Notes

Silation of Alcohols and Aldehydes Catalyzed by Bisacetylacetonatochlorocyclopentadienylzirconium(IV)

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Silation reactions catalyzed by homogeneous transition metal complexes have been known to be useful for the preparation of various silyl compounds.[1] Most of the reactions are catalyzed by late transition metal complexes and little attention has been paid to early transition metal catalysts. Catalytic activities of titanocene and zirconocene derivatives for the dehydrogenative coupling of organosilanes have been described (eq. 1).[2,3]

$$nRSiH_3 \xrightarrow[(M=Ti,\ Zr)]{Cp_2MMe_2} H\!-\!\left(\!\begin{array}{c}R\\ |\\ Si\\ |\\ H\end{array}\!\right)_{\!n}\!-\!H \quad + \quad (n\text{-}1)\ H_2 \qquad (1)$$

Recently catalytic activations of the organosilanes by group 4 metallocene derivatives have been utilized for the olefin hydrosilations.[4] *O*-silations of alcohols and aldehydes are important reactions for the synthesis of silyl ethers.[5] However, only a few complexes have been used as the homogeneous catalysts for *O*-silations of alcohols and aldehydes and most of the homogeneous catalysts known to date are late transition metal complexes.[6]

In this paper we wish to report the *O*-silation reaction of aldehydes and alcohols with phenylsilane catalyzed by a mixture of *n*BuLi and [CpZr(acac)$_2$Cl] (**1**) under the mild conditions. Compound **1** can be prepared from the reaction of [Cp$_2$ZrCl$_2$] and 2*n*BuLi with 2,4-pentanedione,[7] or from [Cp$_2$ZrCl$_2$] and 2,4-pentanedione in the presence of NEt$_3$.[8] The former method gives the higher yield of **1** than the latter. When a catalytic amount of **1** and 1 equiv of *n*BuLi were added to a mixture of 1-propanol and phenylsilane (**2**) in THF, initially yellow solution turned orange with evolution of H_2 gas. Tri(propoxy)phenylsilane was isolated from the reaction mixture after flash chromatography and characterized spectroscopically.[9] In a typical procedure, a mixture of **2** (21.9 mmol) and alcohol (16.1 mmol) was added to a THF solution of **1** (0.2 mmol) and *n*BuLi (0.2 mmol) at -78 °C and stirred for 48 hrs at room temperature. The resulting mixture was subjected to the GC/MS after removing the metal moieties by passing through Florisil. All manipulations were carried out under nitrogen atmosphere using either standard inert-atmosphere techniques or nitrogen filled glove box. The solvent, phenylsilane and alcohols were saturated with nitrogen gas before use. The results of the *O*-silation reaction of the alcohols catalyzed by **1** and *n*BuLi are summarized in Table 1. The alcoholysis of phenylsilane by **1** and *n*BuLi produced trialkoxyphenylsilane with the yield of 79-92%. We have identified the formation of [Ph$_2$Si(OCH$_2$CH$_3$)H] in case of ethanol. In case of 1-butanol, 14% of bis(butoxy)phenylsilane and 7% of butoxyphenylsilane were formed in addition to the tris(butoxy)-phenylsilane.

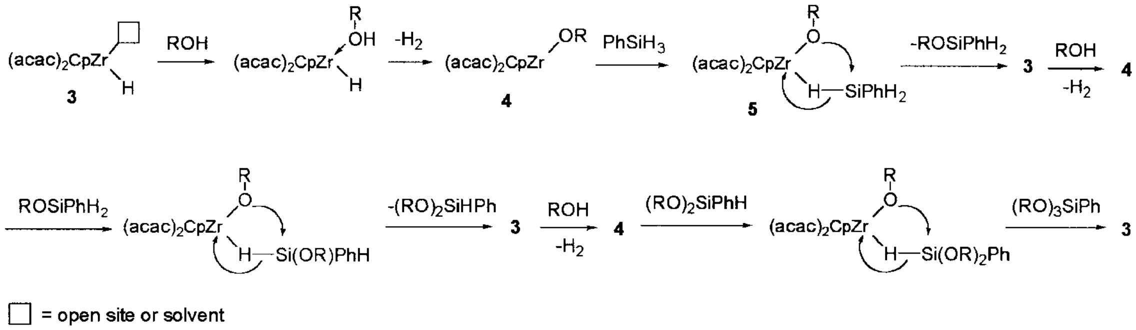
Table 1. *O*-silation products of alcohols with phenylsilane catalyzed by [Cp(acac)$_2$ZrCl] and *n*BuLi

Alcohols	Products	GC yield (%)[a]
Ethanol	PhSi(OCH$_2$CH$_3$)$_3$	85
	Ph$_2$Si(OCH$_2$CH$_3$)H	9
1-Propanol	PhSi(OCH$_2$CH$_2$CH$_3$)$_3$	92
1-Butanol	PhSi(OCH$_2$CH$_2$CH$_2$CH$_3$)$_3$	79
	PhSi(OCH$_2$CH$_2$CH$_2$CH$_3$)$_2$H	14
	PhSi(OCH$_2$CH$_2$CH$_2$CH$_3$)H$_2$	7
Allylalcohol	PhSi(OCH$_2$CH=CH$_2$)$_3$	83

[a]Yield calculated by GC based on [alcohol]$_i$

The reaction pathway for the reaction is under speculative. However, it is most probable that the *O*-silation reaction is undergoing through the formation of complex (**3**) as shown in Scheme 1. It has been suggested that the hydridosilylzirconocene formed by the reaction of [Cp$_2$ZrMe$_2$] with **2** is an active species for the catalytic polymerization of **2**, and hydridosilylzirconocene is also active species for the catalytic *O*-silation of alcohol or aldehyde with **2**.[10]

For the present discussion, hydridosilylzircornium complex as a catalytic intermediate was precluded. To have vacant site for the oxidative addition of **2**, metal center had to be reduced from Zr(IV) to Zr(II) and reductively eliminated compound containing cyclopentadieny or acetylacetonate ligand should be formed. However, GC/MS spectra of reaction mixture of **1**, *n*BuLi and 2equiv of **2** did not contain any cyclopentadieny or acetylacetonate moieties. Based on



Scheme 1

the results, hypothesis for the alcololysis of silanes by **1** and *n*BuLi were suggested in Scheme 1. It involves the butylation of **1** by *n*BuLi, followed by β-hydride elimination to form **3**, and the formation of alkoxide with evolution of hydrogen molecules to give **4**. Formation of an intermediate η^2-H-SiPhH$_2$ complex of type **5** then undergoes nucleophilic attack by OR to give ROSiPhH$_2$ and **3**. Further reaction of **4** with ROSiPhH$_2$ or (RO)$_2$SiPhH$_2$ followed by nucleophilic attack by OR gives dialkoxyphenylsilane or trialkoxyphenylsilane, respectively. To explain the alcoholysis of silanes by IrH$_2$L$_2$(MeOH)(HSiR$_3$) (L=PAr$_3$ or PCy$_3$), η^2-H-SiPhH$_2$ complex and nucleophilic attack by alcohol have been postulated.[6] M···H-Si interaction has been proposed in compound of the type IrH$_2$L$_2$(MeOH)(HSiR$_3$) (L=PAr$_3$ or PCy$_3$)[6] and CpMn(CO)LHSiR$_3$ (L=phosphine or CO) and supported by X-ray and neutron diffraction studies[11-13] and theoretical calculation.[14]

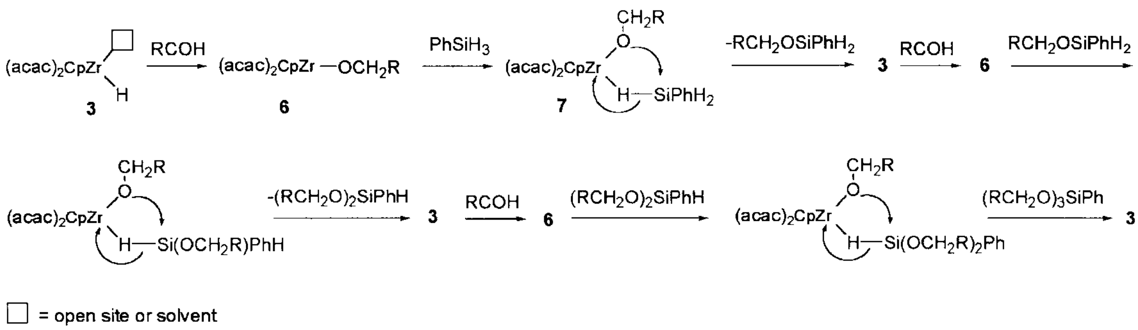
O-silation reaction of aldehydes with phenylsilane catalyzed by the mixture of *n*BuLi and **1** was similarly performed. In a typical procedure, a mixture **2** (21.9 mmol) and aldehyde (16.1 mmol) was added to a THF solution of **1** (0.2 mmol) and *n*BuLi (0.2 mol) at -78 °C and stirred for 48 hr at room temperature. The resulting mixture was subjected to the GC/MS after removing the metal moieties by passing through Florisil. The results of the *O*-silation reaction catalyzed by **1** and *n*BuLi are summarized in Table 2. Alkoxyphenylsilanes were produced with over 70%. In case of crotonaldehyde 9% of bis(butoxy)crotoxyphenylsilane was observed, which could be formed by hydrogenation of double bond in crotoxy groups. In case of benzaldehyde trialkoxyphenylsilane compound was major product in the yield of 92%, and 8% of dialkoxyphenysilane was observed. These results are comparable with the reaction of benzaldehyde in the dimethylzirconocene system.[4c,4d] When a mixture of benzaldehyde and **2** was catalytically activated by dimethylzirconocene, the hydrogenation product of benzaldehyde such as benzyl alcohol was found as a major product instead of *O*-hydrosilation product.[4c]

Table 2. *O*-silation products of aldehydes with phenylsilane catalyzed by [Cp(acac)$_2$ZrCl] and *n*BuLi

Aldehydes	Products	GC yield (%)[a]
Acetaldehyde	PhSi(OCH$_2$CH$_3$)$_3$	87
	PhSi(OCH$_2$CH$_3$)$_2$H	13
Propionaldehyde	PhSi(OCH$_2$CH$_2$CH$_3$)$_3$	58
	Ph$_2$Si$_2$(OCH$_2$CH$_2$CH$_3$)$_4$	35
Butyraldehyde	PhSi(O(CH$_2$)$_3$CH$_3$)$_3$	90
	PhSi(O(CH$_2$)$_3$CH$_3$)H$_2$	10
Isobutyraldehyde	PhSi(OCH$_2$CH(CH$_3$)$_2$)$_2$H	53
	PhSi(OCH$_2$CH(CH$_3$)$_2$)H$_2$	47
Crotonaldehyde	PhSi(OCH$_2$CH=CHCH$_3$)$_3$	61
	PhSi(OCH$_2$CH=CHCH$_3$)(OCH$_2$CH$_2$CH$_2$CH$_3$)$_2$	9
Benzaldehyde	PhSi(OCH$_2$Ph)$_3$	92
	PhSi(OCH$_2$Ph)$_2$H	8

[a]Yield calculated by GC based on [aldehyde]$_i$

A plausible reaction pathway for the hydrosilation of aldehydes is similarly suggested as in the case of the alcoholysis of phenylsilane by **3**, and shown in Scheme 2. It involves the formation of alkoxide complex type of **6**, followed by reaction with **2** to give an intermediate η^2-H-SiPhH$_2$ complex type



Scheme 2

of **7**. Nucleophilic attack by OCH_2R gives $RCH_2OSiPhH_2$ and **3** and further reaction of **6** with $RCH_2OSiPhH_2$ or $(RCH_2O)_2SiPhH_2$ followed by nucleophilic attack by OCH_2R gives dialkoxyphenylsilane or trialkoxyphenylsilane, respectively.

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9. A solution of *n*BuLi (125 μL, 0.2 mmol, 1.6 M) in hexane was added to a solution of **1** (0.078 g, 0.2 mmol) in THF (5 mL) at -78 °C. The mixture was stirred for 10 min, and a solution of phenylsilane (2.70 mL, 21.9 mmol) and 1-propanol (1.20 mL, 16.1 mol) in THF (10 mL) was then added at 0 °C. The resultant mixture was stirred for 24 hr at room temperature. Flash chromatography (5% ethyl acetate in hexane) furnished $(CH_3CH_2CH_2O)_3SiPh$ (1.02 g, 3.61 mmol, 53% yield) as a yellow liquid: IR (neat) 3072 (m), 3051 (m), 2936 (vs), 2876 (vs), 2735 (w), 1593 (w), 1464 (s), 1431 (s), 1391 (s), 1381 (m), 1304 (w), 1261 (m), 1084 (vs), 1016 (vs), 920 (m), 899 (m), 845 (vs), 797 (m), 735 (vs), 700 (vs) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77-7.40 (m, 5H), 3.84 (t, J = 6.6 Hz, 2H), δ 1.68 (m, 2H), δ 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 134.70, δ 131.04, δ 130.11, δ 127.64, δ 64.54, δ 25. 52, δ 10.08; GC/MS spectrum m/z 282 [M]+.
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