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Dehydrogenative coupling of alcohols and carboxylic acids with hydrosilanes catalyzed by a salen-Mn(v) complex[†]

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A Mn(v)-salen complex was found to be an effective catalyst for the dehydrogenative coupling of hydroxyl groups with hydrosilane. The reaction conditions were optimized with different silanes and efficient dehydrogenative coupling was achieved by using triethoxysilane and diphenylsilane. Various alcohols and phenols and a limited number of carboxylic acids were converted into the corresponding silyl ethers and silyl esters. A range of functional groups such as chloro, nitro, methoxy, carbonyl and carbon-carbon multiple bonds are tolerated in the reaction.

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Introduction

Si-O bond-containing compounds such as silvl ethers and silyl esters are important chemicals with an assortment of applications. For example, silvl ethers are commonly employed for protecting hydroxyl groups in multi-step syntheses,¹ and serve as precursors to silicone polymers.² They are also valuable for surface modifications, constructing organic-inorganic hybrids, functionalizing silica materials and tethering organometallic catalysts.³ Silyl esters are useful for protecting carboxylic acid groups¹ and poly(silyl ester)s are an interesting class of degradable materials with tunable degradation profiles.⁴ The standard method for the synthesis of silvl ethers and silvl esters is treating alcohol and carboxylic acid substrates with chlorosilanes, for which the HCl by-product is neutralized with a stoichiometric amount of bases such as imidazole and diisopropylethylamine.⁵ Moreover, the corrosiveness and hydrolytic sensitivity of chlorosilanes make them inconvenient for handling and storage. For tertiary and hindered alcohols, the use of more expensive silvl triflate reagents is required.⁶ Hexamethyldisilazane (HMDS) has also been utilized for silyl ether synthesis, but it usually takes longer reaction times and the ammonia by-product needs to be removed continuously.⁷

Dehydrogenative coupling of alcohols and carboxylic acids with hydrosilanes has emerged as an alternative for the synthesis of silyl ethers and silyl esters. Compared to chlorosilanes, hydrosilanes are generally less prone to hydrolysis and easier to handle. The dehydrogenative coupling reaction is a single-step process with high atom economy, generating hydrogen gas as the only by-product. Due to these attractive features, a number of catalysts have been reported for the dehydrogenative coupling of alcohols and hydrosilanes. They are typically complexes of various transition metals,⁸ while metal-free systems such as N-heterocyclic carbenes⁹ and Lewis acid $B(C_6F_5)_3$ (ref. 10) have also been developed for the process. In comparison, only a few catalytic systems are available for the dehydrogenative coupling of carboxylic acids and hydrosilanes.¹¹

Recent concerns about sustainability have led to significant efforts towards the development of catalytic systems derived from inexpensive, biocompatible and abundant metals.^{12,13} Taking this into consideration, manganese is of particular interest, since its global reserve is one of the largest among transition metals and it is an essential element for biological systems. Traditionally, manganese complexes have been extensively investigated in oxidation reactions, and their applications in other types of transformations have only been explored more recently.¹⁴ During the course of our study on high-valent transition metal catalysts for hydrosilylations,¹⁵ we observed that hydroxyl groups reacted with hydrosilanes in the presence of a Mn(v) complex, $[MnN(salen-3,5^{-t}Bu_2)]$ (1), that is readily available and can be easily prepared.¹⁶ Herein, we report our study on the dehydrogenative coupling of alcohols and carboxylic acids with hydrosilanes catalyzed by the Mn complex 1.

Results and discussion

Dehydrogenative coupling of alcohols and silanes: screening

In the initial experiments, we examined the dehydrogenative coupling reaction by taking benzyl alcohol as a template substrate. Various hydrosilanes were examined under different conditions in the presence of 0.5 mol% (*vs.* alcohol) MnN



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 Table 1
 Dehydrogenative coupling of benzyl alcohol with hydrosilanes^a

$\bigcirc CH_2OH + R'_{4-n}SiH_n \xrightarrow{MnN (0.5 mol \%),} \bigcirc CH_2O-SiH_{n-1}R'_{4-n} + H_2$						
Entry	Silane	BnOH : silane	Products	<i>T</i> (°C)	<i>t</i> (h)	Conversion ^b (%)
1 ^c	Ph ₂ SiH ₂	2:1	(PhCH ₂ O) ₂ -SiPh ₂	80	2.5	89
2	Ph_2SiH_2	2:1	(PhCH ₂ O) ₂ -SiPh ₂	80	3	85
3 ^c	Ph_2SiH_2	1:1	PhCH ₂ O-SiHPh ₂ ^d	80	1	90
4	PhMe ₂ SiH	1:1	N.R.	80	72	—
5	^t BuMe ₂ SiH	1:1	N.R.	80	24	_
6	Et ₃ SiH	1:1	N.R.	80	24	_
7	Ph ₃ SiH	1:1	PhCH ₂ OSiPh ₃	80	72	57
8	PhSiH ₃	1:1	(PhCH ₂ O) ₂ -SiHPh ^e	80	1.5	90
9 ^c	(EtO) ₃ SiH	1:1	PhCH ₂ O-Si(OEt) ₃	80	0.67	98
10	(EtO) ₃ SiH	1:1	PhCH ₂ O-Si(OEt) ₃	80	1	94
11	(EtO) ₃ SiH	1:1	PhCH ₂ O-Si(OEt) ₃	RT	7	90
12^{f}	(EtO) ₃ SiH	1:1	N.R.	80	12	—

^{*a*} Reaction conditions: substrate (0.7–0.8 mmol), silanes (one or two equivalents), PhSiMe₃ (10 mol%, as internal standard) and MnN catalyst 1 (0.5 mol%). ^{*b*} Determined by ¹H NMR on the basis of consumption of Ph₂CH₂OH or silane. ^{*c*} Reaction was performed under N₂. ^{*d*} Dialkoxy silyl ether was observed as a minor product. ^{*e*} Mono and trialkoxy silyl ethers were observed as minor products. ^{*f*} Catalyst was not used.

complex 1, and the selected results are presented in Table 1. Primary PhSiH₃, secondary Ph₂SiH₂ and tertiary (EtO)₃SiH hydrosilanes reacted readily with PhCH₂OH to produce the corresponding silvl ethers, with (EtO)₃SiH being the fastest among them (entries 3 vs. 9, 8 vs. 10). According to the product analysis of the crude reaction mixture, monoalkoxysilane Ph₂SiH(OCH₂Ph) was produced when one equivalent of Ph₂SiH₂ was employed, with a small amount of dialkoxysilane $Ph_2Si(OCH_2Ph)_2$ (entry 3). When the ratio of alcohol: Ph_2SiH_2 was 2:1, dialkoxysilane Ph₂Si(OCH₂Ph)₂ was produced as the predominant product (entry 2). In this case, the time profile of the reaction monitored by ¹H NMR spectroscopy shows rapid consumption of Ph₂SiH₂ and buildup of Ph₂SiH(OCH₂Ph), followed by slower disappearance of Ph₂SiH(OCH₂Ph) (Fig. 1). Similar to the Mn-catalyzed



Fig. 1 Time profiles for the reaction of benzyl alcohol with Ph_2SiH_2 (one equiv.).

hydrosilylation of carbonyl compounds,^{15*a*} the coupling reaction could be carried out at room temperature with extended reaction time (entry 11). Running the reaction under inert nitrogen atmosphere could shorten the reaction time (entries 1 *vs.* 2, 9 *vs.* 10), though the effect seems to be less substantial than that in hydrosilylation. Thus, subsequent reactions were performed without extrusion of air for convenience. On the other hand, tertiary silanes such as PhMe₂SiH, ^tBuMe₂SiH and Et₃SiH exhibited no reactivity, while Ph₃SiH showed reasonable conversion with prolonged reaction time (72 h), likely due to their electronic and steric characters (entries 4–7). In a control experiment, no reaction between PhCH₂OH and (EtO)₃SiH was observed after 12 h without adding the catalyst (entry 12).

Alcohol substrate scope

Having established the activity of complex 1 in the dehydrogenative coupling reactions, we moved on to a variety of alcohol substrates including primary, secondary, tertiary, cyclic and phenolic alcohols (Table 2). Under specified reaction conditions, most of the alcohols yielded the corresponding silyl ethers with >90% conversions and slightly lower isolated yields. Unlike primary alcohols, the dehydrogenative coupling of secondary and tertiary alcohols with Ph2SiH2 afforded monoalkoxysilanes as the primary product, even when excess alcohols were used (entries 2-4). This observation indicates that it was more challenging to couple the last Si-H bond with a bulky alcohol because of the steric crowding. For example, when 2 equivalents of a tertiary alcohol (^tBuOH) were allowed to react with Ph_2SiH_2 , only ~50% of the alcohol was consumed, even after prolonged reaction time (6 h). Addition of another equivalent of Ph₂SiH₂ led to the complete conversion of ^tBuOH within 2.5 h and the monoalkoxysilane was the predominant product detected (Table 2, entry 3). Similarly, reaction of a secondary alcohol, cyclohexanol, with Ph₂SiH₂ resulted in the formation of the monoalkoxysilane

Table 2 MnN-catalyzed dehydrogenative coupling of various alcohols with silanes⁴

Entry	Silane ^b	Products	<i>t</i> (h)	Conv. ^c (%)
1	Ph_2SiH_2 (0.5)	Ph, Ph	7.5	95 (81)
2	Ph_2SiH_2 (1.0)		1.5	96 (67)
3	Ph_2SiH_2 (1.0)		8.5	97 (79)
4	Ph_2SiH_2 (1.0)		1	95 (63)
5	Ph_2SiH_2 (0.5)	Ph Ph Si.	3	85 (50)
6^d	Ph_2SiH_2 (0.5)	Ph O Ph Ph Ph Si	2.7	95 (80)
7	(EtO) ₃ SiH (1.0)	$O-Si(OEt)_3$	1	90 (65)
8	(EtO) ₃ SiH (1.2)	O-Si(OEt) ₂	1.5	95 (81)
9	(EtO) ₃ SiH (1.2)		2.5	95 (73)
10	(EtO) ₃ SiH (1.0)	Ph $O-Si(OEt)_3$	3	98 (64)
11	(EtO) ₃ SiH (1.0)	Ph O-Si(OEt)a	4	98 (71)
12	(EtO) ₃ SiH (1.4)		5	96 (65)
13	(EtO) ₃ SiH (1.3)	O-Si(OEt) ₃	2.5	90 (64)
14	(EtO) ₃ SiH (1.0)	O-Si(OEt) ₃	2.8	90 (72)
15 ^e	(EtO) ₃ SiH (1.0)	O-Si(OEt) ₃	0.67	99
16	(EtO) ₃ SiH (1.0)		3	98 (81)
17	(EtO) ₃ SiH (1.3)	MeO-Si(OEt) ₃	1.5	90 (78)
18	(EtO) ₃ SiH (1.2)	^t Bu	2	95 (73)
19	(EtO) ₃ SiH (1.2)	$O_2N \longrightarrow O - Si(OEt)_3$	4	100 (90)
20	(EtO) ₃ SiH (1.3)	CI	1	95 (57)

^{*a*} Reaction conditions: substrate (0.7–0.8 mmol), silane and MnN catalyst (0.5 mol%) at 80 °C. ^{*b*} The equivalent amounts of silanes used (ν s. alcohol). ^{*c*} Determined by ¹H NMR on the basis of consumption of alcohol and/or silane; isolated yields in parenthesis. ^{*d*} Reaction under N₂. ^{*e*} 1 mol% catalyst used.

as the major product with 95% conversion in 1 h (Table 2, entry 4).

To examine the chemoselectivity of the dehydrogenative coupling process, we further worked with alcohol substrates having different functional groups such as C=C and C=C multiple bonds (Table 2, entries 11–13 and 15), since such groups may react with silanes under catalytic conditions.¹⁷ All these alcohols were converted to silyl ethers with excellent conversions. There were no side products of hydrosilylation/

hydrogenation of double and triple bonds with silanes. It is noted that saturated primary alcohols seem to be more reactive towards dehydrogenative coupling with triethoxysilane than unsaturated ones, as it took less reaction time (entries 8 vs. 11 & 12). The time profile of their reactions under identical conditions with 1 equivalent of $(EtO)_3SiH$ confirms that butan-1-ol has the fastest reaction time among them, though the difference is not large (Fig. 2). Nevertheless, this suggests that even though the double and triple bonds are not reactive



Fig. 2 Comparison of reactions of three primary aliphatic alcohols with $({\rm EtO})_3{\rm SiH}~(1\,{:}\,1).$

towards hydrosilanes under these conditions, they may still inhibit the coupling, presumably by coordinating to the active metal site. Since the Mn complex is known to catalyze the hydrosilylation of ketones,^{15*a*} a multifunctional substrate, 5-hydroxy-2-pentanone was tested for the coupling reaction (entry 14). Only the hydroxyl group reacted with silane under these conditions, and the ketone moiety was preserved in the isolated product. The preference for hydroxyl groups over carbonyls has been observed in other catalytic systems.^{8*j*,*l*,*r*}

To further probe the selectivity and electronic effect of different functional groups, we performed dehydrogenative coupling reactions of a series of para-substituted phenolic substrates and (EtO)₃SiH (Table 2, entries 16-20). Chloro, nitro and methoxy groups were tolerated in the reaction and dehydrogenative coupling proceeded with high conversion and decent yields within a few hours. When the reactions of 1:1 (EtO)₃SiH: phenols under otherwise identical conditions were monitored by ¹H NMR, the silane conversion profile indicated that both electron-withdrawing and electron-donating groups lead to faster reactions (Fig. 3), with the exception of *p*-nitrophenol, for which the reaction was considerably slower and featured an induction period. The peculiarity of para-NO2-substituted benzaldehyde and acetophenone has been noticed previously in hydrosilylation reactions,^{15a} though the reason behind it is still unclear.

To extend the scope of dehydrogenative coupling reactions, several diols were also examined under the same conditions and the results are summarized in Table 3. Diol substrates tend to be more demanding for the coupling because of the competing formation of cyclic and polymeric species. When 1,4-butanediol was allowed to react with two equivalents of $(EtO)_3SiH$, bissilylated $(EtO)_3SiO(CH_2)_4OSi(OEt)_3$ was the only product as expected (entry 1). When a slight excess of Ph₂SiH₂ was used, the seven-membered cyclic dioxasilacycle



Fig. 3 Reactions of substituted phenols p-X-C₆H₄OH (X = H, OMe, NO₂, Cl, ^tBu) with (EtO)₃SiH (1:1).

was obtained as the major product (entry 2). Similarly, treatment of pinacol with one equivalent of Ph_2SiH_2 or $PhMeSiH_2$ afforded five-membered cyclic dioxasilacycles as the major products (entries 3 and 4).⁸⁵

In another set of experiments, we repeated the reaction between benzyl alcohol and triethoxysilane to test the reusability of the catalyst. After the reaction was nearly complete (~60 min), second equivalents of alcohol and silane (1:1 molar ratio) were added to the reaction mixture, and with vigorous bubbling, >90% of the substrates were consumed within 30 min. A third addition of the 1:1 mixture of PhCH₂OH and (EtO)₃SiH led to a similar outcome (Fig. 4). These results suggested that the catalyst can be effectively reused without much loss in reactivity.

Dehydrogenative coupling of carboxylic acids and silanes

Based on the results of the alcohols, we next extended this process to the dehydrogenative coupling of carboxylic acids and silanes to synthesize silyl esters. Several reactions were performed in several solvents at different temperatures to optimize the reaction conditions, and selected results are listed in Table 4. Among the solvents tested, CDCl₃ has generally given rise to better conversions. Compared with the dehydrogenative reactions of alcohols, reactions of carboxylic acids are much slower, even with increased catalyst loading. Both aromatic (entry 1) and aliphatic carboxylic acids (entries 2 & 3) undergo dehydrogenative coupling reactions with (EtO)₃-SiH to yield the corresponding silyl esters.

Mechanistic consideration

During the reactions, one of the most notable features was the conspicuous change in color of the starting MnN complex from green to reddish brown, then to dark yellow, and finally to pale yellow, similar to the observations in hydrosilylation reactions.^{15*a*} The color change can be attributed to the reduction of Mn(v) to lower oxidation states such as Mn(m) and Mn(n),¹⁸ and appears to be correlated with the progress of the reaction. The observation that the reactions upon second

Table 3 MnN-catalyzed dehydrogenative coupling of diols with silanes^a

Entry	Silane	Diol: silane	Product(s)	<i>t</i> (h)	$\operatorname{Conv.}^{b}(\%)$
1	(EtO) ₃ SiH	1:2		3	90 (56)
2	Ph ₂ SiH ₂	1:1.2	SiPh ₂	3.5	70 (65)
3	Ph_2SiH_2	1:1	Si <ph Ph</ph 	5.5	95
4	PhMeSiH ₂	1:1	Si<	5	98

^{*a*} Substrate (0.7–0.8 mmol), silane and MnN catalyst (0.5 mol%) at 80 °C. ^{*b*} Determined by ¹H NMR on the basis of consumption of diols and/ or silane; isolated yields in parenthesis.



and third additions of the reactants took place even faster, as discussed earlier (see Fig. 4), is in agreement with the

hypothesis that Mn(v) is not the actual active species and it needs to be reduced first to act as the active catalyst. Conversely, when there was no reaction between the hydroxyl groups and tertiary hydrosilanes such as PhMe₂SiH, Et₃SiH and ^tBuMe₂SiH, the reaction mixture retained the same green color. In these cases, the less active tertiary hydrosilanes were not able to reduce manganese(v), and as a result, catalytic dehydrogenative coupling did not occur. Hence, we believe that the activation of manganese by reduction is a crucial step for the reactivity.

Conclusion

In conclusion, we have reported a Mn–salen complex for the effective synthesis of silyl ethers and silyl esters *via* dehydrogenative coupling of alcohols, phenols and carboxylic acids with hydrosilanes. The coupling reaction is compatible with a variety of functional groups, and seems to involve a reduced Mn active species. Our future studies will be focusing on the mechanistic understanding of the current dehydrogenative coupling reactions and further extension of the methodology to other applications.

Table 4 MnN-catalyzed dehydrogenative coupling of carboxylic acids with (EtO)₃SiH^a

Entry	Substrate	Acid : silane	Solvent	Products	<i>t</i> (h)	Conversion ^{b} (%)
1	ОН	1:1	CDCl ₃		32	73
2	Ph OH	1:1.3	$CDCl_3$	Ph O-Si(OEt) ₃	29	77
3	ОН	1:1	C_6D_6	O-Si(OEt) ₃	28	52

^{*a*} Reaction conditions: substrate (0.4–0.6 mmol), (EtO)₃SiH and 1 (1 mol%); 80 °C. ^{*b*} Determined by ¹H NMR on the basis of consumption of acids and/or silane. Repeated attempts at isolation of silyl esters by column chromatography on silica led to decomposition, and isolated yields were not obtained.

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