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Zirconocene-Catalyzed Silylation of Alkenes with Chlorosilanes**

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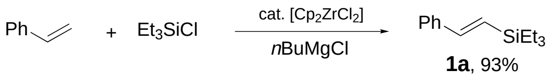
Organosilanes play an important role in organic synthesis as useful intermediates in a number of synthetic transformations.[1] To date, a variety of procedures have been developed for the introduction of silyl functionalities into organic molecules. The most straightforward and practical methodology for C–Si bond formation involves electrophilic trapping of the corresponding organometallic reagents of main group metals with chlorosilanes. An attractive alternative is the transition metal catalyzed silylation of unsaturated compounds,[1, 2] as exemplified by the hydrosilylation of alkenes and alkynes.[2a, 3] The reactions in this category proceed not only with silanes containing one or more hydrogen atoms, but also with various silylating reagents such as disilanes,[2c, d] silacyclobutanes or silacyclopropanes,[4] silyl cyanides,[5] silylgermanes,[6] silylstannanes,[7] silylselenides,[6] and iodosilanes.[8]

Although chlorosilanes are the most readily available silylating reagents, their use in catalytic silylation has not yet been achieved. This is probably due to the difficulty of the oxidative addition of the Si–Cl bonds to transition metal centers.[9] We report herein the first example of the transition metal catalyzed silylation of alkenes with chlorosilanes as well as silylsulfides, silylselenides, and silyltellurides. This reaction proceeds under mild conditions with a catalytic amount of a zirconocene complex[10] in the presence of a Grignard reagent to give alkenylsilanes and/or allylsilanes.

For example, styrene reacted with chlorotriethylsilane in refluxing THF in the presence of nBuMgCl and a catalytic amount of zirconocene dichloride (conditions A) to give the E isomer of alkenylsilane **1a** in 93% yield and with greater than 99% regio- and stereoselectivities [Eq. (1)]. In this reaction, only a trace amount of Et$_3$SinBu (<5%) was formed as a byproduct, probably through the direct reaction of Et$_3$SiCl with nBuMgCl.



1a, 93%

(1)

Table 1 summarizes the results of the silylation of styrene using different reagents and catalysts. When [Cp$_2$TiCl$_2$] was

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Table 1. Silylation of styrene with R_3SiX in the presence of $R'MgX'$ and a catalytic amount of $[Cp_2MCl_2]$.[a]

Entry	R_3SiX	$R'MgX'$	M	Product	Yield [%][b]
1	Et_3SiCl	*n*BuMgCl	Zr	**1a**	93 (84)
2	Et_3SiCl	*n*BuMgCl	Ti	**1a**	21
3	Et_3SiCl	*n*BuMgCl	Hf	**1a**	0[c]
4	Et_3SiCl	*s*BuMgCl	Zr	**1a**	78
5	Et_3SiCl	EtMgBr	Zr	**1a**	57
6	Me_3SiCl	*n*BuMgCl	Zr	**1b**	48
7	Me_3SiSPh	*n*BuMgCl	Zr	**1b**	92 (86)
8	$Me_3SiSePh$	*n*BuMgCl	Zr	**1b**	89
9	$Me_3SiTePh$	*n*BuMgCl	Zr	**1b**	48

[a] Conditions: styrene (1.0 mmol), R_3SiX (2.0 mmol), $R'MgX'$ (1.5 mmol), $[Cp_2MCl_2]$ (0.05 mmol), THF (1.7 mL), reflux, 40 min. [b] Yield according to NMR spectroscopy. The yield of the isolated product is given in parentheses. [c] No reaction.

used instead of $[Cp_2ZrCl_2]$, **1a** was obtained in only 21 % yield (entry 2). Under the same conditions, $[Cp_2HfCl_2]$ was ineffective (entry 3). The use of *s*BuMgCl and EtMgBr in place of *n*BuMgCl afforded **1a** in yields of 78 and 57 %, respectively (entries 4 and 5), but no reaction took place with MeMgCl and *t*BuMgCl. When Me_3SiCl was used as the silylating reagent, (*E*)-2-phenyl-1-(trimethylsilyl)ethylene (**1b**) was obtained in only a moderate yield along with unchanged styrene, probably because of the low boiling point of Me_3SiCl (entry 6). This problem was solved by employing Me_3SiSPh, which afforded **1b** in an excellent yield (entry 7). The reaction also proceeded when $Me_3SiSePh$ and $Me_3SiTePh$ were used as the silylating reagents (entries 8 and 9).

Results from reactions with some other representative alkenes are shown in Table 2. Use of 4-methylstyrene yielded the corresponding alkenylsilane **2** in 91 % yield (entry 1; *p*-Tol = 4-MeC_6H_4). A reaction at 80 °C with ethylene (1 atm at 20 °C in an autoclave, conditions B) gave **3** in 75 % yield based on nPr_3SiCl (entry 2). Interestingly, when *β*-methylstyrene was employed as an internal alkene, allylsilane **4a** was obtained in 22 % yield as the sole product rather than the corresponding alkenylsilane (entry 3). This result can be explained by assuming that in the reaction medium *β*-methylstyrene isomerized to allylbenzene, which then underwent silylation to give **4a**. Indeed, when allylbenzene was employed **4a** was obtained in 46 % yield under the same conditions (entry 4, conditions A). It is noteworthy that under conditions C the reaction proceeded smoothly at room temperature to yield **4a** in 87 % yield (entry 4). A trimethylsilyl group could be introduced efficiently by the use of either Me_3SiCl or Me_3SiSPh (entries 5 and 6). A similar reaction of allyltrimethylsilane with Me_3SiCl afforded 1,3-bis(trimethylsilyl)propene (**5**) in 73 % yield as a 1:1 mixture of stereoisomers (entry 7). Alkenes having a simple alkyl substituent also afforded the corresponding alkenylsilane **6** and **7** in 74 and 70 % yields, respectively (entries 8 and 9), along with byproducts which may involve stereoisomers of the corresponding allylsilanes. The product selectivities—that is, alkenylsilanes versus allylsilanes—can be rationalized by assuming the common intermediate **8**. Alkenylsilanes and/or allylsilanes result from *β*-elimination with abstraction of H^a or H^b with concomitant formation of butane and "Cp_2Zr". This mechanism accounts for the selective formation of allylsilanes **4** from allylbenzene; that is, the *β*-elimination from **8** proceeds exclusively at the benzylic side when R = Ph in favor of conjugated double bond formation by abstraction of H^b. In the cases of 1-butene and 1-octene (R = Me, *n*-C_5H_{11}), H^a was abstracted predominantly, giving rise to **6** and **7**.

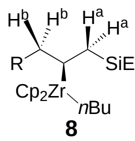

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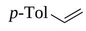
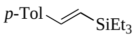
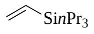
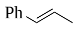
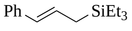
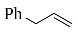
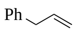
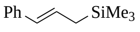
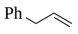
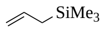
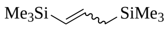
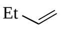
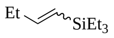
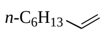
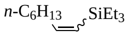
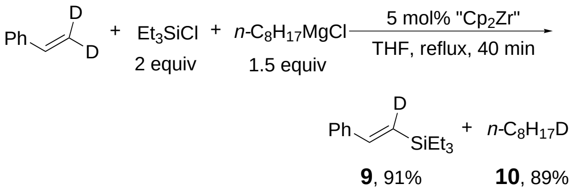
Table 2. Silylation of alkenes with R_3SiX in the presence of *n*BuMgCl and a catalytic amount of $[Cp_2ZrCl_2]$.

Entry	Alkene	R_3SiX	Conditions[a]	*T* [°C]	Product	Yield [%][b]
1		Et_3SiCl	A	66	 **2**	91 (90)
2	$CH_2{=}CH_2$	nPr_3SiCl	B	80	 **3**	75[c]
3		Et_3SiCl	A	66	 **4a**	22[d]
4		Et_3SiCl	A C	66 20	**4a**	46 87 (82)
5		Me_3SiCl	C	20	 **4b**	82 (73)
6		Me_3SiSPh	C	20	**4b**	69
7		Me_3SiCl	C	20	 **5** (*E*:*Z*=52:48)	73 (69)
8		Et_3SiCl	D	20	 **6** (*E*:*Z*=74:26)	74
9		Et_3SiCl	C	20	 **7** (*E*:*Z*=27:73)	70

[a] For details of conditions A – D, see the Experimental Section. [b] Yield according to NMR spectroscopy. The yield of the isolated product is given in parentheses. [c] Based on nPr_3SiCl. [d] Unchanged alkene was recovered (67 %).

To prove the *β*-elimination mechanism the following labeling experiment was performed. The reaction of $PhCH{=}CD_2$ with Et_3SiCl (2 equiv) and *n*-$C_8H_{17}MgCl$ (1.5 equiv) in the presence of "Cp_2Zr" (5 mol %), prepared in situ from $[Cp_2ZrCl_2]$ and *n*BuMgCl (2 equiv),[11] was conducted under reflux for 40 min [Eq. (2)]. Addition of benzaldehyde in order to trap the remaining *n*-$C_8H_{17}MgCl$ followed by quenching with aqueous 0.1 N HCl gave nearly equal amounts of monodeuterated products **9** (deuterium content > 98 %) and **10** (deuterium content > 95 %).[12] This result supports that one of the deuterium atoms of $PhCH{=}CD_2$ was transferred to the terminal carbon atom of the octyl group by *β*-elimination from **11**.



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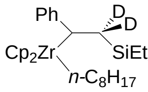

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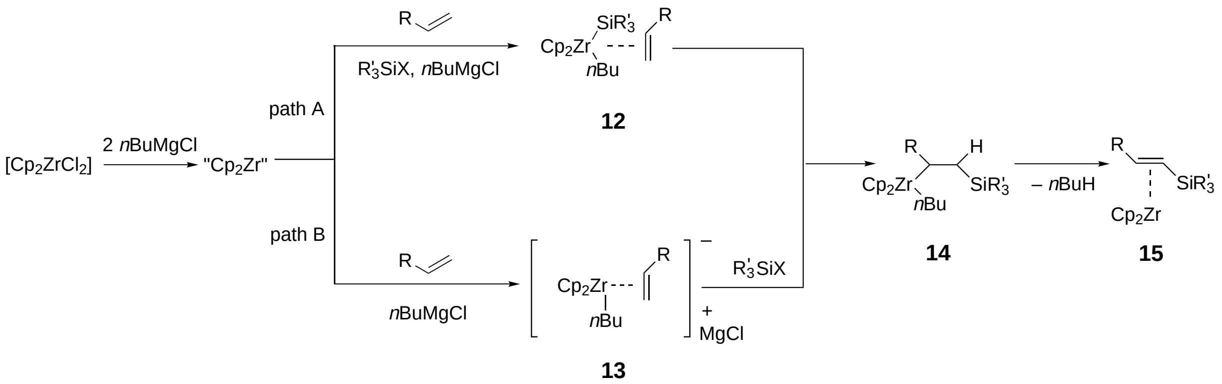

Scheme 1. Plausible pathways for the zirconocene-catalyzed silylation reaction. R = alkyl, aryl, H; R'' = Me, Et, nPr; X = Cl, SPh, SePh, TePh.

We also conducted several control experiments in order to elucidate the reaction pathway leading to dialkylzirconocene intermediates such as **8** or **11**. Since a small amount of the corresponding silane R_3SiH is formed as a by-product (< 5 %) in the present silylation reaction and since it is known that zirconocene complexes catalyze the addition of R_3SiH to alkenes,[13] we first examined whether hydrosilylation is involved. When a reaction similar to that in entry 5 of Table 2 was carried out in the presence of Et_3SiH, only **4b** was obtained as the silylated product in 86 % yield, and unchanged Et_3SiH was recovered. This result rules out the intermediacy of R_3SiH. We then examined the role of Grignard reagents. The reaction of a stoichiometric amount of "Cp_2Zr", generated in situ as described above, with allylbenzene (1 equiv) and Et_3SiCl (1 equiv) failed to give **4a** or saturated silylation product $PhCH_2CH_2CH_2SiEt_3$, even after quenching the resulting mixture with aqeous HCl. However, a similar reaction in the presence of one equivalent of nBuMgCl afforded **4a** in 72 % yield. These results indicate that nBuMgCl does in fact promote the C–Si bond formation.

Although the detailed mechanism of this silylation reaction has not been clarified yet, it is possible that **12** or **13** (Scheme 1) serves as the key intermediate leading to the dialkylzirconocene complex **14**. The former has a Zr–Si bond which undergoes alkene insertion (path A).[14] In path B a zirconate complex **13** directly reacts with chlorosilanes at the olefinic terminal carbon atom to give **14**.[15] The resulting dialkyl complex **14** undergoes β-elimination to afford **15**, which acts as a source of "Cp_2Zr" to complete the catalytic cycle.

In conclusion, a novel silylation reaction of alkenes with chlorosilanes and related silylating reagents has been developed by the use of a zirconocene catalyst. This reaction is promoted by Grignard reagents, giving rise to alkenylsilanes and/or allylsilanes under mild conditions. It is suggested that the product selectivities are determined at the β-elimination step from the dialkylzirconocene intermediates.

Experimental Section

Conditions A: (E)-1-Phenyl-2-(triethylsilyl)ethylene (**1a**): nBuMgCl (0.90 M in THF, 2.30 mL, 2.07 mmol) was added to a mixture of styrene (145 mg, 1.39 mmol), Et_3SiCl (420 mg, 2.79 mmol) and $[Cp_2ZrCl_2]$ (20.0 mg, 0.07 mmol) at 20 °C under nitrogen. After the mixture was heated at reflux for 40 min, aqueous 1 N HCl (2 mL) was added at 0 °C, and the mixture was again warmed to 20 °C. A saturated solution of aqueous NH_4Cl (50 mL) was added, and the product was extracted with diethyl ether (50 mL). The organic phase was dried over $MgSO_4$ and evaporated to give a yellow crude product (93 % yield according to NMR spectroscopy). Purification by column chromatography on silica gel with hexane as the eluent afforded 255 mg (84 %) of **1**.

Conditions B: Ethenyltripropylsilane (**3**): A magnetic stirring bar, nPr$_3$SiCl (257 mg, 1.33 mmol), and $[Cp_2ZrCl_2]$ (15.0 mg, 0.05 mmol) were placed in a 50-mL stainless steel autoclave equipped with a pyrex glass insert. nBuMgCl (0.90 M in THF, 3.00 mL, 2.70 mmol) was added at 20 °C under nitrogen, and the autoclave was purged with ethylene several times and then charged with ethylene (about 2 mmol) at 1 atm and 20 °C. After the mixture was heated at 80 °C for 40 min, the autoclave was opened and aqueous 1 N HCl (3 mL) was added at 0 °C. A workup similar to that for **1a** afforded **3** in 75 % yield (according to NMR spectroscopy) based on nPr$_3$SiCl.

Conditions C: (E)-1-Phenyl-3-(triethylsilyl)-1-propene (**4a**): nBuMgCl (0.90 M in THF, 3.90 mL, 3.51 mmol) was added to a mixture of allylbenzene (137.5 mg, 1.16 mmol), Et_3SiCl (438 mg, 2.91 mmol), and $[Cp_2ZrCl_2]$ (34.0 mg, 0.12 mmol) at 20 °C under nitrogen. Stirring of the solution for 4 h at 20 °C followed by workup similar to that for **1a** gave a yellow crude product (87 % yield according to NMR spcetroscopy). Purification by column chromatography on silica gel with hexane as the eluent afforded 226 mg (82 %) of **4a**.

Conditions D: 1-(Triethylsilyl)-1-butene (**6**): A 50-mL pyrex glass vessel containing a magnetic stirring bar, Et_3SiCl (750 mg, 4.98 mmol), and $[Cp_2ZrCl_2]$ (58.0 mg, 0.20 mmol) was cooled at −78 °C. The gas was then evaculated under reduced pressure, and 1-butene (2.01 mmol, 45 mL, 1 atm and 20 °C) was introduced. Afterwards nBuMgCl (0.9 M in THF, 6.60 mL, 5.94 mmol) was added at the same temperature, the vessel was sealed, and the solution was stirred for 24 h at 20 °C. Workup similar to that for **1a** gave **6** as a pale yellow crude product (E/Z = 74/26) in 74 % yield (according to NMR spectroscopy) based on 1-butene.

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A Robust (10,3)-a Network Containing Chiral Micropores in the Ag^I Coordination Polymer of a Bridging Ligand that Provides Three Bidentate Metal-Binding Sites[**]

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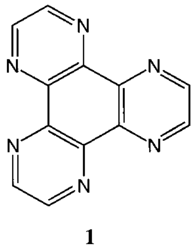
A major goal in the crystal engineering of coordination polymers is the design and synthesis of microporous networks that maintain structural integrity upon exchange or loss of channel guest molecules. One strategy to achieve more robust framework structures that we have been developing is to harness the powerful chelate effect by employing bridging ligands that bind metal centers strongly at chelating sites. The planar ligand 1,4,5,8,9,12-hexaazatriphenylene (hat, **1**) provides a pleasingly symmetrical array of three bidentate sites at which metal centers can realistically be expected to be strongly and predictably bound, each site closely resembling those in the classical chelating agents 2,2′-bipyridine and 1,10-phenanthroline. The ligand hat has already been put to use to bind trios of metal ions in discrete molecular species,[1] but our interest is to generate infinite networks.



1

A particularly appealing aspect of connecting ligands providing two or more bidentate sites is that when a metal center takes on three of them the metal itself adopts the role of three-connecting node. Ligands such as hat, therefore, in combination with appropriate metal centers provide access, in principle, to a range of intriguing and little known three-connected nets whose topologies have been catalogued by Wells.[2]

One feature of hat of potentially great interest and usefulness is its delocalized π-electron system which may provide facile electronic communication between attached metal centers; such communication throughout an extended 3D network could lead to unusual properties. Intense interest has been focussed on the photophysical properties associated with the metal-to-ligand charge transfer chromophores in complexes of 2,2′-bipyridine and related ligands and upon binuclear and oligonuclear mixed-valence complexes of bridging ligands containing pyridine and pyrazine residues,[3] including hat itself.[4] We believe that mixed-valence 3D coordination polymers of planar bridging ligands with delocalized π-electron systems, of which hat is only one example, may provide unique physical properties; the generation of such systems is one of our long-term objectives. The results reported here are part of an initial exploratory study of the

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