FULL PAPER

Selective Construction of C–C and C=C Bonds by Manganese Catalyzed Coupling of Alcohols with Phosphorus Ylides

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Abstract. Herein, we report the manganese catalyzed coupling of alcohols with phosphorus ylides. The selectivity in the coupling of primary alcohols with phosphorus ylides to form carbon–carbon single (C–C) and carbon–carbon double (C=C) bonds can be controlled by the ligands. In the conversion of more challenging secondary alcohols with phosphorus ylides the selectivity towards the formation of C–C vs. C=C bonds can be controlled by the reaction conditions, namely the amount of base. The scope and limitations of the coupling reactions were thoroughly evaluated by the conversion of 21 alcohols and 15 ylides. Notably, compared to existing methods, which are based on precious metal complexes as catalysts, the present catalytic system is based on earth abundant manganese catalysts.

The reaction can also be performed in a sequential one-pot reaction generating the phosphorus ylide in situ followed manganese catalyzed C–C and C=C bond formation. Mechanistic studies suggest that the C–C bond was generated via a borrowing hydrogen pathway and the C=C bond formation followed an acceptorless dehydrogenative coupling pathway.
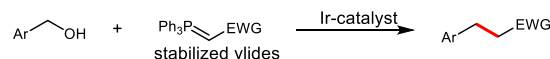
Keywords: manganese; acceptorless dehydrogenative coupling; borrowing hydrogen; Wittig reaction; alcohols

Introduction

The formation of carbon-carbon bonds is of fundamental importance in organic synthesis and numerous methods have been developed in this regard. However, in view of the depletion of fossil resources chemists and the chemical industry are urged to find alternative raw materials. In this respect alcohols are of particular importance since they are not only readily available products from the petrochemical industry but also biomass derived alternative feedstocks.[1] The conversion of alcohols to fine chemicals is therefore an interesting and growing research area. In this regard the transition-metal-catalyzed borrowing hydrogen reactions and acceptorless dehydrogenative coupling emerged as important tools in the construction of chemical bonds using alcohols as starting materials.[2] Most of the reported catalysts for these reactions are based on precious transition metals (Ir, Rh, Ru, Pd etc.). However, recently the use earth-abundant transition-metal catalysts, in particular Mn-complexes, attracted great attention.[3] In respect to the formation of carbon-carbon bonds elegant procedures for the construction of C–C bonds by combining borrowing hydrogen reactions with the α-alkylation of carbonyl compounds have been reported.[4] Whereas acceptorless dehydrogenative coupling emerged as a tool for the construction of C=C bonds.[5] However, typically an

excess base in these reactions is required which often results in the formation of by-products, poor functional group tolerance and limitations regarding the coupling partners, respectively.
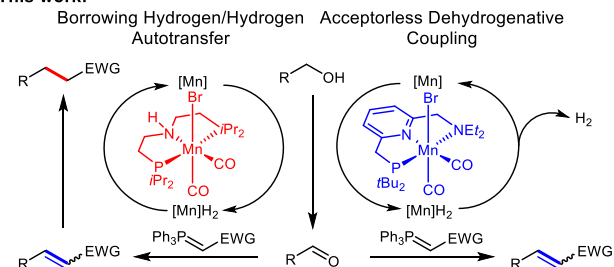

Williams: Alkane synthesis via borrowing hydrogen reaction (ref. 7)

Milstein: Alkene synthesis via acceptorless dehydrogenative coupling (ref.10)
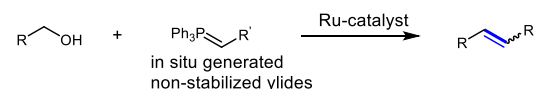
This work:

Scheme 1. Manganese catalyzed C–C and C=C bond formation via borrowing hydrogen and acceptorless dehydrogenative coupling.

The use of phosphorus ylides as coupling partners should allow to overcome these limitations. Notably, the group of Williams first reported a borrowing hydrogen protocol for the synthesis of alkanes from primary alcohols and phosphorus ylides by an indirect Wittig reaction (Scheme 1).[6] The initial step of the reaction sequence is the dehydrogenation of the alcohol into an aldehyde catalyzed by an iridium[6-7] or ruthenium[8] complex. The reaction with stabilized ylides and subsequent hydrogenation of the formed double bond leads to alkanes as major products, rather than alkenes.

Alonos et al. reported the use of nickel nano particles for the acceptorless dehydrogenative coupling of alcohols with semi-stabilized ylides.[9] More recently, Milstein and co-workers described the selective synthesis of alkenes by the ruthenium catalyzed acceptorless dehydrogenative coupling of alcohols with in situ generated, non-stabilized ylides under homogenous conditions.[10] This strategy has been further elaborated by others using acridine-derived ruthenium pincer[11] as well as diruthenium complexes[12] as catalysts. Until now, the use of phosphorus ylides as coupling partners required mainly precious metal catalysts for the borrowing hydrogen reactions and acceptorless dehydrogenative coupling, respectively. Notably, the selective formation of carbon-carbon single or double bonds from alcohols and phosphorus ylides in the presence of a homogeneous abundant metal catalyst has not been reported. Another unsolved challenge so far is the control of the selectivity either by the ligand or reaction conditions, respectively.
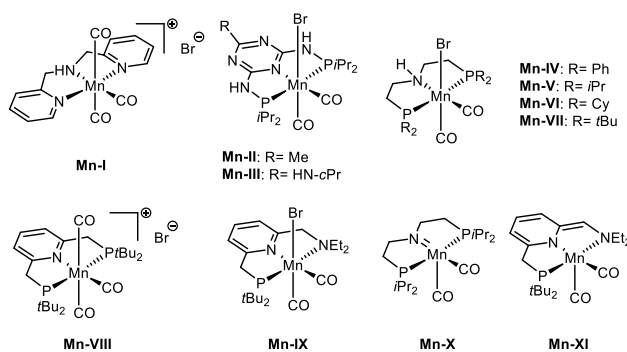

Figure 1. Manganese complexes Mn-**I**–Mn-**XI** explored in this work.

Inspired by the above reports and driven by our interest in the use of earth-abundant pincer catalysts[13] and catalytic Wittig reactions,[14] we envisioned to develop a method for the selective construction of C–C and C=C bonds from alcohols and phosphorus ylides catalyzed by a manganese complex. In this regard we identified complexes Mn-**I**–Mn-**XI** as potential catalysts (Figure 1). Recently, these catalysts have been reported as excellent catalysts for various transformations based on (de)hydrogenation reactions e.g. by the groups of Beller,[15] Kempe,[5c, 16] Liu,[17] Leitner[18] and Milstein.[4a, 5a, 5e, 19] Herein, we report the

unprecedented manganese catalyzed divergent coupling of alcohols with stabilized phosphorus ylides for the selective construction of C–C and C=C bonds.

Results and Discussion

Initially we studied the chemoselectivity and catalytic performance of complexes Mn-**I**–Mn-**XI** in the one-pot coupling reaction of benzyl alcohol **1a** with ylide **2a** (Table 1). Even though the conversion under our initial conditions in the presence of Mn-**I** was low, the selectivity towards the saturated product **3aa** which was obtained in 14 % yield was >90 % (entry 1). Catalysts Mn-**II** and Mn-**III** gave higher conversions but only moderate chemoselectivity were observed and both products **3aa** and **4aa** were formed (entries 2 and 3). Complexes Mn-**IV**–Mn-**VII** are based on commercially available ligands and were successfully used in (de)hydrogenation and borrowing hydrogen reactions before. In the presence of these catalysts, full conversion of alcohol **1a** was achieved (entries 4–6). Notably, catalyst Mn-**IV** and Mn-**V** gave selectively the saturated product **3aa** in excellent yields of 96 % and 97 % respectively. Although full conversion was achieved with catalyst Mn-**VI** the selectivity was only moderate and the products **3aa** and **4aa** were obtained in 86 % and 12 % respectively (entry 6). In contrast the use of catalyst Mn-**VII** led to low conversion and selectivity (entry 7). Furthermore, complexes Mn-**VIII** and Mn-**IX** were used as catalysts. Mn-**VIII** which was reported to be an excellent catalyst for the acceptorless dehydrogenative coupling of alcohols and amines gave a conversion of 87 % (entry 8).[20]

Table 1. Catalyst screening for the borrowing hydrogen reaction and acceptorless dehydrogenative coupling between alcohol **1a** and ylide **2a**.[a]

Entry	[Mn]	Conv. 1a/ %	Yield 3aa/ %[b]	Yield 4aa/ %[b]
1	Mn-**I**	14	13	-
2	Mn-**II**	71	53	17
3	Mn-**III**	68	47	20
4	Mn-**IV**	>99	96	traces
5	Mn-**V**	>99	97	traces
6	Mn-**VI**	>99	86	12
7	Mn-**VII**	16	7	8
8	Mn-**VIII**	87[c]	4	16
9	Mn-**IX**	22	traces	21
10[d]	Mn-**X**	99	94	traces
11[d]	Mn-**XI**	24	traces	22
12[e]	Mn-**IX**	92	traces	83

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), [Mn] (2.5 mol%), KO*t*Bu (2.5 mol%), 1,4-dioxane, 110 °C, 12 h. [b] Conversion, yield and *E/Z* selectivity were determined by GC-FID using mesitylene as the internal standard. [c] The formation of several by-products was observed. [d] No base

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was added. [e)] [Mn] (7.5 mol%), KO*t*Bu (7.5 mol%), 1,4-dioxane, 120 °C, 30 h.

However, only unsatisfying yields of **3aa** and **4aa** were achieved and several by-products were observed. Interestingly, in the presence of Mn-**IX** the selective formation of unsaturated product was observed and **4aa** was obtained in 21 % yield (entry 9). Under the reaction condition Mn-**V** and Mn-**IX** are deprotonated by the added base (KO*t*Bu) which leads in situ to the formation of the activated complexes Mn-**X** and Mn-**XI**, respectively.[4c, 19b] The direct use of these complexes gave comparable results to the in situ system (entry 5 vs. 10 and entry 9 vs. 11). Based on these results we evaluate the effect of different reaction parameters on the performance of complexes Mn-**V** for the selective preparation of the saturated product **3aa** and Mn-**IX** for the synthesis of the unsaturated product **4aa** (See SI for details). Notably, slight modification in the reaction conditions led to an increased yield of 87 % for the selective formation of the α,β-unsaturated product **4aa** in the presence of catalyst Mn-**IX** (entry 12).

Subsequently, we evaluate the substrate scope and limitation of the ligand-controlled coupling of various primary alcohols **1** and phosphorus ylides **2** yielding the respective C–C and C=C bond products (Scheme

2). At first, we studied the reaction between primary alcohols **1a**–**1o** and ylide **2a** in the presence of catalyst Mn-**V** under the optimized conditions (Scheme 2). Compound **3aa** which is the product of the test reaction was isolated in 91 % yield. Although in some cases the reaction time and temperature had to be adjusted, differently substituted benzyl alcohols gave the corresponding saturated products **3ba**–**3ha** in isolated yields up to 86 %. Furfuryl alcohol (**1k**) and benzothiazole derivative (**1l**) were also smoothly converted to the desired products **3ka** and **3la** in 73 % and 80 % yield, respectively. Notably, non-benzylic alcohols such as cyclohexylmethanol (**1m**) could be converted to yield **3ma** in 66 % yield. The conversion of **1n** gave **3na** in 82 % yield. Interestingly, the hydrogenation of the cyclohexenyl motif was not observed. The conversion of *n*-hexanol (**1o**) led to **3oa** in 80 % yield.

We turned our attention to the scope in respect to the ylide. The reaction of **1a** with various stabilized ylides **2b**–**2i** gave the desired products **3ab**–**3ai** in yields up to 90 %. Interestingly, the conversion of **2j** gave not the expected saturated product **3aj**, but cinnamonitrile (**4aj**) in 86 % yield. We were also interested in the scalability of the reaction and performed the synthesis of the drug intermediate **3af** on a 10 mmol scale affording the desired product in 71 % yield.[21]
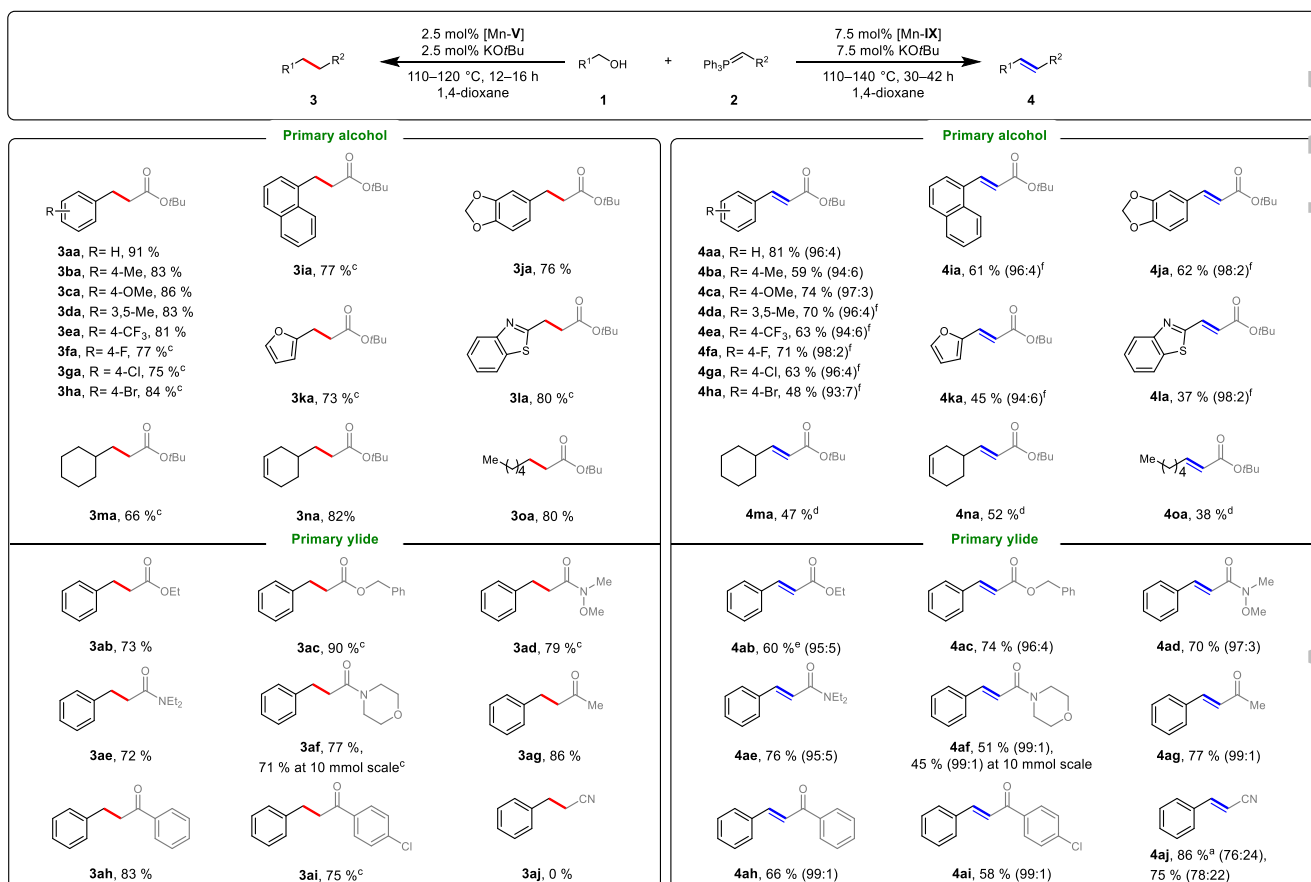
Scheme 2. Scope of the ligand-controlled C–C[a] and C=C[b] bond formation by manganese catalysts. [a)] Reaction conditions: **1** (1.0 equiv.), **2** (1.2 equiv.), Mn-**V** (2.5 mol%), KO*t*Bu (2.5 mol%), 1,4-dioxane, 110 °C, 12 h. Isolated yields are given. [b)]

Reaction conditions: **1** (1.0 equiv.), **2** (1.1 equiv.), Mn-**IX** (7.5 mol%), KO*t*Bu (7.5 mol%), 1,4-dioxane, 120 °C, 30 h. Isolated yields are given. *E/Z* selectivity is given in brackets. [c)] 120 °C, 16 h. [d)] KO*t*Bu (0.55 mmol, 1.1 equiv.), 140 °C, 30 h, yield determined by ^{1}H-NMR with mesitylene as the internal standard, **4** was obtained in a mixture with **3** (<20%). [e)] 110 °C, 42 h. [f)] Mn-**IX** (10.0 mol%), KO*t*Bu (10.0 mol%), 120 °C, 30 h.

Subsequently we studied the synthesis of the respective acceptorless dehydrogenative coupling products **4** under the optimized conditions. Thus, aromatic and heteroaromatic substrates **1a**–**1l** were converted with ylide **2a** in the presence of complex Mn-**IX**. In all cases the respective saturated compounds **3** were not observed while the unsaturated products **4** were obtained in isolated yields up to 81 % and *E*-selectivity ≥94 %. Under the standard conditions no conversion was achieved for aliphatic alcohols **1m**–**1o** as substrates and only starting material was recovered. This indicates that the dehydrogenation step is hampered. However, in the presence of stochiometric amounts of base the alcohols **1m**–**1o** reacted with ylide **2a** to give the corresponding product **4m**–**4o** in moderate yields up to 52%. Even though in the latter cases the unsaturated products were the major products they were obtained in a mixture with the saturated compounds **3** (<20 %). Next, we studied the scope in respect to the ylide and converted **1a** with various ylides **2b**–**2j**. In contrast to complex Mn-**V**, the use of Mn-**IX** enabled the synthesis of the corresponding unsaturated products **4ab**–**4aj** in yields up to 77 % and *E*-selectivity up to 99 %. Also, for this series the scalability of the reaction was studied. The conversion **1a** with **2f** on a 10 mmol scale gave the desired product **4af** in 45 % yield.

Furthermore, we tested the performance of both catalysts Mn-**V** and Mn-**IX** in the reaction of secondary alcohols and ylides (Scheme 3, see SI for further details). Initially, we studied the conversion of alcohols **1p** and **1q** with ylide **2a** in the presence of Mn-**V**. Under the standard reaction conditions, no conversion was achieved while at higher reaction temperatures (140 °C) only the unsaturated products **4pa** and **4qa** were obtained in 71 % and 75 % yield, respectively.
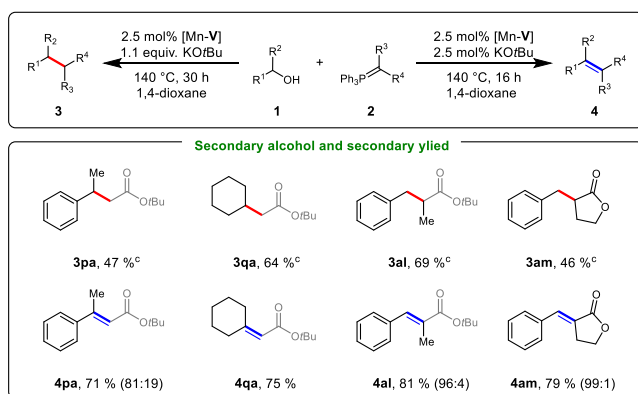

Scheme 3. Scope of the secondary alcohols for C–C[a] and C=C[b] bond formation by manganese catalysts. [a)] Reaction conditions: **1** (1.0 equiv.), **2** (1.2 equiv.), Mn-**V** (2.5 mol%),

KO*t*Bu (0.60 mmol, 1.1 equiv.), 1,4-dioxane, 140 °C, 30 h. Yields were determined by ^{1}H-NMR. [b)] Reaction conditions: **1** (1.0 equiv.), **2** (1.2 equiv.), Mn-**V** (2.5 mol%), KO*t*Bu (2.5 mol%), 1,4-dioxane, 140 °C, 16 h. Isolated yields are given. The *E/Z* ratio was determined by ^{1}H-NMR and is given in brackets. [c)] **4** was observed as a by-product in ≤10 %.

The conversion of secondary ylides **2l** and **2m** with **1a** also led to the unsaturated products and **4al** and **4am** were obtained in yields up to 81 %. These results indicate that the borrowing hydrogen pathway is hampered due to the inability of the manganese complex to hydrogenate the highly substituted α,β-unsaturated carbonyl compound. Typically, these substrate require precious metal catalysts to undergo hydrogenation via borrowing hydrogen.[21] In this respect, Huang and co-workers reported the use of Ir-pincer complexes for the reduction of α-branched unsaturated intermediates to yield saturated products via borrowing hydrogen reactions.[22] Most recently, Leitner and Maji's group reported a methodology for synthesis of cycloalkanes from diols and secondary alcohols or ketones.[18b, 23] In their mechanistic studies they showed that manganese pincer complexes can reduce α-branched unsaturated intermediates to saturated products under an excess amount of base (>1 equiv.). Inspired by these reports the reaction of secondary substrates in the presences of catalyst Mn-**V** and an excess amount of KO*t*Bu was explored. Notably, under these conditions the corresponding saturated products **3pa**, **3qa**, **3al** and **3am** were obtained in yields up to 69 %. However, the hydrogenation of the unsaturated intermediate was still incomplete and compounds **3** were obtained in a mixture with **4** as the minor product (≤10 %). The use of catalyst Mn-**IX** allowed only the conversion primary alcohol **1a** with secondary ylides **2l** and **2m** (See SI for details).

Finally, we turned our attention to the functionalisation of bio-based substrates (Scheme 4). The conversion of prenol (**1r**), cinnamyl alcohol (**1s**) and geraniol (**1t**) with **2a** in the presence of catalyst Mn-**V** selective formation of the conjugated α,β-unsaturated esters **4ra**–**4ta** in up to 83 % yield. Notably, the conjugated system is not hydrogenated under the reaction conditions or even at higher H₂ pressures of 10 bars (See SI for details). In contrast the reaction of **2a** with citronellol (**1u**) gave as expected the saturated product **3pa** in 81 % isolated yield. This reaction was also performed on larger scale (10 mmol) yielding **3ua** in 70 % proving once more the scalability. Subsequently menthol-**2o**, testosterone-**2p** and cholesterol-based ylide **2q** were converted with benzyl alcohol (**1a**). In the presence of catalyst Mn-**V** the

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saturated menthol derivative **3ao** was obtained in 83 % yield while the steroid derivatives **3ap** and **3aq** were isolated in 63 % and 70 % yield, respectively. In contrast catalyst Mn-**IX** proved to be suitable for the synthesis of the corresponding unsaturated products. Thus, conversion of **2o–2q** with **1a** led to the unsaturated products **4ao–4aq** in isolated yields up to 71 %.
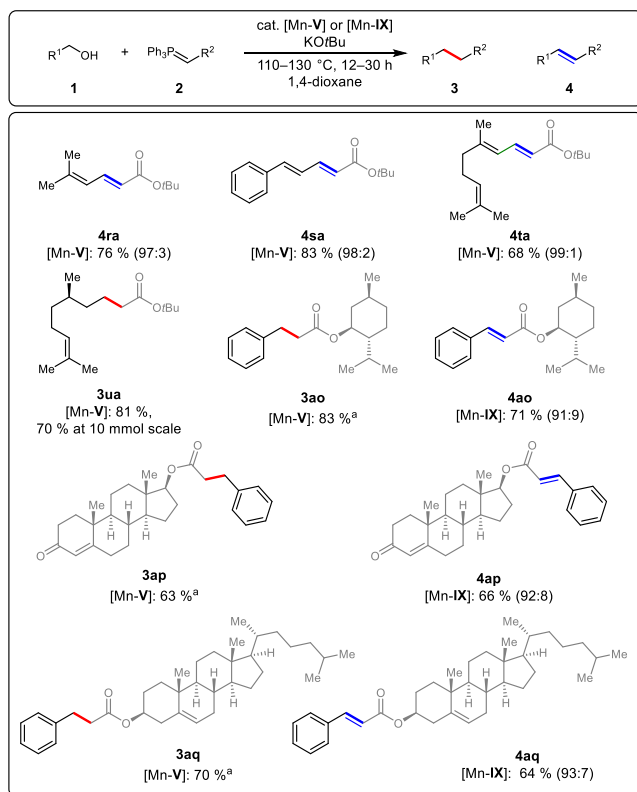

Scheme 4. Reaction scope for bio-based substrates. Reaction conditions: **1** (1.0 equiv.), **2** (1.2 equiv.), Mn-**V** (2.5 mol%), KO*t*Bu (2.5 mol%), 1,4-dioxane, 110 °C, 12 h or Mn-**IX** (7.5 mol%), KO*t*Bu (7.5 mol%), 1,4-dioxane, 120 °C and 30 h. Isolated yields are given, and *E*/*Z* ratio determined by ^{1}H-NMR. [a] 130 °C and 24 h.
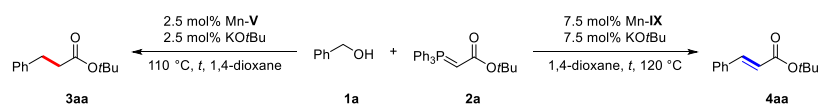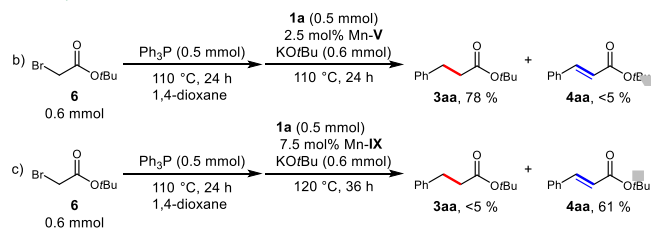
So far, the ylides **1** were prepared prior to the coupling reaction. The in situ generation of the ylide would be a more direct approach making the isolation of the ylide redundant. To evaluate the feasibility of this approach we extend the reaction sequence to the in situ formation of the ylide (Scheme 5).
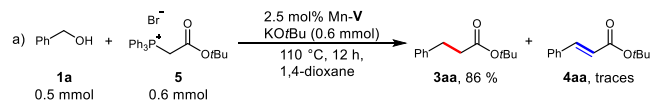
Scheme 5. Extending the manganese-catalyzed borrowing hydrogen and acceptorless dehydrogenative coupling reaction by the in situ generation of the phosphorus ylide **2a**.

Initially we used phosphonium salt **5** instead of ylide **2a** for the conversion with **1a** in the presence of catalyst Mn-**V** under the standard reaction conditions. Notably, equimolar amounts of the base (KO*t*Bu) in respect to **5** were used to enable the in situ formation of the ylide **2a** (Scheme 5a). Under these conditions the desired borrowing hydrogen product **3aa** was obtained in 86 % yield. Subsequently, we performed the sequential one-pot synthesis of **3aa** starting from Ph₃P and **6** leading to the desired product in 78 % yield (Scheme 5b, see SI for details). In the presence of catalyst Mn-**IX** this reaction sequence also allows the synthesis of the acceptorless dehydrogenation coupling product **4aa** in 61 % yield (Scheme 5c).
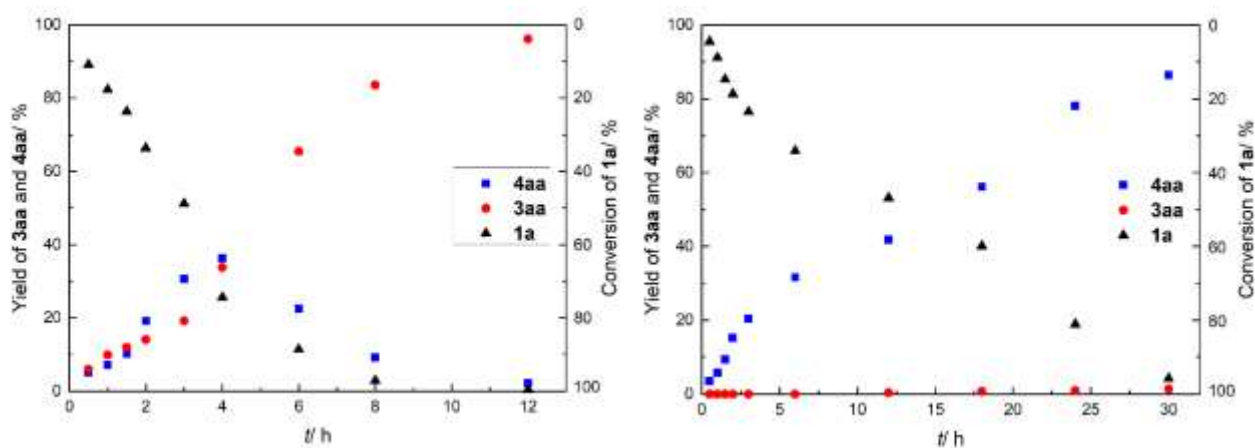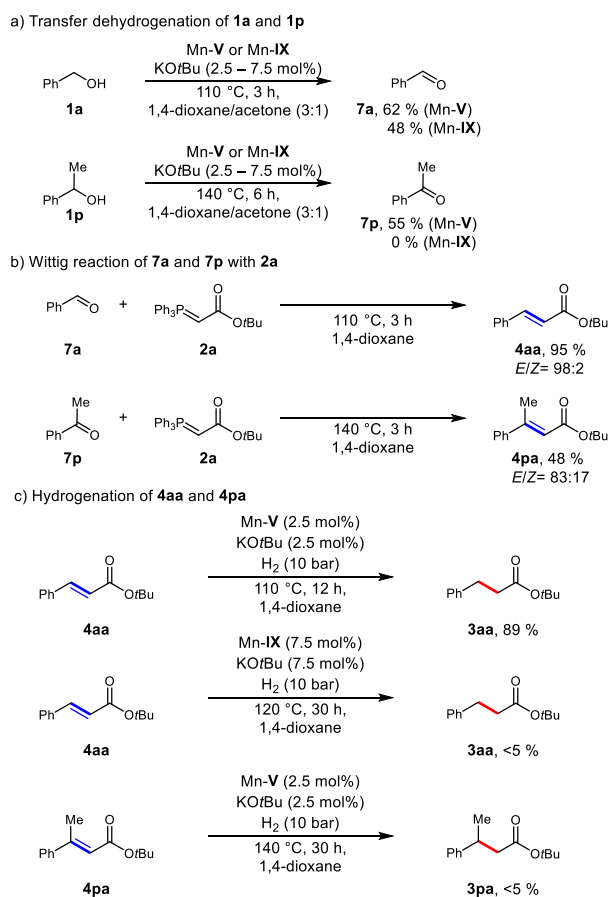
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Figure 2. Reaction profile for the conversion of benzylic alcohol (**1a**) with **2a** to the saturated product **3aa** in the presence of catalyst Mn-**V** (left) and the unsaturated product **4aa** using catalyst Mn-**IX** (right).

Scheme 6. Control experiments.

Considering the ability of the two complexes for selective construction of C–C and C=C bonds, we were interested in the reaction profile and mechanism of these transformations. Thus, under the optimized reaction conditions, we recorded the reaction profiles

for the conversion **1a** with **2a** to the saturated and unsaturated products **3aa** and **4aa** in the presence of catalyst Mn-**V** and Mn-**IX**, respectively (Figure 2). When Mn-**V** was used as catalyst, the formation of **4aa** as an intermediate was observed reaching a maximum after 4 h and 72 % conversion of **1a** (Figure 2, left). Hydrogenation of intermediate **4aa** over time led to a gradually decreased until it finally was fully converted. After 12 h the yield of **4aa** was <1 % and **3aa** was observed in 97 %. In contrast, in the presence of Mn-**IX** the only observed product was **4aa** (Figure 2, right). While the complex Mn-**V** is a well-known (de)hydrogenation manganese catalyst,[15a, 15b, 24] the (de)hydrogenation in presence of Mn-**IX** has not been reported so far. Therefore, several control experiments were performed under the standard reaction conditions to explain the observed reactivity (Scheme 6). First, the transfer-dehydrogenation of primary **1a** and secondary alcohol **1p** in the presence of Mn-**V** and Mn-**IX** were investigated (Scheme 6a). The conversion of **1a** using acetone as a hydrogen acceptor led to the formation of benzaldehyde **7a** which indicates the ability of both catalysts to dehydrogenate primary alcohols. However, only Mn-**V** facilitated the dehydrogenation of the secondary substrate **1p** while Mn-**IX** showed no conversion. As expected, the subsequent Wittig reaction between **7a** and **7p** with **2a** leads to the unsaturated product **4aa** and **4pa**, respectively (Scheme 6b). Additionally, the reduction of **4aa** by using molecular hydrogen (10 bar) was performed in presence of both complexes. Interestingly only the use of Mn-**V** led to hydrogenation of **4aa**. In contrast, when Mn-**IX** is used as a catalyst the conversion of **4aa** to **3aa** was below 5 % even after 30 h at 120 °C (Scheme 6c). These results indicate that the reaction between primary alcohol and ylides can either follow the traditionally borrowing hydrogen or acceptorless dehydrogenative coupling pathways depending on the ligand and reaction conditions.

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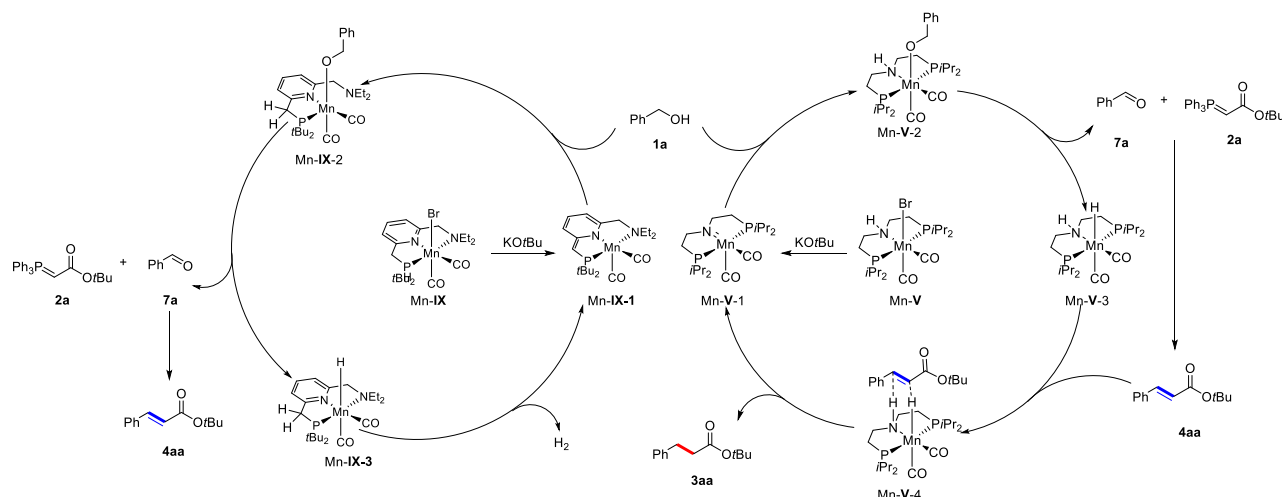
Scheme 7. Proposed reaction mechanism.

Based on the experimental results and the previous literature reports,[7] we propose the mechanism depicted in Scheme 7. The formation of saturated products **3** in the presence of Mn-**V** is initiated by the deprotonation of Mn-**V** by KO*t*Bu under formation of the amido complex Mn-**V**-1. The dehydrogenation of the alcohol **1** occurs via formation of an Mn-alkoxy amino complex Mn-**V**-2, which is followed by *β*-hydride elimination to give the carbonyl compound **7** and manganese hydride complex Mn-**V**-3. The Wittig reaction between the carbonyl compound **7** and ylide **2** leads to the corresponding unsaturated product **4**. Hydrogenation of the carbon-carbon double bond in **4** yields the saturated product **3** and thereby regenerating the amido complex Mn-**V**-1. In case of Mn-**IX**, the active catalyst Mn-**IX**-1 is also formed by deprotonation with KO*t*Bu. Subsequently, the intermediate complex Mn-**IX**-2 is formed, in analogy to the previously reported formation of an alkoxy complex through O-H activation by metal-ligand cooperation resulting in rearomatization of the pincer ligand.[20] Subsequently, the carbonyl compound **7** is liberated forming the hydride complex Mn-**IX**-3. As described above, the unsaturated product **4** is formed by the Wittig reaction between **7** and ylide **2**. However, in contrast to Mn-**V**-4, the hydride complex Mn-**IX**-4 cannot reduce the alkenes **4** under the reaction conditions. In this case, the dearomatized species Mn-**IX**-1 is regenerated by reductive elimination of molecular hydrogen.

Conclusion

A manganese-catalyzed C–C and C=C bond formation reaction between alcohols and phosphorus ylides via borrowing hydrogen and acceptorless dehydrogenative coupling is reported. The initial screening and optimization studies indicated that depending on the ligand and reaction conditions one or the other reaction pathway is favoured. A well-known PNP-Mn catalyst

proved to be suitable for the selective coupling of primary alcohols with primary phosphorus ylides to form the saturated products via borrowing hydrogen reactions. In contrast a PNN-Mn catalyst led to the respective acceptorless dehydrogenative coupling product. Both catalysts were applied to the coupling of a wide range of differently functionalized substrates. In total 65 C–C and C=C bond products were isolated in up to 91% yield. It was observed that the reaction of sterically hindered secondary alcohols and ylides led exclusively to the corresponding C=C products. However, in the presence of stochiometric amounts of KO*t*Bu the saturated products were also accessible using a PNP-Mn catalyst. The substrate scope was further extended to the conversion of 7 bio-based substrates. Notably, several reactions were performed on a 10 mmol scale indicating the scalability of the protocol. Moreover, it was shown that the Mn-catalyzed borrowing hydrogen and acceptorless dehydrogenative coupling reactions can be extended by the in situ generation of the phosphorus ylide in a one-pot reaction.

Experimental Section

General Procedure 1 – Mn-V catalyzed C–C bond formation reaction: In a Schlenk vessel, Mn-**V** (7.200 mg, 0.0125 mmol, 2.500 mol%) and KO*t*Bu (1.380 mg, 0.0125 mmol, 2.500 mol%) were dissolved in 1,4-dioxane (2.5 mL) under argon. The mixture was stirred for 5 min at 23 °C. Subsequently, the alcohol **1** (0.5 mmol, 1.0 equiv.) and ylide **2** (0.6 mmol, 1.2 equiv.) were added in one portion. The Schlenk vessel was placed in a preheated oil bath (110–130 °C) and the mixture was stirred for 12–24 h. The reaction mixture was cooled to 23 °C. After removal of all volatiles in vacuo the crude mixture was purified by column chromatography on silica gel to afford the desired products.

General Procedure 2 – Mn-IX catalyzed C=C bond formation reaction: In a Schlenk vessel, Mn-**IX** (17.90 mg, 0.0375 mmol, 7.500 mol%) and KO*t*Bu (4.140 mg, 0.0375 mmol, 7.500 mol%) were dissolved in 1,4-dioxane (2.5 mL) under argon. The mixture was stirred for 5 min at 23 °C. Subsequently, the alcohol **1** (0.5 mmol, 1.0 equiv.) and ylide

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2 (0.6 mmol, 1.2 equiv.) were added in one portion. The Schlenk vessel was placed in a preheated oil bath (110–120 °C) and the mixture was stirred for 30–42 h. The reaction mixture was cooled to 23 °C and vented carefully. After removal of all volatiles in vacuo the crude mixture was purified by column chromatography on silica gel to afford the desired products.

Acknowledgements

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FULL PAPER

Selective Construction of C–C and C=C Bonds by Manganese-catalyzed Coupling of Alcohols with Phosphorus Ylides

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Xin Liu and Thomas Werner*

Borrowing Hydrogen/Hydrogen Autotransfer

Acceptorless Dehydrogenative Coupling

31 exampes
up to 91 % yield

34 exampes
up to 81 % yield