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Activation of silanes by Grubbs' carbene complex $Cl_2(PCy_3)_2Ru{=}CHPh$: dehydrogenative condensation of alcohols and hydrosilylation of carbonyls

Sarah V. Maifeld, Reagan L. Miller and Daesung Lee*

Department of Chemistry, University of Wisconsin, Madison, WI 53706, USA

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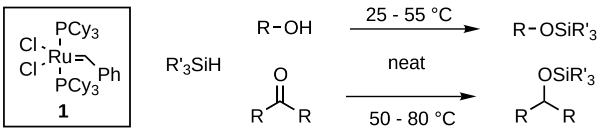
Abstract—This manuscript describes two catalytic methods for silyl ether synthesis using Grubbs' catalyst $Cl_2(PCy_3)_2Ru{=}CHPh$. Silyl ethers are obtained from the reaction of a variety of silanes with alcohols by dehydrogenative condensation and by the hydrosilylation of carbonyl compounds. Both reactions occur under neat conditions. © 2002 Elsevier Science Ltd. All rights reserved.

In recent years, olefin metathesis chemistry has emerged as a powerful synthetic tool. The tremendous growth in this area can primarily be attributed to the development of new catalysts such as Grubbs' ruthenium–carbene complex $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**) and its congeners.[1] This catalyst has demonstrated remarkable efficiency promoting ring opening, ring closing as well as cross metathesis reactions while displaying tolerance toward a wide variety of common functional groups. Furthermore, a growing number of newly discovered catalytic processes mediated by this complex broaden its synthetic utility beyond olefin metathesis.

Complex **1** has been shown to catalyze the Kharasch addition of chloroform across alkenes[2] as well as the removal of allyl groups from amines.[3] Noels and co-workers demonstrated that **1** promotes the atom transfer radical polymerization (ATRP) of methyl methacrylate,[4] while Grubbs et al. built a difunctional catalyst retaining ATRP activity and used it for the synthesis of diblock copolymers.[5] Complex **1** has been also shown to act as an effective pre-catalyst for hydrogenation of olefins, transfer hydrogenation of ketones, and dehydrogenative oxidations of alcohols.[6] Adding to this list of synthetically useful transformations, our studies show a new twofold use of complex **1** to activate a variety of silanes in the presence of alcohols or carbonyl compounds, yielding the corresponding silyl ethers (Scheme 1).

Silyl ethers comprise one of the most widely used classes of protecting groups in synthetic chemistry due to their ease of formation and selective removal in the presence of other protecting groups.[7] In addition, silyl ethers function as temporary tethers in organic synthesis, adapting many intermolecular reactions as more favorable intramolecular processes.[8] Although the conventional silylation procedure is straightforward and dependable, its reliance on environmentally undesirable solvents such as CH_2Cl_2 and DMF as well as excess amine bases makes the synthesis of silyl ethers an excellent target for greener methodology.

In our effort to develop a convenient and environmentally benign route to silyl ethers, we investigated the activation of silicon–hydrogen bonds by a variety of transition metal complexes.[9,10] Our initial efforts found that ruthenium–carbene complex **1** is an effective catalyst for the condensation of alcohols and silanes, showing no indication of competing olefin metathesis even with a terminal alkene (Table 1). In the presence of 0.5 mol% of **1**, these reactions efficiently give complete conversion of the substrate alcohols to the corresponding silyl ethers in nearly quantitative yield.[11] Generally, dialkyl aryl (Me_2PhSiH) and alkyl diaryl (Ph_2MeSiH) silanes react more efficiently than either trialkyl (Et_3SiH, *tert*-$BuMe_2SiH$) or trialkoxy silanes



Scheme 1.

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* Corresponding author. Tel.: (608) 265-8431; fax: (608) 265-4534; e-mail: dlee@chem.wisc.edu

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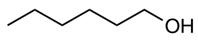
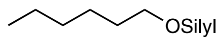
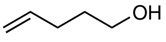
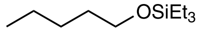
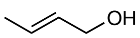
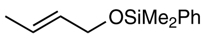
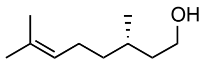
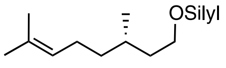
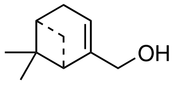
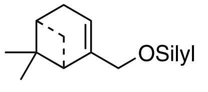
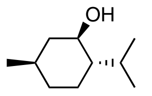
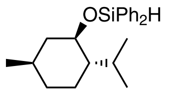
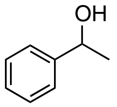
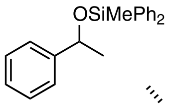
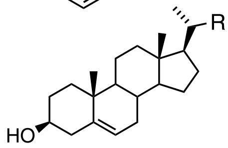
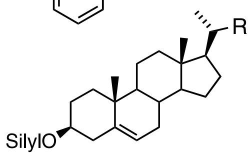
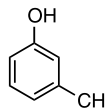
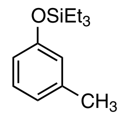
Table 1. Dehydrogenative condensation of alcohols and silanes catalyzed by **1**[a]

entry	alcohol	silane	temp (°C) / h	silyl ether	yield (%)[b]
1		Me_2PhSiH	25 / 0.25	 (Silyl = $SiMe_2Ph$)	>95
2		t-$BuMe_2SiH$	45 / 6	Silyl = $SiMe_2t$-Butyl	>95
3		$(EtO)_3SiH$	35 / 5.5	Silyl = $Si(OEt)_3$	>95
4		Et_3SiH	25 / 0.5		75
5		Me_2PhSiH	25 / 2		>95[c]
6		Me_2PhSiH	25 / 2	 (Silyl = $SiMe_2Ph$)	>95
7		t-$BuMe_2SiH$	45 / 8	Silyl = $SiMe_2t$-Butyl	
8		Me_2PhSiH	25 / 1	 (Silyl = $SiMe_2Ph$)	>95
9		Et_3SiH	35 / 2.5	Silyl = $SiEt_3$	>95
10		$(EtO)_3SiH$	35 / 5.5	Silyl = $Si(OEt)_3$	>95[c]
11		Ph_2SiH_2	25 / 0.25		>95
12		Ph_2MeSiH	35 / 3		>95
13	 (R = isohexyl)	Me_2PhSiH	25 / 1	 (Silyl = $SiMe_2Ph$)	>95
14		Et_3SiH	35 / 4	Silyl = $SiEt_3$	>95
15		Et_3SiH	55 / 8		>95

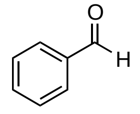
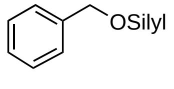
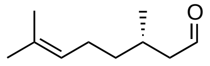
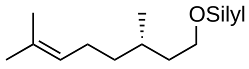
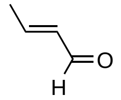
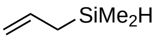
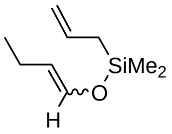
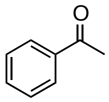
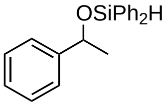
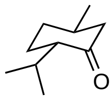
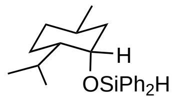
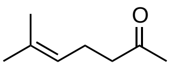
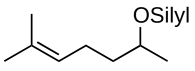
[a] 0.5 mol% **1**, 1 mmol silane, 1 mmol alcohol

[b] Yields were reported on the basis of ^1H NMR of the crude reaction mixture

[c] Partial hydrogenation was observed

($(EtO)_3SiH$). In particular, diphenylsilane (Ph_2SiH_2) reacts vigorously with (1*R*,2*S*,5*R*)-menthol yielding the silyl ether almost immediately at ambient temperature (entry 7). Although trialkyl silanes may react at 25°C (entry 4), most reactions involving trialkyl silanesrequired gentle heating (ca. 55°C) to complete triethylsilyl (TES) or *tert*-butyldimethyl silyl (TBS) ether formation in a reasonable timeframe (entries 2, 7, 9, 14 and 15). Triethoxysilane ($(EtO)_3SiH$) is even less reactive, requiring longer reaction times (entries 3 and 10). A less reactive aromatic alcohol, *m*-cresol, reacted with Et_3SiH to form the TES ether efficiently but also required a higher temperature and a longer reaction time (50°C, 8 h) (entry 15). Solid alcohols, if suitably miscible with silanes, provided the respective silyl ethers without any use of solvent (entry 11); immiscible alcohols required a minimal amount of solvent to partially wet the reaction affording smooth silylation (entries 14 and 15). Since **1** has been shown to effect the hydrogenation of unsaturated systems,[6a] it is not surprising that some olefinic alcohols undergo hydrogenation by **1** with the hydrogen gas generated in situ from the condensation between alcohols and silanes. The terminal double bond of 4-penten-1-ol was hydrogenated com-

Table 2. Hydrosilylation of carbonyl compounds catalyzed by **1**[a]

entry	substrate	silane	temp (°C) / h	silyl ether	yield (%)[b]
1		Me_2PhSiH	50 / 3	 Silyl = $SiMe_2Ph$	>95
2		Et_3SiH	50 / 1	Silyl = $SiEt_3$	>95
3		t-$BuMe_2SiH$	80 / 0.5	Silyl = $SiMe_2t$-Bu	>95
4		Et_3SiH	80 / 1	 Silyl = $SiEt_3$	>85
5		Ph_2MeSiH	80 / 0.5	Silyl = $SiPh_2Me$	>85
6			50 / 0.5		>95
7		Ph_2SiH_2	50 / 2		>95
8		Ph_2SiH_2	50 / 3		>80[c]
9		Et_3SiH	80 / 6	 Silyl = $SiEt_3$	85
10		t-$BuMe_2SiH$	80 / 6	Silyl = $SiMe_2t$-Bu	42

[a] 1.0 mol% **1**, 1 mmol silane, 1.1 mmol carbonyl

[b] Yields were reported on the basis of ^1H NMR of the crude reaction mixture

[c] 3:1 mixture of axial and equatorial silyl ethers

pletely (entry 4) while a *trans*-disubstituted alkene showed less than 50% hydrogenation (entry 5). The extent of hydrogenation of tri-substituted alkenes depends on reaction temperature and silane structure. No loss of unsaturation was detected when β-(*S*)-citronellol was reacted at 25°C with Me_2PhSiH (entry 6); however, at 45°C with less reactive *tert*-$BuMe_2SiH$, partial hydrogenation was observed (entry 7). Similarly, at 35°C, the cyclic tri-substituted double bond in (*R*)-myrtenol was completely retained in reactions with Et_3SiH but underwent slight hydrogenation (5–10%) with $(EtO)_3SiH$ (entries 9 and 10).

After demonstrating the generality of **1** as a catalyst for dehydrogenative condensation between alcohols and silanes, we sought to extend **1**'s utility by investigating its potential as a catalyst for the hydrosilylation of aldehydes and ketones.[12] In most cases, we found that 1 mol% of **1** promoted the hydrosilylation of aldehydes and ketones with a variety of silanes in good yields (Table 2).

In contrast to dehydrogenative condensation between alcohols and silanes, hydrosilylation reactions mediated by **1** required higher temperatures (>50°C), which generated a slightly increased amount of silyl byproduct. This impurity could be avoided by employing a substoichiometric amount of silane.

In general, silanes in both hydrosilylation and dehydrogenative condensation reactions showed similar reactivity profiles. Diphenylsilane, an extremely reactive silane in previous dehydrogenative condensation reactions, underwent hydrosilylation at 50°C with ketones (entry 7, 8) while the hydrosilylation of ketones by trialkylsilanes was sluggish even at elevated temperatures and in the presence of excess silane (entry 9, 10). Reaction between an α,β-unsaturated aldehyde such as crotonaldehyde with allyldimethylsilane yielded a 1.4:1 mixture of *trans* and *cis* silyl enol ethers, respectively; higher reaction temperatures gave rise to the allylic silyl ether resulting from 1,2-hydrosilylation of the carbonyl.

In summary, we have demonstrated that Grubbs' ruthenium carbene complex **1** activates a variety of silanes affording silyl ethers from dehydrogenative condensation with alcohols and hydrosilylation of carbonyls. Current studies in our laboratory are aimed toward developing this newly discovered reactivity for further application.

Acknowledgements

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11. In some cases, a small amount of silyl byproduct was produced presumably from the dehydrocondensation of two silanes or the formation of siloxanes. However, for most cases, filtering the reaction through a short plug of silica to remove catalyst provides pure silyl ethers.
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