Selective synthesis of monohydrosilanes by the reactions of organoytterbium iodides with dihydrosilanes

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Monohydrosilanes can be prepared selectively in high yields from the reaction of various aryl and alkyl iodides with ytterbium metal followed by the reaction with dihydrosilanes.

Recently, lanthanoid complexes with the pentamethylcyclopentadienyl ligand and its analogues have been reported to catalyze the hydrosilylation reactions of alkenes and alkynes, as well as cyclization/silylation and polymerization of silanes.[1,2] Marks and coworkers and others reported that the reactions of $Cp*_2LnCH(SiMe_3)_2$ ($Cp* = C_5Me_5$, Ln = La, Nd, Sm) with $PhSiH_3$ gave $CH_2(SiMe_3)_2$, while $Cp*_2YMe(THF)$ converted $PhSiH_3$ to $PhMeSiH_2$.[2] However, applications of lanthanoid complexes to direct alkylation or arylation of silanes are still limited. Evans *et al.* reported the synthesis of divalent organolanthanoid σ-complexes (RLnI) from organic iodides and lanthanoid metals in THF.[3] We have explored the chemistry of RLnI and found some unique reactivity toward various electrophiles.[4] In our continuing study on the organolanthanoid chemistry, we have found that the monohydrosilanes can be prepared selectively from the reaction of excess divalent organoytterbium σ-complexes (RYbI) with dihydrosilanes [eqn. (1)]. Here, we report these results.

$$RI + Yb \xrightarrow{THF} RYbI \xrightarrow{R'R''SiH_2} R'R''RSiH \quad (1)$$
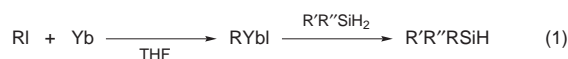
First, we studied the reaction of various arylytterbium σ-complexes (ArYbI) with dihydrosilanes [eqn. (2)] and results are summarized in Table 1.

As shown in entry 1 in Table 1, when the reaction was carried out using an equimolar amount of iodobenzene **1a**, Yb metal and $MePhSiH_2$ **2a**, the monosilane **3a** was formed only in 64% yield. However, when the ratio of **1a** and Yb to **2a** was doubled, **3a** was obtained quantitatively (entry 2). Most of the substrates **1a**–**g** and **1i**–**m** (entries 2–15 and 17–26) reacted smoothly with ytterbium metal to produce arylytterbium iodides, and successive treatment with dihydrosilanes gave selectively monohydrosilanes **3a**–**g**, **3a'**–**g'** and **3i**–**m'** in high yields. For *o*-chloroiodobenzene **1h** (entry 16), many by-products were formed, and the isolation of the desired product **3h** was unsuccessful. Under the present conditions, arylytterbium iodides displayed high reactivity toward not only methylphenylsilane but also diphenylsilane. In addition, dimers of silanes were not formed in this reaction.[5]

On the other hand, different results were obtained in the reaction of aliphatic iodides [eqn. (3)] as shown in Table 2. Primary alkyl iodides such as 1-iodoethane, 1-iodoheptane and isobutyl iodides (**1n**–**p**) proceeded smoothly to afford monohydrosilanes **3n**–**p** in high yields (entries 15–17). By contrast, for bulky **1q**, the yield of **3q** was low (entry 4). In the reactions of secondary and tertiary iodides **1r**–**t**, the reaction proceeded slowly to give small amounts of the monosilanes **3r**–**t**. These results indicate that steric factors of the substrates plays an important role in the reaction. It seems curious that no reaction occurs with α-methoxy-substituted **1u** although Yb metal reacts with **1u** to form $(MeOCH_2)YbI$ (entry 8).

In similar reactions of Grignard reagents and organolithiums, the former give monosubstituted silanes in low yields even

Table 1 Reaction of arylytterbium(II) iodides with dihydrolsilane **2a** and **2a'**[a]

$$\text{ArI} + \text{Yb} \xrightarrow[\text{THF}]{} \xrightarrow[\substack{\text{RPhSiH}_2 \\ \textbf{2a}: R = Me \\ \textbf{2a'}: R = Ph \\ \text{room temp.}}]{} \text{ArRPhSiH} \quad (2)$$

1   **3**

Entry	Substrate	Ar	Dihydrosilane	t/h	Product	Yield(%)[b]
1	**1a**	Ph	**2a**	8	**3a**	64[c]
2		Ph	**2a**	2	**3a**	>99
3			**2a'**	1	**3a'**	99
4	**1b**	*o*-MeOC$_6$H$_4$	**2a**	2	**3b**	97
5			**2a'**	8	**3b'**	96
6	**1c**	*m*-MeOC$_6$H$_4$	**2a**	1	**3c**	>99
7			**2a'**	2	**3c'**	95
8	**1d**	*p*-MeOC$_6$H$_4$	**2a**	8	**3d**	93
9			**2a'**	4	**3d'**	78
10	**1e**	*o*-MeC$_6$H$_4$	**2a**	1	**3e**	99
11			**2a'**	2	**3e'**	>99
12	**1f**	*m*-MeC$_6$H$_4$	**2a**	2	**3f**	>99
13			**2a'**	1	**3f'**	>99
14	**1g**	*p*-MeC$_6$H$_4$	**2a**	1	**3g**	>99
15			**2a'**	2	**3g'**	98
16	**1h**	*o*-ClC$_6$H$_4$	**2a**	8	**3h**	—[d]
17	**1i**	*m*-ClC$_6$H$_4$	**2a**	4	**3i**	92
18			**2a'**	8	**3i'**	80
19	**1j**	*p*-ClC$_6$H$_4$	**2a**	2	**3j**	>99
20			**2a'**	4	**3j'**	89
21	**1k**	*o*-CF$_3$C$_6$H$_4$	**2a**	8	**3k**	>99
22			**2a'**	4	**3k'**	>99
23	**1l**	α-Naphthyl	**2a**	2	**3l**	>99
24			**2a'**	1	**3l'**	97
25	**1m**	2-Thienyl	**2a**	4	**3m**	>99
26			**2a'**	4	**3m'**	>99

[a] See footnote † for reaction conditions. [b] GC yield based on **2a** and **2a'**. [c] Yb:RI:$MePhSiH_2$ = 1:1:1 and unreacted $MePhSiH_2$ recovered. [d] Complex mixture obtained.

Table 2 Reaction of alkylytterbium(II) iodides with methylphenylsilane **2a**[a]

$$\text{RI} + \text{Yb} \xrightarrow[\text{THF}]{} \xrightarrow[\substack{\textbf{2a} \\ \text{room temp.}}]{} \text{RPhSiMeH} \quad (3)$$

1   **3**

Entry	Substrate	R	t/h	Product	Yield(%)[b]
1	**1n**	Et	8	**3n**	>99
2	**1o**	*n*-C$_7$H$_{15}$	8	**3o**	89
3	**1p**	Bu^i	8	**3p**	>99
4	**1q**	Bu^{t}CH$_2$	24	**3q**	50
5	**1r**	Pr^i	4	**3r**	10[c]
6	**1s**	*c*C$_6$H$_{11}$	8	**3s**	18
7	**1t**	Bu^t	72	**3t**	Trace
8	**1u**	MeOCH$_2$	72	**3u**	—[d]

[a] See notes as to the other reaction conditions. [b] GC yield based on **2a**. [c] Isolated yield. [d] Methylphenylsilane recovered.

under refluxing conditions,[6] while the latter afford tetra-substituted silanes rather than monosubstituted silanes.[7] By contrast, the present reaction of organoytterbium iodides with dihydrosilanes proceeds smoothly under mild conditions and gives monosubstituted silanes exclusively. Thus this reaction should be a useful method for the synthesis of mono-hydrosilanes.

In conclusion, we have demonstrated that monohydrosilanes can be prepared selectively and conveniently from the reaction of dihydrosilanes with excess divalent organoytterbium σ-complexes under mild conditions.

Notes and references

† *Typical reaction procedure*: Yb metal (173 mg, 1.0 mmol) was placed in a 50 ml Schlenk tube. Then, THF (4.0 ml) and *p*-iodoanisole (234 mg, 1.0 mmol) were successively added at 0 °C under argon and the mixture stirred for 30 min at this temperature to give a red–brown solution of the ArYbI complex. Then, methylphenylsilane (61 mg, 0.5 mmol) was added. The mixture was then heated to room temperature and stirred for 4 h. Usual workup followed by a silica gel column chromatography (*n*-hexane–benzene) gave *p*-anisylmethylphenylsilane **3d** in 79% (90 mg) yield. The GC yields were determined using *n*-tetradecane, *n*-nonadecane and *n*-eicosane for aromatic iodides, 1-iodonaphthalene and aliphatic ioidides, respectively, as an internal standard. Yields are based on dihydrosilanes.

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