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Hydrosilylation of Ketones: From Metal–Organic Frameworks to Simple Base Catalysts

Daniele Addis,[a] Shaolin Zhou,[a] Shoubhik Das,[a] Kathrin Junge,[a] Hendrik Kosslick,[a, b] Jörg Harloff,[b] Henrik Lund,[a, b] Axel Schulz,*[a, b] and Matthias Beller*[a]

The catalytic reduction of carbon–heteroatom multiple bonds under mild conditions constitutes an important transformation in organic synthesis and the pharmaceutical as well as agrochemical industry.[1] Obviously, high selectivity and broad tolerance towards functional groups are key factors for the acceptance and application of novel methodologies. In addition to molecular hydrogen and hydrogen transfer reagents,[2] hydrosilanes are commonly used as reducing agents.[3]

Since the early reports three decades ago,[4] the asymmetric and non-asymmetric hydrosilylations of prochiral ketones relied mainly on precious-metal-based catalysts, such as rhodium,[5] ruthenium,[6] and iridium.[7] However, less-expensive metals, such as titanium,[8] tin,[9] and copper[10] were explored, too.[11] More recently, efforts have been devoted to the development of more-benign and available bio-relevant metal catalysts based on iron[12] and zinc complexes.[13]

Notably, silanes have also been used as reducing reagents in the presence of acid,[14] fluoride ions,[15] or base,[14a,15b,16] although in many cases harsh reaction conditions and large amounts of salt or base were required. Clearly, each of these procedures has its merits as well as limitations. Either the cost of the metal catalyst, toxicity of the residual metal in the product, operational difficulties (such as low temperature −50 to −70 °C), or the use of complex ligand systems limit their applications. Hence, the development of novel catalysts continues to attract academic and industrial interest.

Based on the recent work of groups including ourselves on iron-, zinc-, and copper-catalyzed reductions,[17,18] we started a joint program to explore the catalytic performance of heterogeneous catalysts for the hydrosilylation of ketones.[19] In particular, we were attracted by the use of so-called metal–organic frameworks (MOFs), an important class of porous crystalline materials.[20] Because of their high porosity and surface area, these materials may also find applications in catalysis.[21]

At the starting point of our investigations, we used the known $\{Cu_3(BTC)_2\}$ (BTC = 1,3,5-benzenetricarboxylate) material (Figure 1)[22] in the hydrosilylation of acetophenone. To the best of our knowledge, this and similar MOFs have not been applied in such reductions.[23]

In exploratory experiments, the variation of the reaction temperature and solvent were performed in the presence of different silanes. To determine product yields conveniently by GC, NaOH (1 M) in methanol was added after 16 hours to hydrolyze the corresponding silyl ether to 1-phenylethanol. Selected catalytic results are shown in Table 1. Whilst

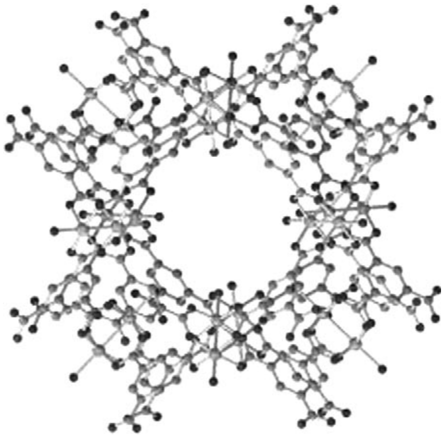

Figure 1. Structure of the $\{Cu_3(BTC)_2\}$ pore.

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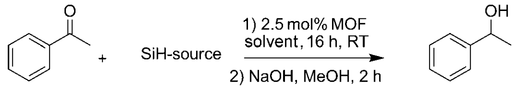
[a] D. Addis, S. Zhou, S. Das, Dr. K. Junge, Dr. H. Kosslick, H. Lund,
Prof. Dr. A. Schulz, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Straße 29a
D-18059 Rostock (Germany)
Fax: (+49) 381-1281-5000
E-mail: matthias.beller@catalysis.de

[b] Dr. H. Kosslick, Dr. J. Harloff, H. Lund, Prof. Dr. A. Schulz
Institut für Chemie, Universität Rostock
Albert-Einstein-Straße 3
D-18059 Rostock (Germany)
Fax: (+49) 381-1281-5000
E-mail: axel.schulz@uni-rostock.de

poly(methylhydrosiloxane) (PMHS), $(EtO)_2MeSiH$, and Ph_2SiH_2 did not lead to the desired 1-phenylethanol, the reaction proceeded smoothly when the more reactive phenylsilane was used (Table 1, entries 4–6). Even in the presence of only 1 mg of $\{Cu_3(BTC)_2\}$, which corresponds to around 1 mol % of copper, we obtained >99 % yield of 1-phenylethanol within 1 hour. With respect to the solvent, the best results were observed in toluene and diethyl ether. Other solvents, such as ethyl acetate, dichloromethane, and *n*-hexane also worked, but gave significantly lower yields.

Table 1. Hydrosilylation of acetophenone with $\{Cu_3(BTC)_2\}$: variation of silanes and solvents.



Entry[a]	$Cu_3(BTC)_2$ [mg]	Silane	Solvent	*T* [°C]	Yield [%]
1	7.5	$(EtO)_2MeSiH$	THF	65	<1
2	7.5	Ph_2SiH_2	toluene	RT	6
3	7.5	PMHS	toluene	RT	<1
4	7.5	$PhSiH_3$	toluene	RT	>99
5	1	$PhSiH_3$	toluene	RT	99
6[b]	1	$PhSiH_3$	toluene	RT	99
7[b]	1	$PhSiH_3$	AcOEt	RT	74
8[b]	1	$PhSiH_3$	CH_2Cl_2	RT	40
9[b]	1	$PhSiH_3$	Et_2O	RT	94
10[b]	1	$PhSiH_3$	THF	RT	81
11[b]	1	$PhSiH_3$	*n*-hexane	RT	38

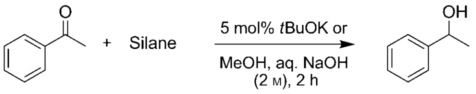
[a] Reaction conditions: MOF (0.0125 mmol), acetophenone (0.5 mmol), toluene (2 mL), then addition of the silane (1.3 equiv $(EtO)_2MeSiH$; 2 equiv Ph_2SiH_2; 3 equiv PMHS; 2 equiv $PhSiH_3$). After 16 h, NaOH in methanol (2 mL, 1 M) was added to the solution at 0 °C and the mixture was left to stir for 2 h at RT. Yield was determined by GC analysis (50 m Lipodex E, 95–200 °C) with diglyme as an internal standard; [b] Reaction time: 1 h. THF = tetrahydrofuran, Ac = acetyl.

Noteworthy, in toluene and diethyl ether the blue color of $\{Cu_3(BTC)_2\}$ did not change during the reaction. However, in the other solvents the reaction solution turned black a few minutes after the addition of silane. Apparently, in the latter cases, leaching of copper ions and formation of copper(0) took place. This effect proceeded within minutes in *n*-hexane, whilst in toluene it was only observed after 2 days. It is important to note that not only the solvent played a crucial role in preventing the formation of elemental copper, because reduction to copper(0) could also be observed in toluene after 20 minutes, if no ketone was added.

Based on these initial promising results, we tested 15 different MOF-based materials in the standard reaction under the optimized conditions (2 equivalents of $PhSiH_3$, toluene, room temperature). In addition to various copper-based MOFs, different zinc-, iron-, and one chromium-containing metal-organic framework were considered and gave product yields in the range 30–80 %.[23] However, there was no clear trend observed with respect to the size of the pores or the coordinating metal. Hence, we wanted to investigate in more detail what was happening in the reaction media. In order to confirm any leaching effect, a second hydrosilylation reaction with acetophenone was performed with the filtrate of a $\{Cu_3(BTC)_2\}$-catalyzed reaction. To our surprise, we again obtained near-complete conversion (98 %) and 94 % yield of 1-phenylethanol, apparently thus demonstrating significant catalyst leaching.

Moreover, we looked for the activity of any acidic or basic impurities present in the reaction. To our surprise, smooth reduction of acetophenone took place in the presence of base in methanol at room temperature. Whilst it is known that phenylsilane undergoes alcoholysis with alcohol and base,[24] there have been no reports on the reduction of ketones under such conditions. In the presence of 5 mol % of *t*BuONa or an inexpensive 1 M solution of NaOH in methanol, the starting material disappeared quickly, leading to the formation of the corresponding silyl ether in good to quantitative yield (Table 2). Interestingly, apart from $PhSiH_3$, other less expensive silanes, such as $(EtO)_2MeSiH$ and Ph_2SiH_2 worked well in this benchmark reduction.

Table 2. Base-catalyzed hydrosilylation of acetophenone.[a]



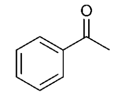
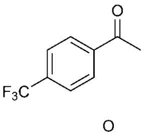
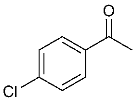
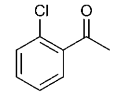
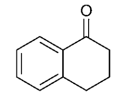
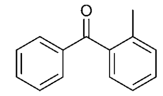
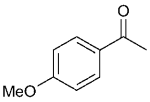
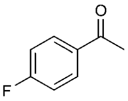
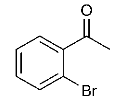
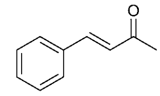
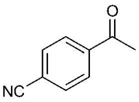
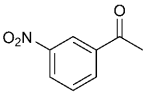
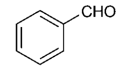
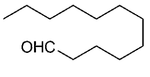
Entry[a]	Base [5 mol %]	Silane [2 equiv]	Conv. [%]	Yield [%]
1	*t*BuOK	$(EtO)_2MeSiH$	>99	98
2	*t*BuOK	$PhSiH_3$	>99	98
3	*t*BuOK	Ph_2SiH_2	>99	96
4	*t*BuONa	$(EtO)_2MeSiH$	>99	95
5	*t*BuONa	$PhSiH_3$	99	96
6[b]	NaOH	$PhSiH_3$	60	60

[a] Reaction conditions: acetophenone (0.5 mmol), toluene (2 mL), silane (2 equiv). After 1 h, NaOH (2 M) was added to the solution at 0 °C and the mixture was stirred for 2 h at RT. Yield was determined by GC analysis (50 m Lipodex E, 95–200 °C) with diglyme as an internal standard. [b] 1 mmol acetophenone, addition of the silane (2 equiv). After 0.5 h, NaOH in methanol (2 mL, 1 M) was added to the solution at 0 °C and the mixture was left to stir for 2 h at RT.

The performance of these simple bases was quite unexpected, considering the reaction of ketones and aldehydes with stoichiometric amounts of pentacoordinated hydrosilanes[25] or with more complex lithium amino-alkoxides.[26]

In order to demonstrate the general applicability of these convenient procedures, we investigated the hydrosilylation of different ketones in the presence of: A) a 2 M solution of NaOH in methanol and B) catalytic amounts (5 mol %) of *t*BuOK. Under the latter conditions, complete formation of the corresponding silyl ether was obtained within a few minutes. The two procedures are compared in Table 3. In general, the reactions catalyzed by potassium *tert*-butoxide gave somewhat higher yields compared to NaOH. However, in the case of 4-phenylbut-3-en-2-one, NaOH gave the allylic alcohol in 76 % yield, whilst *t*BuOK gave only 46 % yield (Table 3, entry 10). Acetophenones containing electron-withdrawing substituents (Cl, Br, F, CF_3-, CN, NO_2), in the *ortho*-, *meta*-, or *para*-positions provided their corresponding benzyl alcohols in moderate to good yields (48–92 %) in the

Table 3. Hydrosilylation of different ketones in the presence of base: substrate scope.

Entry	Ketone	Yield NaOH (A) [%][a]	Yield *t*BuOK (B) [%][b]
1		60	99
2		70	77
3		10	58
4		38	67
5		50	60
6		<1	66
7		30	58
8		15	73
9		<1	48
10		76	46
11		52	90
12		48	92
13		75	91
14		97	99

[a] Ketone or aldehyde (1 mmol), silane (2 equiv $PhSiH_3$). After 0.5 h, NaOH in methanol (2 mL, 1 M) was added to the solution at 0 °C and the mixture was left to stir for 2 h at RT; [b] *t*BuOK (5.6 mg), acetophenone (1 mmol), silane (2 equiv $PhSiH_3$). After 0.5 h, NaOH in water (2 M) was added to the solution at 0 °C and the mixture was left to stir for 2 h at RT.

presence of 5 mol% *t*BuOK (Table 3, entries 2–4, 8, 9, 11, 12). Notable is the chemoselective reduction of the carbonyl group in the presence of halides, nitro, and cyano substituents. 4-Methoxyacetophenone bearing an electron-donating substituent on the phenyl ring showed a decreased reactivity yielding the corresponding alcohol in 58% yield (Table 3, entry 7). In addition to substituted acetophenones, tetralone reacted well both in the presence of NaOH and *t*BuOK (Table 3, entry 5). Whilst diaryl ketones did not react in the presence of NaOH, hydrosilylation took place smoothly with the more reactive alkoxide (Table 3, entry 6). Finally, we demonstrated that aldehydes were also easily reduced under these conditions to give high yields of the corresponding alcohols (Table 3, entries 13 and 14).

In summary, we report a convenient and general hydrosilylation of aromatic ketones and two aldehydes. Based on the exploration of the catalytic potential of MOFs in the reduction of acetophenone, we discovered that simple and inexpensive bases, such as NaOH (2 M) in methanol or catalytic amounts of *t*BuOK, promote this reaction. This procedure works well with 12 different aromatic ketones and two aldehydes under mild conditions (room temperature, air) tolerating other sensitive functional groups.

Experimental Section

$\{Cu_3(BTC)_2\}$-catalyzed hydrosilylation of ketones: A 10 mL oven-dried Schlenk tube containing a stirrer bar, was charged with 1 mg $\{Cu_3(BTC)_2\}$. After purging with argon (argon/vacuum three cycles), anhydrous toluene (2 mL) followed by the ketone (1 mmol) were added and the reaction mixture was stirred at RT for 10–15 min. The $PhSiH_3$ (0.18 mL, 2 equivalents) was added using a syringe under argon. The reaction mixture was further stirred for 30 min at RT, then cooled to 0 °C followed by the sequential addition of diglyme (80 μL) as a GC standard (in case of analysis by GC), and 1 M NaOH in methanol (2 mL) with vigorous stirring (caution: The reaction mixture bubbled briefly but vigorously upon the addition of the base). The reaction mixture was further stirred for an hour (or until the organic layer became colorless/pale yellow) at room temperature and was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered (an aliquot was removed for GC analysis), and concentrated under vacuum. The residue was purified by column chromatography on silica gel using an ethyl acetate/*n*-hexane mixture (20 to 40%) to afford the desired product.

Reduction of ketones with base in methanol: A 10 mL oven-dried Schlenk tube containing a stirrer bar was purged with argon (argon/vacuum three cycles), anhydrous toluene (2 mL) followed by ketone (1 mmol) and $PhSiH_3$ (0.18 mL, 2 equivalents) were added using a syringe under argon. The reaction mixture was further stirred for 30 min at RT, then cooled to 0 °C followed by the sequential addition of diglyme (80 μL) as a GC standard (in case of analysis by GC), and 1 M NaOH in methanol (2 mL) with vigorous stirring (caution: The reaction mixture bubbled briefly but vigorously upon the addition of the base). The reaction mixture was further stirred for an hour (or until the organic layer became colorless/pale yellow) at room temperature and was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered (an aliquot was removed for GC analysis), and concentrated under vacuum. The residue was purified by column chromatography on silica gel using an ethyl acetate/*n*-hexane mixture (20 to 40%) to afford the desired product.

***t*BuOK-catalyzed hydrosilylation of ketones:** A 10 mL oven-dried Schlenk tube containing a stirrer bar, was charged with *t*BuOK (5.6 mg, 5 mol %). After purging with argon (argon/vacuum three cycles), anhydrous toluene (2 mL) followed by ketone (1 mmol). The $PhSiH_3$ (0.18 mL, 2 equivalents) was slowly added using a syringe under argon (fast gas evolution was observed). The reaction mixture was further stirred for 30 min at RT, then cooled to 0 °C followed by the sequential addition of diglyme (80 μL) as a GC standard (in case of analysis by GC), and 2 M NaOH in water (2 mL) with vigorous stirring (caution: The reaction mixture bubbled briefly but vigorously upon the addition of the base). The reaction mixture was further stirred for an hour (or until the organic layer became colorless/pale yellow) at room temperature and was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered (an aliquot was removed for GC analysis) and concentrated under vacuum. The residue was purified by column chromatography on silica gel using an ethyl acetate/*n*-hexane mixture (20 to 40 %) to afford the desired product.

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Keywords: base · hydrosilylation · ketones · metal–organic frameworks

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