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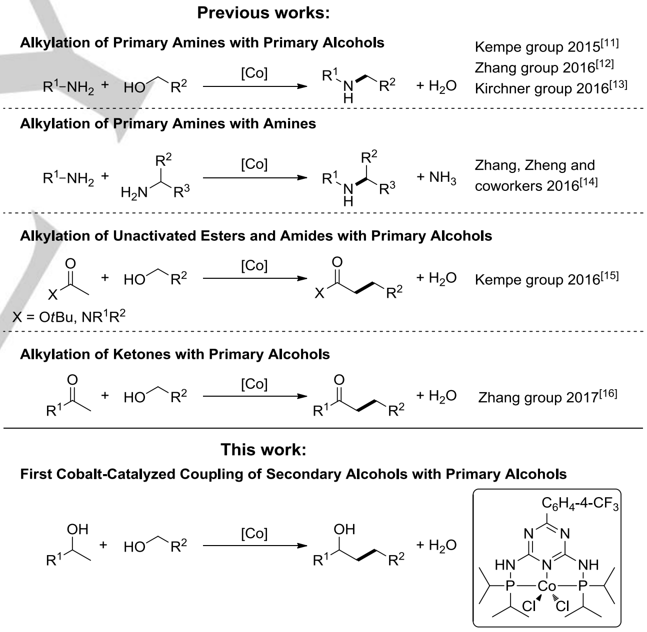
Cobalt-Catalyzed Alkylation of Secondary Alcohols with Primary Alcohols via Borrowing Hydrogen/Hydrogen Autotransfer

Frederik Freitag,[a] Torsten Irrgang,[a] and Rhett Kempe*[a]

Alcohols are promising sustainable starting materials since they can be obtained from abundant and indigestible biomass. The substitution of expensive noble metals in catalysis by earth abundant 3d metals, such as Mn, Fe or Co, (nonprecious or base metals) is a related key concept with respect to sustainability. Herein, we report on the first cobalt-catalyzed alkylation of secondary alcohols with primary alcohols. Easy-to-synthesize and easy-to-activate PN_5P-pincer ligand stabilized Co complexes developed in our laboratory mediate the reaction most efficiently. The catalysis is applicable to a broad substrate scope and proceeds under relatively mild conditions. We have even demonstrated the coupling of a variety of purely aliphatic alcohols with a base or nonprecious metal catalyst. Mechanistic studies indicate that the reaction follows the borrowing hydrogen or hydrogen autotransfer concept.

The borrowing hydrogen/hydrogen autotransfer methodology (BH/HA) is a prominent example of an alcohol re-functionalization concept.[1, 2] The alcohol is dehydrogenated to a carbonyl compound, followed by a reaction with a nucleophile and subsequent reduction with the “borrowed” hydrogen. Because of dwindling crude oil reserves and growing public awareness for the consequences of climate change, the search for alternative carbon resources is getting increasingly urgent.[3, 4] In this regard, alcohols are promising as starting materials due to the possibility of obtaining them from abundantly available, indigestible and barely used biomass (lignocellulose).[5-7] The direct hetero-coupling of two alcohols follows the BH/HA concept and exclusively uses alcohols as starting materials. This reaction has been reported to proceed employing a multitude of noble metal catalysts.[8] However, noble metals are rare and their conservation is a key issue with regard to a sustainable future. One possible approach is the replacement of precious metals in key technologies by more abundant metals. Beside Mn[9], and Fe[10], especially Co complexes[11-17] have been disclosed as highly active and selective catalysts for a variety of reactions following the BH/HA mechanism (see Scheme 1). Iron-[18] and nickel-based[19] homogenous catalysts have been described for the alkylation of secondary alcohols by primary alcohols.[20] Unfortunately, the substrate scope is limited, especially for the nickel catalyzed version. A broadly applicable catalyst system based on a nonprecious metal, which is capable of coupling aromatic, as well as purely aliphatic alcohols remains unknown. Herein, we report on the first cobalt-catalyzed version of the hetero-alkylation of alcohols by alcohols following the BH/HA concept. The catalyst is able to couple substituted 1-phenylethanol derivatives with primary aromatic or aliphatic alcohols as well as secondary aliphatic alcohols with primary aromatic or aliphatic alcohols. Triazine-based PN_5P pincer ligand complexes developed in our laboratory are most efficient in these reactions. They are easily and nearly quantitatively obtainable in two steps from commercially available and inexpensive starting materials. In addition, the precatalysts self-activate under basic conditions.[11, 15, 21] The related pyridine-based PN_3P pincer ligand class was introduced by Haupt and coworkers[22, 23] and has intensively been studied by the Kirchner group[24].



Scheme 1. Cobalt-Catalyzed C-C- and C-N-Coupling Reactions based on BH/HA.

The coupling of 1-phenylethanol (**1a**) and benzyl alcohol (**2a**) to **3a** was chosen as a model reaction (Table 1, top). Common reaction parameters were optimized starting with precatalyst **4a** (for further details see SI). Eight different cobalt-based $PN_{3\text{-}5}P$ complexes and $CoCl_2$ were tested (Table 1), in order to find the most suitable precatalyst for the model reaction. All reactions using precatalysts with pyridine backbone (Table 1, **5a**-**c**, entries 6-8) yielded no product. These results could be explained by the low hydrogenation activity of the pyridine-based

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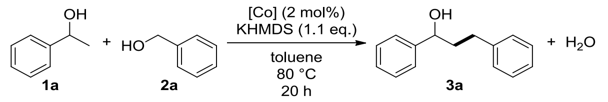
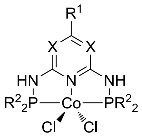
complexes.[21] Hydrogenation/reduction is a key step in BH/HA reactions. When $CoCl_2$ (Table 1, entry 9) was used, **3a** was obtained in only 2 % yield. In contrast, the triazine-based complexes (Table 1, **4a**-**e**, entries 1-5) were much more active. The yield of **3a** improved to 25 % (Table 1, entry 3) with **4c** as the best precatalyst.

Table 1. Precatalyst Screening.[a]



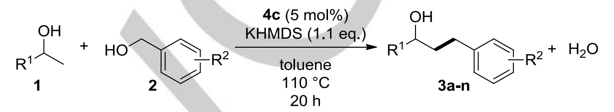
Entry	Precatalyst	Yield [%][b]
1	**4a**: R^1 = Ph; R^2 = *i*Pr	12
2	**4b**: R^1 = NH-C_3H_5; R^2 = *i*Pr	24
3	**4c**: R^1 = 4-F_3C-C_6H_4; R^2 = *i*Pr	25 (90[c])
4	 X = N (**4**), CH (**5**) **4d**: R^1 = Me; R^2 = *i*Pr	16
5	**4e**: R^1 = Me; R^2 = Cy	23
6	**5a**: R^1 = H; R^2 = *i*Pr	0 (3[c])
7	**5b**: R^1 = Me; R^2 = *i*Pr	0 (5[c])
8	**5c**: R^1 = H; R^2 = Ph	0 (1[c])
9	$CoCl_2$	2

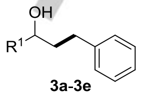
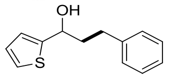
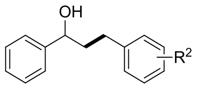
[a] **1a** (1.5 mmol), **2a** (1.0 mmol), KHMDS (potassium bis(trimethylsilyl)amide, 1.1 mmol), 2 mol% (20 µmol) precatalyst, toluene (2 mL), 80 °C (oil bath), 20 h, closed system. [b] Determined via GC analysis. [c] Yields determined via GC for the alkylation under optimized reaction conditions: **1a** (1.5 mmol), **2a** (1.0 mmol), KHMDS (1.1 mmol), 5 mol% (50 µmol) precatalyst, toluene (2 mL), 110 °C (oil bath), 20 h, closed system.

The conversion of **2a** was quantitative and the yield of **3a** could be increased to 90 % by further optimization of the reaction conditions regarding temperature and catalyst loading. In summary, the reaction proceeded best in toluene, with 1.1 eq. KHMDS, a reactant **1**/**2** ratio of 1.5:1.0 and precatalyst **4c** (5 mol%) at 110 °C for 20 h.

Next, the substrate scope for the alkylating system was investigated under these conditions. It seemed most reasonable to us to start with reactants derivable from the aromatic model substrates **1a** and **2a**, from which **3a** had been isolated in 76 % of yield. At first, aromatic secondary alcohols **1** with different substitution patterns were reacted with benzyl alcohol (**2a**). Methoxy-, methyl- and chloro- (Table 2, entries 2-4) functionalities were introduced in *para* position of **1** with nearly identical isolated yields. *m*-Chloro-1-phenylethanol (Table 2, entry 5) gave the corresponding product in a slightly lower yield of 61 %. Even a reactant with a potentially catalyst-inhibiting thiophene motif (Table 2, entry 6) gave **3f** in an acceptable 44 % yield. After that, primary alcohols derived from benzyl alcohol were varied and used in combination with 1-phenylethanol (**1a**), giving rise to products with methyl group in *ortho*-, *meta*- and *para*-position of the phenyl ring (Table 2, entries 7-9) in yields of isolated 73-79 %. The electron-rich 2- and 4-methoxybenzyl alcohols (Table 2, entries 10, 11) gave the corresponding products in 69 (**3j**) and 77 % (**3k**). However, the reaction time had to be prolonged to 44 h for the *ortho* substituted reactant (Table 2, entry 10). This might be due to the methoxy substituent being much closer to the hydroxyl group and thus causing steric hindrance.

Table 2. Substrate Scope of Aromatic Alcohols (**1** and **2**).[a]

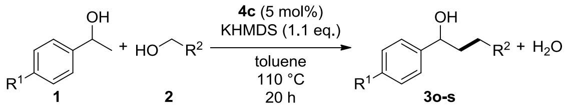


Entry	Product (**3a**-**n**)		R^1	R^2	Yield [%][b]
1		**3a**	C_6H_5	H	76
2	 **3a-3e**	**3b**	4-OMe-C_6H_4	H	80
3		**3c**	4-Me-C_6H_4	H	77
4		**3d**	4-Cl-C_6H_4	H	79
5		**3e**	3-Cl-C_6H_4	H	61
6	 **3f**	**3f**	C_4H_3S	H	44
7		**3g**	C_6H_5	2-Me	74
8		**3h**	C_6H_5	3-Me	73
9		**3i**	C_6H_5	4-Me	79
10[c]	 **3g-3n**	**3j**	C_6H_5	2-MeO	69
11		**3k**	C_6H_5	4-MeO	77
12		**3l**	C_6H_5	4-Cl	60
13		**3m**	C_6H_5	4-Br	49
14[d]		**3n**	C_6H_5	3,4-$(CH)_4$	64

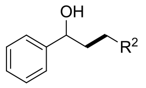
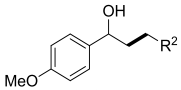
[a] **1** (1.5 mmol), **2** (1.0 mmol), KHMDS (1.1 mmol), 5 mol% **4c** (50 µmol), toluene (2 mL), 110 °C (oil bath), 20 h, closed system. [b] Yields of isolated products. [c] Reaction time: 44 h. [d] 130 °C (oil bath).

p-Chloro- and *p*-bromobenzyl alcohol (Table 2, entries 12, 13) were converted into products **3l** (60 %) and **3m** (49 %), in order to prove tolerance of the catalytic system for halides. The lower yield of **3m** is due to dehalogenation. Next, we investigated the reaction of aliphatic primary alcohols with aromatic secondary alcohols. Therefor **1a** was alkylated with the two unbranched alcohols 1-hexanol (Table 3, entry 1) and 1-octanol (Table 3, entry 2), which delivered the products in nearly identical yields of 49 (**3o**) and 51 % (**3p**). Cyclopropylmethanol was employed as a branched example of an aliphatic reactant, giving the corresponding product **3q** in a slightly higher 63 % yield. 4-Methoxyphenylethanol was also tested in combination with 1-hexanol (Table 3, entry 4) and 1-octanol (Table 3, entry 5), in order to show that these findings are not restricted to 1-phenylethanol (**1a**). Thus, products **3r** and **3s** were obtained in a 46 and a 49 % isolated yield.

Table 3. Reaction of aromatic secondary alcohols (**1**) and aliphatic primary alcohols (**2**).[a]



1 **2** **3o-s**

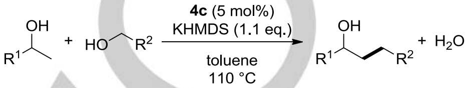
Entry	Product (**3o**-**s**)		R^1	R^2	Yield [%][b]
1	 **3o-3q**	**3o**	H	*n*-pentyl	49
2		**3p**	H	*n*-heptyl	51
3		**3q**	H	cyclopropyl	63
4	 **3r-3s**	**3r**	OMe	*n*-pentyl	46
5		**3s**	OMe	*n*-heptyl	49

[a] **1** (1.5 mmol), **2** (1.0 mmol), KHMDS (1.1 mmol), 5 mol% **4c** (50 µmol), toluene (2 mL), 110 °C (oil bath), 20 h, closed system. [b] Yields of isolated products.

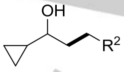
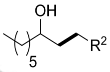
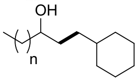
Since the incorporation of primary aliphatic alcohols was possible, we investigated the substrate scope for aliphatic secondary alcohols. Consequently, 1-cyclopropylethanol, as a branched aliphatic substrate, was applied along with benzyl alcohol (Table 4, entry 1), delivering product **3t** in 72 % yield. Furthermore, 1-octanol (Table 4, entry 2) as an unbranched, and cyclohexanemethanol (Table 4, entry 3) as a branched alcohol, were coupled with 1-cyclopropylethanol into **3u** (62 %) and **3v** (54 %). Linear secondary alcohols were also successfully deployed in the reaction. 2-Octanol was alkylated with 3-phenylpropanol (Table 4, entry 4) in a 40 %, with 1-octanol (Table 4, entry 5) in a 50 % and with cyclohexanemethanol (Table 4, entry 6) even in a 70 % yield. Because of the rather high yield of the latter, it seemed to be a suitable substrate for examining how the length of the carbon chain influences the alkylation. Thus, 2-hexanol (Table 4, entry 7) and 2-pentanol (Table 4, entry 8) were coupled with cyclohexanemethanol and the products were isolated in a 66 (**3z**) and a 59 % (**3aa**) yield, respectively. Consequently, the yields seem to decrease slightly towards smaller carbon chains of the secondary alcohols.

After having shown the substrate scope especially for aliphatic alcohols, further investigations were conducted gaining insight into the mechanism of the catalysis. A time-conversion-plot revealed that the alkylation between the model substrates **1a** and **2a** had finished after about 10 h.

Table 4. Coupling of aliphatic secondary alcohols (**1**) with primary alcohols (**2**).[a]



1 **2** **3t-aa**

Entry	Product (**3t**-**aa**)		R^1	R^2	Yield [%][b]
1	 **3t-3v**	**3t**	cyclopropyl	C$_6$H$_5$	72
2		**3u**	cyclopropyl	*n*-heptyl	62
3		**3v**	cyclopropyl	cyclohexyl	54
4	 **3w-3x**	**3w**	*n*-hexyl	(CH$_2$)$_3$C$_6$H$_5$	40
5		**3x**	*n*-hexyl	*n*-heptyl	50
6	 **3y**, **3z**, **3aa**	**3y**	*n*-hexyl (n = 5)	cyclohexyl	70
7		**3z**	*n*-butyl (n = 3)	cyclohexyl	66
8		**3aa**	*n*-propyl (n = 2)	cyclohexyl	59

[a] **1** (1.5 mmol), **2** (1.0 mmol), KHMDS (1.1 mmol), 5 mol% **4c** (50 µmol), toluene (2 mL), 110 °C (oil bath), 20 h, closed system. [b] Yields of isolated products.

The oxidation of starting materials **1a** and **2a**, as a key step of the BH/HA mechanism, was investigated separately, in an open system each. The depletion of the reactants, as well as the produced compounds, imply that the oxidation of alcohols is possible with the herein reported cobalt catalyst. As a second key step, the postulated intermediates (chalcone, its corresponding ketone, and the unsaturated alcohol) were reduced to **3a**. The usage of hydrogen and precatalyst **4c** resulted in 17, 84 and 80 % yields, respectively. Other experiments demonstrated that the equilibrium of the alkylation tends strongly to the alkylated products, since no back reaction is observed. The investigations indicate that the reaction proceeds via the BH/HA mechanism (see SI for further details). We have reported the first cobalt-catalyzed version of the alkylation of secondary alcohols with primary alcohols. We used PN$_5$P-pincer ligand complexes of cobalt, developed in our laboratory and demonstrated that they are highly active in this reaction. The catalysts are easy to synthesize from inexpensive starting materials. The catalyst system we have developed is applicable to a broad substrate scope. Even the hetero-coupling of different aliphatic alcohols was demonstrated.

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Keywords: Alcohol • Alkylation • Borrowing Hydrogen/Hydrogen Autotransfer • Cobalt • PNP ligands

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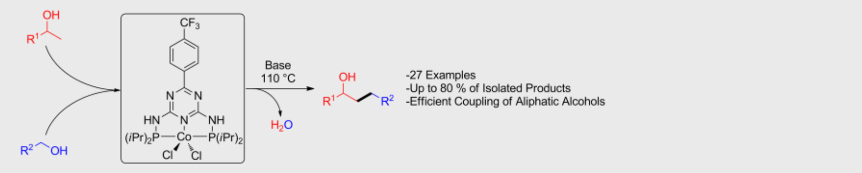

It is all about the al[Co]hol. – The first cobalt catalyst for the alkylation of secondary alcohols with primary alcohols is reported. The system requires mild conditions with a high substrate scope even for aliphatic motifs and yields of the isolated products of up to 80 %.

*Frederik Freitag, Torsten Irrgang, Rhett Kempe**

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Cobalt-Catalyzed Alkylation of Secondary Alcohols with Primary Alcohols via Borrowing Hydrogen/Hydrogen Autotransfer