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Iridium-Catalyzed Hydrosilylation of Sulfur-Containing Olefins

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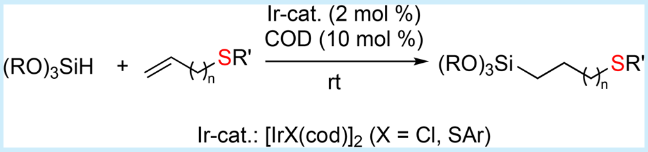
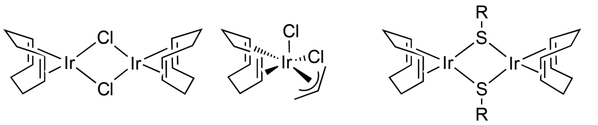
Supporting Information

ABSTRACT: Hydrosilylation of various sulfur-containing olefins with $(RO)_3SiH$ has been achieved using iridium catalysts $[IrX(cod)]_2$ (X = Cl, SPh). The catalysis is applicable to the chemoselective hydrosilylation of thioacetate, which enables the preparation of an industrially important silane coupling agent.



Hydrosilylation of olefins is widely recognized as one of the most important reactions for the production of various organosilicon compounds and materials, such as silicones and silane coupling agents.[1] Platinum catalysts such as Speier's and Karstedt's catalysts have been used in these reactions for more than half a century. However, many problems still remain to be solved, for example, occurrence of side reactions (olefin hydrogenation, olefin isomerization, dehydrogenative coupling, etc.) and deactivation of catalysts by reactive and/or coordinating functional groups of the substrates.[2] On the other hand, organosilicon compounds and materials are nowadays utilized not only as commodity chemicals but also as high-performance materials in a wide range of fields due to their versatile excellent properties. Therefore, there is an increasing demand for the development of new catalyst systems that enable the precise synthesis of highly sophisticated organosilicon materials with a variety of functions. In this regard, limited functional group compatibility of the conventional Pt catalysts is a crucial issue, and continuous studies have been made to overcome the drawbacks. As a result, various catalysts, which exhibit good compatibility toward amino, epoxy, alkoxy, and carbonyl functional groups, have been recently reported.[3−5] On the other hand, examples of selective hydrosilylation of sulfur-containing olefins are still scarce.[6] For example, it is reported that $[H_2PtCl_6]$ and $[RhCl(PPh_3)_3]$ catalyze hydrosilylation of various alkenyl sulfides with a moderate selectivity.[6a] In particular, when using $[RhCl(PPh_3)_3]$, the occurrence of the C−S bond cleavage lead to significant decrease in the product yields. Recently, Vranken et al. reported a hydrosilylation of homoallylic thioethers with $PhMe_2SiH$ catalyzed by $[H_2PtCl_6]$, whereas hydrogenation of the substrates concomitantly proceeded in some cases.[6b] Considering the importance of sulfur-containing organosilicon compounds $(RO)_3Si(CH_2)_3(S)_n(CH_2)_3Si(OR)_3$ (R = Me or Et, n = 2−8) and $(RO)_3Si(CH_2)_3SH$ as useful silane coupling agents in the tire production process,[7] development of new hydrosilylation catalysts that attain direct synthesis of these compounds starting from $(RO)_3SiH$ and sulfur-containing olefins is one of the most challenging topics in the hydrosilylation chemistry.

We thus far developed various hydrosilylation catalysts,[8] some of which exhibit sulfur-functional group tolerance[8a] to give the corresponding hydrosilylation product *albeit* in low yields. In this study, hydrosilylation of various sulfur-containing olefins was successfully achieved using iridium catalysts, $[IrCl(cod)]_2$, **1** (cod = 1,5-cyclooctadiene), $[IrCl_2(\eta^3\text{-}C_3H_5)(cod)]$, **2**, and $[Ir(\mu\text{-}SR)(cod)]_2$ [**3a**, R = Ph; **3b**, R = 4-$Cl(C_6H_4)$; **3c**, R = 4-$MeO(C_6H_4)$; **3d**, R = CH_2CH_2Ph] (Figure 1).



1 **2** **3a**, R = Ph; **3b**, R = 4-Cl(C_6H_4); **3c**, R = 4-MeO(C_6H_4); **3d**, R = Ph(CH_2)$_2$

Figure 1. Iridium catalysts **1**, **2**, and **3a−d**.

Catalytic performance of **1** is summarized in Table 1. Allyl phenyl sulfide **5a** was hydrosilylated with $(MeO)_3SiH$, **4a**, at room temperature in the presence of 2 mol % of **1**, leading to the formation of anti-Markovnikov addition product trimethoxy(3-(phenylthio)propyl)silane **6a** in 85% yield. The yield was slightly improved to 92% when the reaction was performed with additional COD (10 mol %) (Table 1, entry 1). Therefore, hydrosilylation of other olefins was examined under similar reaction conditions. Allyl phenyl sulfide **5a** was also hydrosilylated with $(EtO)_3SiH$, **4b**, and $(EtO)_2MeSiH$ **4c** to give the corresponding hydrosilylated products **6b** and **6c** in 90% and 93% yields, respectively (Table 1, entries 2 and 3). Chemoselective hydrosilylation of allyl thioacetate **5b** was achieved to form the corresponding hydrosilylated product *S*-(3-(trimethoxysilyl)propyl) thioacetate (**6d**, 94%) (Table 1, entry 4). The reaction of allyl methyl sulfide **5c**, homoallyl methyl sulfide **5d**, and methyl pent-4-en-1-yl sulfide **5e** with $(MeO)_3SiH$, **4a**, resulted in the moderate to good product

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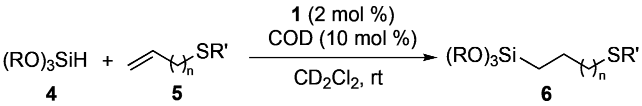
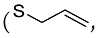
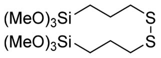
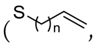
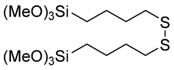
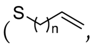
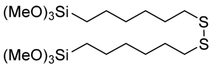
Table 1. Hydrosilylation Reactions of Sulfur-Containing Olefins Catalyzed by 1[a]



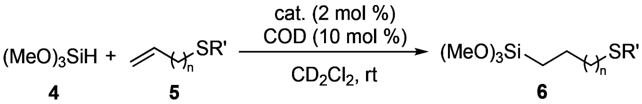
entry	4	5 (R', n)	6 [time, yield (%)[b]]
1	$(MeO)_3SiH$ **4a**	**5a** (Ph, 1)	**6a** [6 h, 92(90)]
2	$(EtO)_3SiH$ **4b**	**5a** (Ph, 1)	**6b** [6 h, 90(87)]
3	$(EtO)_2MeSiH$ **4c**	**5a** (Ph, 1)	**6c** [6 h, 93(89)]
4	**4a**	**5b** (Ac, 1)	**6d** [5 h, 94(90)]
5	**4a**	**5c** (Me, 1)	**6e** [24 h, 42(33)^{c}]
6	**4a**	**5d** (Me, 2)	**6f** [24 h, 70(65)^{d}]
7	**4a**	**5e** (Me, 3)	**6g** [24 h, 77(71)^{e}]
8	**4a**	**5f** (, 1)	 **6h** [6 h, 92(89)]
9	**4a**	**5g** (, 2)	 **6i** [8 h, 94(90)]
10	**4a**	**5h** (, 4)	 **6j** [8 h, 88(85)]

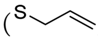
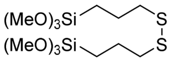
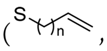
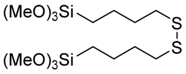
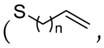
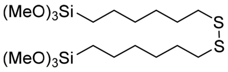
[a]Reaction conditions: **1** (4 μmol), COD (0.02 mmol), silane (0.24 mmol for entries 1–7, 0.48 mmol for entries 8–10), olefin (0.20 mmol) in CD_2Cl_2 (0.5 mL) at rt. [b]NMR yield determined using mesitylene (0.10 mmol) as an internal standard (isolated yield). [c]**5c** (30%) was recovered, and $Me(CH_2)_2SMe$ (18%) was also formed. [d]**5d** (18%) was recovered, and $Me(CH_2)_3SMe$ (10%) was also formed. [e]**5e** (6%) was recovered, and Me(CH2)$_4$SMe (4%) was also formed.

yields, trimethoxy(3-(methylthio)propyl)silane **6e** (42%), trimethoxy(4-(methylthio)butyl)silane **6f** (70%), and trimethoxy(5-(methylthio)pentyl)silane **6g** (77%), respectively (Table 1, entries 5–7). This is probably due to the higher coordination ability of the SMe group compared to SPh and SAc groups. In these reactions, hydrogenation of the starting olefins concomitantly proceeded to give the corresponding hydrogenated products in 18%, 10%, and 4% yields, respectively. Disulfides also underwent hydrosilylation without the occurrence of S–S bond cleavage. Thus, both diallyl disulfide **5f** and dihomoallyl disulfide **5g** smoothly reacted with 2 equiv of $(MeO)_3SiH$, **4a**, at room temperature to form the corresponding bis-hydrosilylated products **6h** and **6i** in good yields (Table 1, entries 8 and 9). In a similar manner, the 1,2-di(hex-5-en-1-yl) disulfide **5h** was also reacted with $(MeO)_3SiH$, **4a**, to afford the product **6j** in excellent yields (Table 1, entry 10).

It was confirmed that conventional Karstedt's catalyst and $[RhCl(PPh_3)_3]$ were not efficient for the hydrosilylation of allyl phenyl sulfide with **4a**, resulting in the recovery of unreacted starting materials with no or 33% of the hydrosilylated product. The reaction was also performed using other iridium catalyst candidates. Either $[Ir(OMe)(cod)]_2$ or $[IrCl(coe)_2]_2$ (coe = cyclooctene) did not exhibit catalytic activity for the hydrosilylation reaction of allyl phenyl sulfide with $(MeO)_3SiH$, **4a**. In contrast, complex **2** exhibited a similar catalytic activity to that of **1**. Thus, the hydrosilylation of allyl phenyl sulfide **5a** with $(MeO)_3SiH$, **4a**, was catalyzed by **2** to form the hydrosilylated product **6a** in 86% yield at the catalyst loading of 4 mol % (Table 2, entry 1). Since **2** is easily converted to **1** on the treatment of $(MeO)_3SiH$, **4a**,[9] hydrosilylation reactions catalyzed either **1** or **2** are likely to proceed following the same reaction mechanism.

Table 2. Hydrosilylation Reactions of Sulfur-Containing Olefins Catalyzed by 2 and 3a–d[a]



entry	cat.	5 (R', n)	6 [time, yield (%)[b]]
1	**2**^{c}	**5a** (Ph, 1)	**6a** [6 h, 86(82)]
2	**3a**	**5a** (Ph, 1)	**6a** [6 h, 91(87)]
3	**3b**	**5a** (Ph, 1)	**6a** [24 h, 66(62)^{d}]
4	**3c**	**5a** (Ph, 1)	**6a** [24 h, 45(41)^{d}]
5	**3d**	**5a** (Ph, 1)	**6a** [24 h, 20(18)^{d}]
6	**3a**	**5b** (Ac, 1)	**6d** [5 h, 92(89)]
7	**3a**	**5c** (Me, 1)	**6e** [24 h, 33(28)^{e}]
8	**3a**	**5d** (Me, 2)	**6f** [24 h, 65(63)^{f}]
9	**3a**	**5f** (, 1)	 **6h** [6 h, 88(85)]
10	**3a**	**5g** (, 2)	 **6i** [8 h, 91(88)]
11	**3a**	**5h** (, 4)	 **6j** [8 h, 91(87)]

[a]Reaction conditions: cat. (4 μmol), COD (0.02 mmol), olefin (0.20 mmol), $(MeO)_3SiH$ (0.24 mmol for entries 1–8, 0.48 mmol for entries 9–11) in CD_2Cl_2 (0.5 mL) at rt. [b]NMR yield determined using mesitylene (0.10 mmol) as an internal standard (isolated yield). [c]4 mol % of **2** (8 μmol) was used. [d]Starting materials were recovered. [e]**5c** (31%) was recovered, and $Me(CH_2)_2SMe$ (30%) was also formed. [f]**5d** (21%) was recovered, and $Me(CH_2)_3SMe$ (11%) was also formed.

Sulfide-bridged dinuclear iridium complex **3a** also showed catalytic activity similar to those of **1** and **2** for the hydrosilylation of allyl phenyl sulfide **5a** with $(MeO)_3SiH$, **4a**, giving the hydrosilylated product **6a** in 91% yield (Table 2, entry 2). To investigate the substituent effect of the bridging sulfide ligand, complexes **3b–d** with different sulfide ligands

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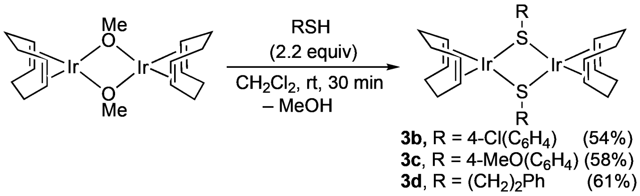
were prepared by a similar procedure for **3a**.[10] Thus, the reaction of $[Ir(OMe)(cod)]_2$ with RSH afforded **3b–d** in good yields (Scheme 1).

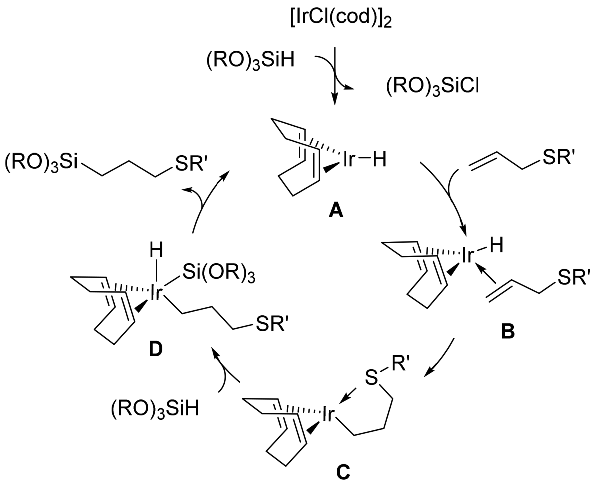
Scheme 1. Preparation of Iridium Complexes 3b–d



Next, hydrosilylation of allyl phenyl sulfide **5a** with $(MeO)_3SiH$, **4a**, was examined in the presence of 2 mol % of **3b–d**. The use of **3b** and **3c**, which have Cl- or MeO-substituted phenyl sulfides, required a longer reaction time than that with **3a** and resulted in the formation of the desired product **6a** in 66% and 45% yields, respectively, after 24 h (Table 2, entries 3 and 4). Complex **3d** bearing phenethyl sulfides exhibited further suppressed activity to produce the product **6a** in 20% yield (Table 2, entry 5). Hydrosilylation reactions of allyl thioacetate **5b** and disulfides **5e–g** were also examined using the most active **3a** (2 mol %) to give the corresponding hydrosilylated products **6d** and **6h–j** in 88–92% yields (Table 2, entries 6, 9–11), whereas hydrosilylation of allyl methyl sulfide **5c** and homoallyl methyl sulfide **5d** resulted in the formation of the desired products **6e** and **6f** in moderate yields (Table 2, entries 7 and 8). These results indicated the comparable catalytic activity of **3a** to that of **1**.

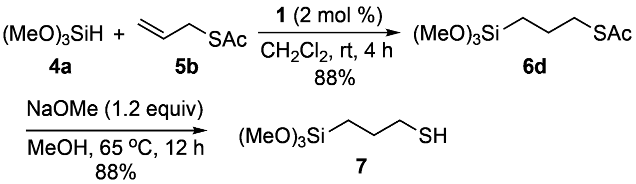
The utility of **1** as a hydrosilylation catalyst is already reported in the alkyne hydrosilylation reactions.[11] DFT studies in the paper supported that the reaction is initiated with the formation of active [Ir(H)(cod)] via reaction of **1** with $(MeO)_3SiH$, **4a**.[12] Considering this report, one possible mechanism is proposed in Scheme 2. Complex **1** initially reacts with $(RO)_3SiH$ to form the hydride species **A** with the formula of [Ir(H)(cod)] and $(RO)_3SiCl$. In the reaction mixture, the coordinatively unsaturated **A** might exist as an adduct with additional coordinated ligands such as solvents, silanes, or other Ir species. Then the coordination of the olefinic part of allyl phenyl sulfide to **A** affords intermediate **B**. The insertion of the double bond into the Ir–H bond and subsequent intramolecular coordination of the S atom to the Ir atom provides intermediate **C**. Oxidative addition of $(RO)_3SiH$ on **C** gives Ir(III) species **D**, from which the reductive elimination of the product regenerate **A**. The mechanistic details (for example, interaction of the Ir atom with the sulfide moiety, etc.) are not clear at this moment, and further detailed mechanistic studies will be performed in due course.

Scheme 2. Plausible Mechanism for the Formation of Hydrosilylated Products



With the effective catalyst **1** in hand, the utility of the system for the synthesis of an industrially important silane coupling agent 3-(trimethoxysilyl)propane-1-thiol (**7**)[13] is demonstrated. Reaction of allyl thioacetate (**5b**, 1.0 g) and $(MeO)_3SiH$ (**4a**, 1.26 g) catalyzed by **1** gave *S*-(3-(trimethoxysilyl)propyl) ethanethioate **6d** in 88% isolated yield, and subsequent hydrolysis of the product with NaOMe (1.2 equiv) in MeOH[14] afforded the desired silane coupling agent 3-(trimethoxysilyl)propane-1-thiol (**7**, 1.31 g, 88% isolated yield) (Scheme 3).

Scheme 3. Preparation of Silane Coupling Agent 7



In summary, hydrosilylation of various sulfur-containing olefins was achieved using iridium catalysts **1–3**. To the best of our knowledge, this is the first example of the efficient hydrosilylation of various sulfur-containing olefins with trialkoxysilanes that are industrially important.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02940.

Experimental procedures and compound characterization data for products (PDF)

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Notes

The authors declare no competing financial interest.

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