, Pd-catalyzed decomposition of phenyl formate to CO and phenol has been reported[18] possibly resulting in a reversible dissociation of the leaving group from the substrate, consumption of the formic acid or non-productive activity of the Pd catalyst. (2-Methoxyphenyl)oxy-substituted **1 ae** performed even worse (Table 1, entry 5).

Comparable behavior to that of **1 aa** was observed with acetate **1 af**, diol **1 ag** and diacetate **1 al** (Table 1, entries 6, 7, and 12, respectively). After 4 h, diformate **1 aj** was found beside **2 a** in the reaction mixtures. Prolongation of the reaction time led to its complete consumption but not to an increase in the yield of **2 a**. The conjecture that diformate **1 aj** is rather unreactive in the catalytic reaction was confirmed when it was subjected directly to the catalysis (Table 1, entry 10). In fact, **2 a** was obtained but only in 18% yield. The critical role of **1 aj** as an impasse in the rearrangement–reduction sequence explains why alkylation of the C2-oxygen atom is favorable as it prevents terminal O-formylation.

Esterification of the benzylic hydroxy group of **1 ab** and **1 ad** with formic acid (substrates **1 ah** and **1 ai**) led to no significant change in yield (Table 1, entries 8 and 9). Benzylic O-acetylation did not prohibit the catalytic transformation either, and formate **2 a** was obtained in 80% yield beside 10% of phenethyl acetate (Table 1, entry 11). In contrast, the O,O-dimethylated substrate **1 am** yielded only 8% of **2 a** under full conversion of the starting material (Table 1, entry 13). Furthermore, the catalytic reaction was tested on two substrates with non-oxygen-based leaving groups. Bromide as leaving group led to formation of **2 a** in 9% yield, but still large amounts of formylated substrate were found in the reaction mixture (Table 1, entry 14). With 1-heptyl sulfide as leaving group, no product **2 a** was observed due to the formation of a dithioacetal from intermediary phenylacetaldehyde (Table 1, entry 15).

Considering that the reaction of 2-methoxy alcohol **1 ab** furnished formate **2 a** in high yield, various substituents were introduced on its phenyl ring in order to study the influence of electronic effects. Introduction of an alkyl group in 2′- or 4′-position made it possible to isolate the respective products in very good yields (Table 2, entries 1 and 8). Methoxy-substituted arenes yielded the desired products in low yields between 34 and 43% independently from the position of substitution (Table 2, entries 3, 7, and 9). With 4′-fluoro- and 4′-chloro-substituted substrates, the corresponding formic esters were obtained in moderate yields of 47 and 53%, respectively (Table 2, entries 5 and 6). The low yields obtained from substrates bearing substituents with a positive mesomeric effect are attributed to the acid-catalyzed formation of oligomers. However, methylthio substitution in 4′-position led to the isolation of formate **2 d** in 73% yield (Table 2, entry 4).

The electron-poor substrate **1 c** bearing a CF_3 group in 4′-position did not react to the desired product probably due to insufficient stabilization of an intermediary benzylic carbocation (Table 2, entry 2). After 4 h, solely the C1-O-formylated substrate was found in the reaction mixture. The situation changed when an additional phenyl substituent was installed at C1. This way, formic ester **2 o** could be isolated in 90% yield and the 4-chloro- and 4-methylthio-substituted analogues in even higher yields (Table 2, entries 14–16). The increased yields compared to the secondary benzylic alcohols are attributed to a better stabilization of the positive charge at C1. An increase in yield was also observed with an alkyl, benzyl and phenyl moiety as additional substituent attached to the benzylic carbon atom. The corresponding products were isolated in good to excellent yields (Table 2, entries 10–13).

Curious if only benzylic alcohols would undergo the reductive rearrangement, the aliphatic tertiary 2-methoxy alcohol **1 r** was subjected to the catalysis. The corresponding aliphatic formate **2 r** was isolated in 74% yield. However, the reaction of entirely aliphatic compounds does not seem to proceed as smoothly as the transformation of aromatic substrates, and **2 r** was obtained as an inseparable mixture with the unreduced rearrangement product.

Similar results were obtained with **1 s** and **1 t** (Table 2, entries 18 and 19). However, **2 u** and **2 v** could be isolated in pure form in moderate yields of 49 and 41%, respectively (Table 2, entries 20 and 21). The bulkier aliphatic substrate **1 w** underwent rearrangement, but the resulting aldehyde was not re-

Table 2. Catalytic reaction of C1-substituted substrates.

Entry[a]	Educt	Product	R^1	R^2	Yield[b] [%]
1	**1 b**	**2 b**	4-*t*-Bu-C_6H_4	H	91
2	**1 c**	**2 c**	4-F_3C-C_6H_4	H	0
3	**1 d**	**2 d**	4-MeO-C_6H_4	H	34
4	**1 e**	**2 e**	4-MeS-C_6H_4	H	73
5	**1 f**	**2 f**	4-F-C_6H_4	H	47
6	**1 g**	**2 g**	4-Cl-C_6H_4	H	53
7	**1 h**	**2 h**	3-MeO-C_6H_4	H	37
8	**1 i**	**2 i**	2-Me-C_6H_4	H	83
9	**1 j**	**2 j**	2-MeO-C_6H_4	H	43
10	**1 k**	**2 k**	Me	Ph	89
11	**1 l**	**2 l**	$(CH_2)_5CH_3$	Ph	95
12	**1 m**	**2 m**	Bn	Ph	92
13	**1 n**	**2 n**	Ph	Ph	80
14	**1 o**	**2 o**	4-F_3C-C_6H_4	Ph	90
15	**1 p**	**2 p**	4-MeS-C_6H_4	Ph	98
16	**1 q**	**2 q**	4-Cl-C_6H_4	Ph	94
17[c]	**1 r**	**2 r**	$(CH_2)_5CH_3$	$(CH_2)_5CH_3$	74
18[c]	**1 s**	**2 s**	*n*Pr	Bn	55
19[c]	**1 t**	**2 t**	Bn	Bn	48
20	**1 u**	**2 u**	*n*Pr	*n*Pr	49
21	**1 v**	**2 v**	-$(CH_2)_5$-		41
22	**1 w**	**2 w**	*i*Pr	*i*Pr	0
23	**1 x**	**2 x**	$PhOCH_2$	H	0
24	**1 y**	**2 y**	$PhOCH_2$	Ph	0

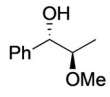
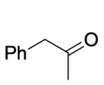
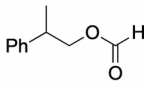
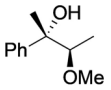
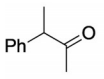
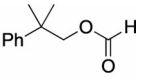
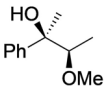
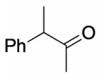
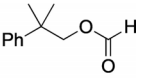
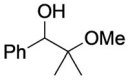
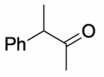
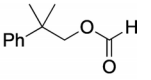
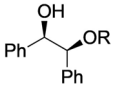
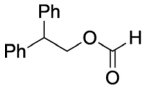
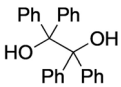
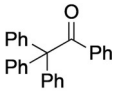
[a] General reaction conditions: $Pd(acac)_2$ (2.28 mg, 750 μmol, 0.75 mol%), **L1** (11.8 mg, 30.0 μmol, 3 mol%), **1 b–1 y** (1.00 mmol, 1 equiv), $CHCl_3$ (2 mL), RT, 2.5 h, then MSA (12.9 μL, 200 μmol, 20 mol%), RT, 30 min, then formic acid (377 μL, 10.0 mmol, 10 equiv), 100 °C, 4 h. Bn = benzyl. [b] Yield of isolated product. [c] Obtained as an inseparable mixture with unreduced aldehyde.

duced. Compounds **1x** and **1y** possessing two different vicinal oxygen substituents yielded benzylic O-formylated substrate and an oligomer, respectively.

In the studied reaction, net migration of a group from C2 to C1 takes place (see below). As it is crucial to understand the selectivity with which this occurs, several C2-substituted substrates were subjected to the catalytic reaction. Introduction of a methyl group at C2 led to the isolation of ketone **4a** as the main product generated through hydrogen migration (Table 3, entry 1). Formate **2k**, the product of methyl migration and subsequent reduction–esterification, was furnished only in traces. Similar results were obtained when another methyl group was installed in the benzylic position (Table 3, entries 2 and 3). Interestingly, the relative configuration of the starting material affected the yield of the isolated ketone **4b** suggesting an at least partially concerted rearrangement mechanism.

The catalytic reaction of substrate **3c** with two methyl groups at C2 provided formate **2z** in 25% yield beside ketone **4b** (18%) and an oligomer, the structure of which could not be determined (Table 3, entry 4). Whereas the formation of **4b** is expected to occur through the rearrangement mechanism presented below under migration of the methyl moiety from C2 to C1, **2z** should be generated in a semi-pinacol rearrangement with phenyl group migration from C1 to C2.

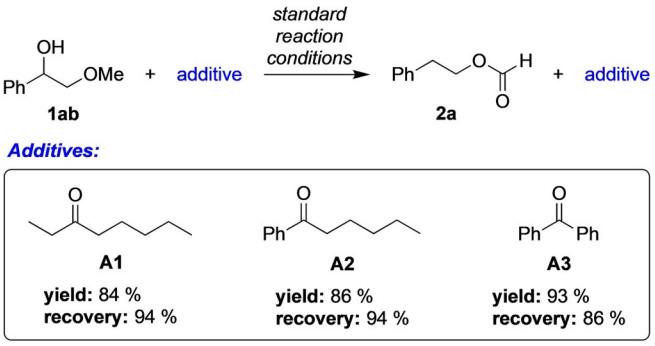
Table 3. Catalytic reaction of C2-substituted substrates.

Entry[a]	Substrate	Product, yield	
1	 **3a** (d.r. = 70:30)	 **4a**, 72 %	 **2k**, traces
2	 **3b**	 **4b**, 37 %	 **2z**, traces
3	 **3b'** (d.r. = 91:9)	 **4b**, 57 %	 **2z**, traces
4	 **3c**	 **4b**, 18 %	 **2z**, 25 %
5	 **3d**, R = Me	 **2n**, 91 %	
6	**3e**, R = H	**2n**, 95 %	
7	 **3f**	 **4c**, 68 %	

[a] General reaction conditions: $Pd(acac)_2$ (2.28 mg, 750 μmol, 0.75 mol%), **L1** (11.8 mg, 30.0 μmol, 3 mol%), **3a–3f** (1.00 mmol, 1 equiv), $CHCl_3$ (2 mL), RT, 2.5 h, then MSA (12.9 μL, 200 μmol, 20 mol%), RT, 30 min, then formic acid (377 μL, 10.0 mmol, 10 equiv), 100 °C, 4 h.

Spurred by migration of the phenyl ring in the catalytic reaction of **3c**, the C2-phenyl-substituted substrate **3d** was tested in the catalysis, and formic ester **2n**, which is formed by migration of a phenyl group, was obtained in excellent yield (Table 3, entry 5). Reaction of the corresponding symmetric diol **3e** provided the same product in similarly good yield (Table 3, entry 6). However, it seems reasonable to assume a (semi-)pinacol rearrangement pathway for these starting materials. Considering that the 2-methoxy alcohol **3d** and the diol **3e** showed similar reactivity, diol **3f** was subjected to the catalytic reaction without previous etherification. Ketone **4c** was obtained as only product showing the selectivity of the reduction step again (Table 3, entry 7).

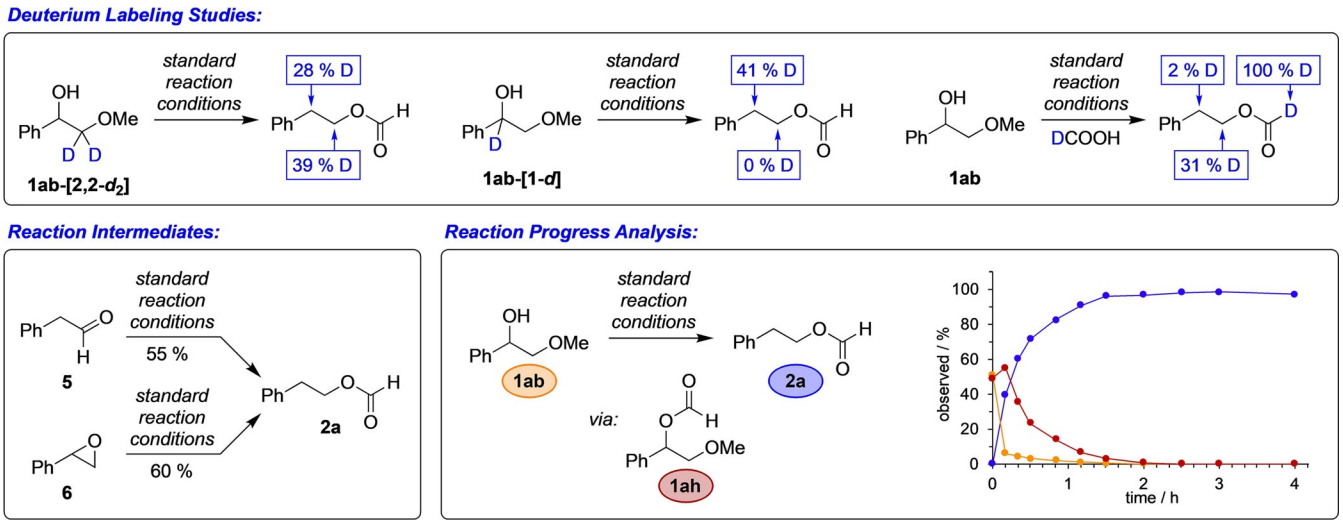
The formation of ketones **4a–4c** and not their reduction products suggests that the reductive step is selective to aldehydes. This chemoselectivity was verified when model substrate **1ab** was successfully reduced in the presence of three different ketones **A1–A3**, which were not converted (Scheme 3).



Scheme 3. Evaluation of the chemoselectivity of the reduction step by reacting model substrate **1ab** in the presence of additives **A1–A3**. General reaction conditions: $Pd(acac)_2$ (1.14 mg, 375 μmol, 0.75 mol%), **L1** (5.92 mg, 15.0 μmol, 3 mol%), **1ab** (76.1 mg, 500 μmol, 1 equiv), **A1–A3** (500 μmol, 1 equiv), $CHCl_3$ (1 mL), RT, 2.5 h, then MSA (6.5 μL, 100 μmol, 20 mol%), RT, 30 min, then formic acid (189 μL, 5.00 mmol, 10 equiv), 100 °C, 4 h. Yields were determined by quantitative GC analysis.

In order to gain mechanistic insights, the progress of the transformation of **1ab** into **2a** was monitored under optimized conditions (Scheme 4). Interestingly, the formylation of the alcoholic substrate was observed at the outset of the reaction. After 2 min at room temperature before heating was started, about 50% of **1ab** had been esterified to **1ah**. Upon heating applied, the amount of **1ah** increased slightly within 10 min, and the fraction of **1ab** dropped under 10%. Parallel to that, about 40% of **2a** formed. In the following 2 h, the amount of **2a** increased as **1ab** and **3ah** were consumed. After that, the yield of **2a** remained constant at its maximum.

In order to understand how product **2a** is formed, the deuterium-labeled substrates **1ab**-[**2,2-d_2**] and **1ab**-[**1-*d***] were employed in the catalytic reaction (Scheme 4). The deuterium distribution in the isolated products suggests a mechanism involving a [1,2]-hydrogen shift from C2 to C1. Reaction of **1ab** with deuterated formic acid yielded a product, which is very likely to be generated in the reduction of phenylacetaldehyde



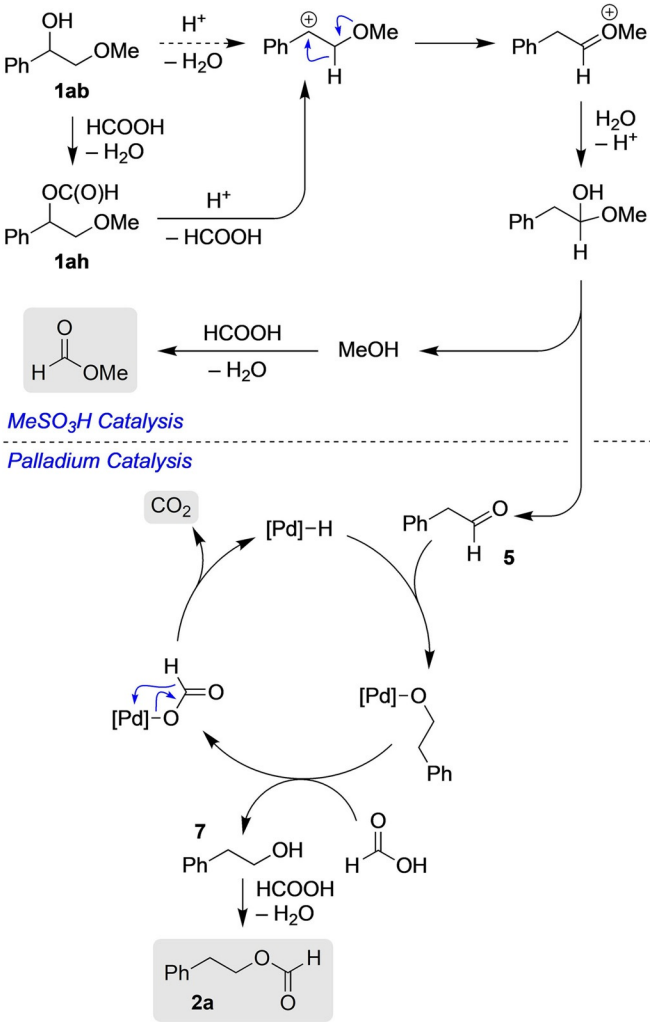
Scheme 4. Mechanistic insights into the catalytic transformation of **1ab**. Given yields were determined by quantitative GC analysis.

(**5**) with formic acid as hydrogen donor. Subjecting **5** to the standard reaction conditions, **2a** was obtained in 55% yield (GC). Formation of **5** from a benzylic cation by [1,2]-hydrogen shift seems very likely. The related acid-catalyzed Meinwald rearrangement[19] of epoxide **6** is expected to comprise this step. Hence, **6** was tested in the catalytic reaction as well, providing 60% of **2a**.

Combining the results of the mechanistic studies, DFT studies on related systems,[20] the substrate screening, and the optimization process, a plausible mechanism was proposed (Scheme 5). After addition of formic acid to the reaction mixture, the alcoholic substrate **1ab** is formylated in a Fischer–Speier esterification.[21] This reaction is fast and takes place at room temperature. In the following rate-determining step, **1ah** undergoes acid-catalyzed extrusion of formic acid to a benzylic cation. In line with that, substrates with substituents stabilizing the positive charge at C1 showed best performances in the catalysis, whereas the electron-poor compound **1c** was O-formylated but not converted to **2c**. The benzylic cation undergoes a [1,2]-hydrogen shift to a carboxonium ion, which is hydrolyzed to aldehyde **5**. Thereby, methanol is released and subsequently trapped as its formic ester. The formation of a carboxonium ion intermediate explains the low yield of **2a** obtained from **1an** but also demonstrates that alternative pathways, for example, a Meinwald-type rearrangement via epoxide **6**, cannot be precluded.

In the Pd-catalyzed reduction step, the aldehyde inserts into the Pd–H bond of a Pd^{II}–hydride complex. Pd^{II}–hydride complexes are known for Pd/**L1** systems and have been studied with great meticulousness.[17,22] From the alkoxide complex, formic acid releases alcohol **7**, which was observed in significant amounts when less than ten equivalents of formic acid were employed in the catalytic reaction. The resulting formate complex regenerates a Pd^{II}–hydride complex via β-hydride elimination. Parallel to that, alcohol **7** is esterified to **2a**.

Although we have not been able to detect a Pd^{II}–hydride complex under the reaction conditions yet, we consider its involvement in the catalytic transformation as very likely. After adding formic acid to a solution of Pd(**L1**)$(acac)_2$ in $CDCl_3$, formation of a hydride complex could be observed proving the



Scheme 5. Mechanistic proposal for the acid/Pd-catalyzed reductive rearrangement of glycol derivative **1ab**.

possibility of its generation from formic acid. Formation of the hydride was accompanied by the appearance of $CDHCl_2$. Reduction of $CDCl_3$ by late-transition-metal hydrides has been reported.[23] Under conditions similar to the ones in the catalytic reaction, we could observe formation of $CDHCl_2$ as well.

Conclusions

To conclude, we report the acid-catalyzed rearrangement of glycol derivatives followed by Pd/**L1**-catalyzed transfer reduction with formic acid as hydrogen donor. In our study, we could demonstrate the presence of a [1,2] hydrogen migratory pathway representing a mechanistic alternative to the previously reported mechanisms relevant for the transformation of lignin model compounds. Furthermore, the selective (transfer) reduction of aldehydes by a Pd/**L1** system has been unknown before. The substrate scope of the described transformation comprises various oxygen-based leaving groups and both aliphatic and aromatic compounds.

Acknowledgements

Financial support from the DFG (Deutsche Forschungsgemeinschaft, FL 878/4-1), the DAAD (Deutscher Akademischer Austauschdienst, fellowship P.K.), and the University of Tübingen is gratefully acknowledged. Regina Oechsner (University of Tübingen) is thanked for technical assistance in the preparation of **1 ae**.

Conflict of interest

The authors declare no conflict of interest.

Keywords: homogenous catalysis · palladium · rearrangement · reduction · tandem reactions

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Manuscript received: January 15, 2020
Accepted manuscript online: January 17, 2020
Version of record online: March 4, 2020

