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Divalent Ytterbium Complex-Catalyzed Homo- and Cross-Coupling of Primary Arylsilanes

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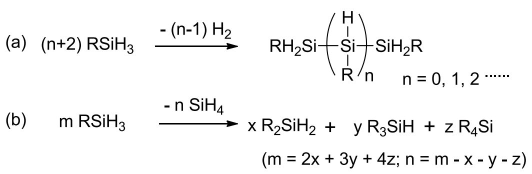
Supporting Information Placeholder

ABSTRACT: Redistribution of primary silanes through C–Si and Si–H bond cleavage and reformation provides a straightforward synthesis of secondary silanes, but the poor selectivity and low efficiency severely hinders the application of this synthetic protocol. Here, we show that a newly synthesized divalent ytterbium alkyl complex exhibits unprecedentedly high catalytic activity towards the selective redistribution of primary arylsilanes to secondary arylsilanes. More significantly, this complex also effectively catalyzes the cross-coupling between electron-withdrawing substituted primary arylsilanes and electron-donating substituted primary arylsilanes to secondary arylsilanes containing two different aryls. DFT calculation indicates that the reaction always involve the exothermic formation of a hypervalent silicon upon facile addition of $PhSiH_3$ to the Yb–E (E = C, H) bond. This hypervalent compound can easily either generate directly the Yb–Ph complex, or indirectly through the formation of Yb–H, that is the key complex for the formation of Ph_2SiH_2.

INTRODUCTION

Hydrosilanes are important reagents in organic and polymer synthesis; the formation and transformation of hydrosilanes are not only of fundamental interests, but are also known to have practical applications.[1] Redistribution of primary silanes provides a straightforward synthesis of secondary silanes.[2] However, the poor selectivity and low efficiency severely hindered the application of this synthetic protocol.[3] Firstly, primary silanes can undergo dehydrocoupling to give oligo- or polysilanes (Scheme 1), where the redistribution is in fact a side reaction.[4] Secondly, the formed secondary silanes may continue the redistribution process to produce tertiary and quaternary silanes.[5] Recently, Hou and coworkers reported that $B(C_6F_5)_3$ catalyzes the redistribution of tertiary silanes, containing electron-rich aromatic substituents, to quaternary silanes but also the cross-coupling of these tertiary silanes with other tertiary (or secondary) silanes to quaternary (or tertiary) silanes with a good selectivity.[6] However, the selective redistribution of primary silanes to secondary silanes as well as the cross-coupling of two different primary silanes to secondary silanes remain unsolved.

Scheme 1. Dehydrocoupling (a) and Redistribution (b) of Primary Silanes

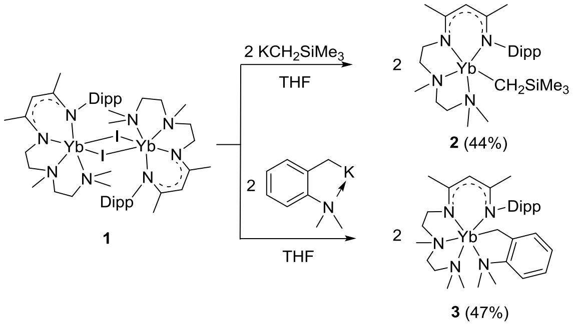


As the largest subgroup of the periodic table, the complexes of rare-earth metals (Ln: Sc, Y, and lanthanides) attract a great attention and important applications as the catalysts for organic and polymer synthesis were found. These complexes are mainly trivalent.[7,8] For the divalent rare-earth metal complexes, they are well known as the reductants in stoichiometric reactions,[9] but their applications in catalysis are very limited.[10] Recently, we have developed a *β*-diketiminato based tetradentate ligand, which stabilizes a series of highly reactive rare-earth metal complexes.[11] To explore further applications of this multidentate ligand, we sought to synthesize divalent ytterbium hydride supported by this ligand. Although there are many rare-earth metal hydrides have been reported,[12] but most of them are the trivalent ones, the divalent ones are very few.[10a,13] During this study, we found that the associated divalent ytterbium alkyl complex can efficiently catalyze the selective redistribution of primary arylsilanes as well as the cross-coupling between electron-withdrawing substituted primary arylsilanes and electron-donating substituted primary arylsilanes.

RESULTS AND DISCUSSION

Divalent ytterbium iodide $[LYb(\mu\text{-}I)]_2$ (**1**, L = $[MeC(NDipp)CHC(Me)NCH_2CH_2N(Me)CH_2CH_2NMe_2]^-$) was synthesized from the reaction of $YbI_2(THF)_2$ with a potassium salt of ligand KL in 66% yield. Treatment of **1** with KCH_2SiMe_3 or $K[CH_2C_6H_4\text{-}o\text{-}NMe_2]$ in THF successfully afforded a divalent ytterbium alkyl or benzyl complex, **2** or **3** (Scheme 2). Complexes **1**-**3** were characterized by NMR spectroscopy (^1H, $^{13}C\{^1H\}$) and elemental analysis, and the structures of **1** and **2** were further confirmed by single-crystal X-ray crystallography. The molecular structure of **2** is shown in Figure 1, while that of **1** is given in the Supporting Information. In complex **2**, the ytterbium ion has a distorted square pyramid coordination environment, with four nitrogen atoms of L forming the basal plane and a carbon atom of alkyl group in the apical position. The Yb–C bond length is 2.499(5) Å, which is similar to that reported in a divalent ytterbium alkyl complex $(Tp^{tBu,Me})YbCH_2SiMe_3$ (2.526(4) Å).[14]

Scheme 2. Synthesis of Divalent Ytterbium Alkyl and Benzyl Complexes



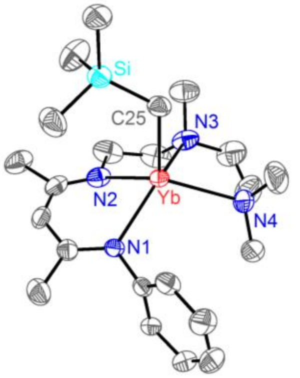
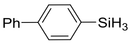
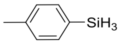
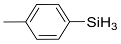
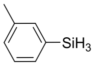
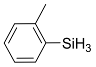
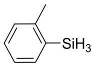
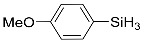
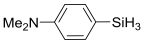
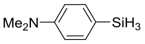
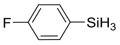
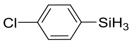
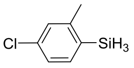


Figure 1. Molecular structure of complex **2** with ellipsoids at 30% probability level (ball and stick representation). Dipp isopropyl groups and hydrogen atoms were omitted for clarity. Selected bond distances [Å]: Yb–C25 2.499(5), Yb–N1 2.403(4), Yb–N2 2.366(5), Yb–N3 2.583(5), Yb–N4 2.571(5).

The ^1H NMR spectral monitoring in C_6D_6 showed that reaction of **2** with 1 equiv. of $PhSiH_3$ rapidly generated $PhSiH_2CH_2SiMe_3$, Ph_2SiH_2, $Ph_2SiHCH_2SiMe_3$, $SiH_3CH_2SiMe_3$, $SiH_2(CH_2SiMe_3)_2$ and some others. A divalent ytterbium hydride was also observed (Yb–*H*: δ 9.26 ppm, $J_{Yb\text{-}H}$ = 394 Hz).[10a,13a] The formation of Ph_2SiH_2, $Ph_2SiHCH_2SiMe_3$, $SiH_3CH_2SiMe_3$ and $SiH_2(CH_2SiMe_3)_2$ clearly indicates a redistribution of $PhSiH_3$. A reaction of **2** with 100 equiv. of $PhSiH_3$ in d_8-toluene in a sealed NMR tube was subsequently carried out, and the reaction at 20 °C was monitored by the ^1H NMR spectroscopy. The plot of the concentrations of $PhSiH_3$ and Ph_2SiH_2 against time is given in Figure S1 of the Supporting Information. The consumption of $PhSiH_3$ and the production of Ph_2SiH_2 are fast during the first 15 min, and then the reaction slows down to reach an equilibrium at about 50 min. The release of SiH_4 (δ = 3.09 ppm, d_8-toluene) was also observed. Considering removal of SiH_4 should influence the equilibrium and promote the conversion of $PhSiH_3$ into Ph_2SiH_2, a reaction of $PhSiH_3$ with 1 mol% of **2** was performed under a N_2 atmosphere and stirred rapidly to facilitate dissipation of SiH_4 gas. In 15 min, 98% of $PhSiH_3$ was consumed and Ph_2SiH_2 was produced in 91% yield, a small amount of Ph_3SiH (4%) was also observed (Table 1, entry 1). Increasing the reaction time to 45 min induces the conversion of Ph_2SiH_2 into Ph_3SiH, decreasing the yield of Ph_2SiH_2 to 71%.

Complex **2** was tested in the redistribution process of other primary silanes (Table 1). By using 1 mol% of **2**, the redistribution of arylsilane with -Ph substituent in *para*-position provides the corresponding diarylsilane in 90% yield at room temperature within 15 min whereas those with -Me or -OMe substituent in *para*-position in 96% and 97% yields within 45 min, respectively. The redistribution of arylsilane with the strong electron-donating NMe_2 group is much slower and provides the diarylsilane in only 34% yield in 45 min at room temperature (the yield can be improved to 61% when the reaction temperature rises to 60 °C). On the other hand, the electron-withdrawing -F or -Cl substituted arylsilanes rapidly undergo the redistribution reaction to give the associated diarylsilanes. Even with 0.5 mol% of **2**, 87% yield can be

Table 1. Redistribution of $RSiH_3$ to R_2SiH_2[a]

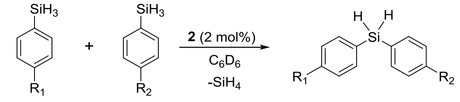
entry	cat.	$RSiH_3$	15 min		45 min	
			conv. (%)[b]	yields (%)[b]	conv. (%)[b]	yields (%)[b]
1	**2**	$PhSiH_3$	98	91	99	71
2	**3**	$PhSiH_3$	97	93	99	75
3	**2**		97	90	99	87
4	**2**		90	87	98	96
5	**2** → **3**		87	86	98	95
6	**2**		90	87	97	93
7	**2**		40	39	67	67
8	**3**		37	37	61	61
9	**2**		90	87	98	97
10	**2**		19	18	37	34
11[c]	**2**		–	–	63	61
12[d]	**2**		70[e]	69[e]	89[f]	87[f]
13[d]	**2**		84[e]	83[e]	94[f]	72[f]
14	**2**		95	92	97	93
15	**2**	$n\text{-}C_6H_{13}SiH_3$	0	0	0	0

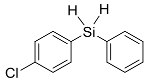
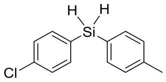
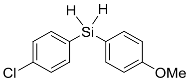
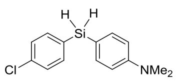
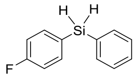
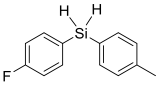
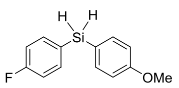
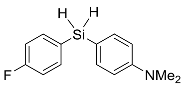
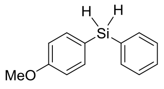
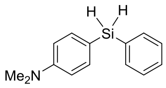
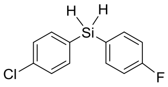
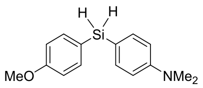
[a] Reactions were conducted open to a N_2 atmosphere with 1 mol% of catalyst in C_6D_6 at r.t., $[RSiH_3]$ = 1.36 mol/L. [b] Determined by ^1H NMR spectroscopy using 1,3,5-trimethylbenzene as the internal standard. [c] Reaction temperature is 50 °C. [d] 0.5 mol% of catalyst. [e] Reaction time was 1 min. [f] Reaction time was 3 min

achieved for the -F substituted substrate in 3 min and 83% yield for the -Cl substituted one in 1 min. The yield of the -Cl containing diarylsilane decreases to 72% in 3 min indicating further redistribution to give the tertiary hydrosilane (p-Cl-C_6H_4)$_3$SiH. The reactivity of these arylsilanes is in the order of Cl > F > H ~ Ph > Me ~ OMe, which is generally in line with the order of their Hammett constants Cl (0.23) > F (0.06) > H (0) ~ Ph (-0.01) > Me (-0.17) > OMe (-0.27).[15] The reactivity of p-NMe_2-phenylsilane is much low. The arylsilane with -Me substituent in *meta*-position also undergoes a quick redistribution reaction to give the product in a high yield, but introducing -Me group at the *ortho*-position decreases the reaction rate (Table 1, entries 6 and 7). For the -Cl substituted substrate, it was also observed that introducing a Me group at the *ortho*-position decreases the reaction rate, and a 92% yield is achieved with 1 mol% of **2** in 15 min (Table 1, entry 14 vs 13). Under similar conditions, alkylsliane such as n-$C_6H_{13}SiH_3$ does not undergo the redistribution reaction. The redistribution of $PhSiH_3$, p-Me-$C_6H_4SiH_3$ or o-Me-$C_6H_4SiH_3$ catalyzed by complex **3** was also studied; the catalytic activity and selectivity of **3** are similar to those of **2** (Table 1, entries 2, 5 and 8).

Compared to the homo-coupling, the cross-coupling of two different primary silanes into secondary silanes is more challenging due to the easy homo-coupling side reactions. Fascinatingly, complex **2** (2 mol%) can efficiently catalyze the cross-coupling of the electron-withdrawing -Cl or -F substituted arylsilane with $PhSiH_3$ or with electron-donating -Me, -OMe or -NMe_2 substituted arylsilane to give the secondary silanes, containing two different aryl groups, in good yields (77%–97% yields) (Table 2). The electron-donating -OMe or -NMe_2 substituted arylsilane reacts with $PhSiH_3$ to give the cross-coupling products in moderate yields (67% and 71% yields). The selectivity for the cross-coupling between the -Cl and -F substituted arylsilanes or the -OMe and -NMe_2 substituted arylsilanes is poor, due to the very similar electronic effects between two reactants. The cross-coupling of p-Cl-$C_6H_4SiH_3$ with $PhSiH_3$ or p-NMe_2-$C_6H_4SiH_3$ catalyzed by **3** was also investigated, which gave the cross-coupling products in 77% and 90% yields in 5 min, respectively, being similar to those catalyzed by **2**. The cross-coupling of p-Cl-$C_6H_4SiH_3$ with p-NMe_2-$C_6H_4SiH_3$ was scaled up to a gram scale with 1 mol% of **2** as the catalyst, and the product p-Cl-$C_6H_4Si(H)_2C_6H_4$-p-NMe_2 was isolated in 89% yield. Since the cross-coupling product has the reactive Si–H bond, it can be easily transferred into other organosilicon compounds. For examples, treatment of p-Cl-$C_6H_4Si(H)_2C_6H_4$-p-NMe_2 with MeLi at room temperature gave p-Cl-$C_6H_4Si(Me)_2C_6H_4$-p-NMe_2 in 99% yield, and that with $LiNMe_2$ at 75 °C provided p-Cl-$C_6H_4Si(NMe_2)_2C_6H_4$-p-NMe_2 in 90% yield (Scheme 3). p-Cl-$C_6H_4Si(H)_2C_6H_4$-p-NMe_2 also reacted with MeOH in the presence of 5 mol% of $KN(SiMe_3)_2$ to produce p-Cl-$C_6H_4Si(OMe)_2C_6H_4$-p-NMe_2 in 98% yield, and with H_2O using 0.3 mol% of $[RhCl(CO)_2]_2$ as a catalyst to afford p-Cl-$C_6H_4Si(OH)_2C_6H_4$-p-NMe_2 in 52% yield.

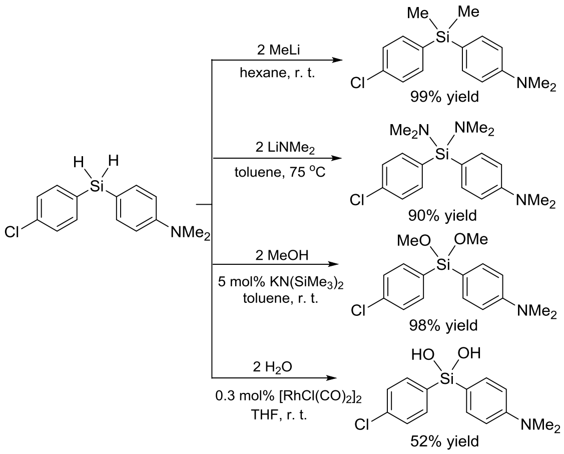
Table 2. Cross-Coupling of Primary Arylsilanes



 78% (5 min)	 97% (5 min)	 86% (5 min)
 88% (5 min)	 77% (5 min)	 91% (5 min)
 84% (5 min)	 87% (5 + 15 min)	 67% (15 + 30 min)
 71% (15 + 30 min)	 ~45% (5 min)	 37% (15 + 30 min)

Reactions were conducted open to a N_2 atmosphere with 2 mol% of catalyst in C_6D_6 for 5 or 15 min at r.t., in some cases the additional 15 or 30 min in the sealed NMR tube were required. The yields of the cross-coupling products were determined by ^1H NMR spectroscopy using 1,3,5-trimethylbenzene as the internal standard.

Scheme 3. Transformation of p-NMe_2-$C_6H_4Si(H)_2C_6H_4$-p-Cl into other Organosilicon Compounds



To study if the redistribution of primary silanes initiated by the divalent ytterbium complex **2** involves trivalent ytterbium catalytic species which may be generated during the reaction, a corresponding trivalent ytterbium alkyl complex $[LYb(CH_2SiMe_3)_2]$ (**4**) was synthesized and applied for the redistribution of $PhSiH_3$. Complex **4** undergoes a quick σ-bond metathesis with $PhSiH_3$, which is evidenced by the ob-

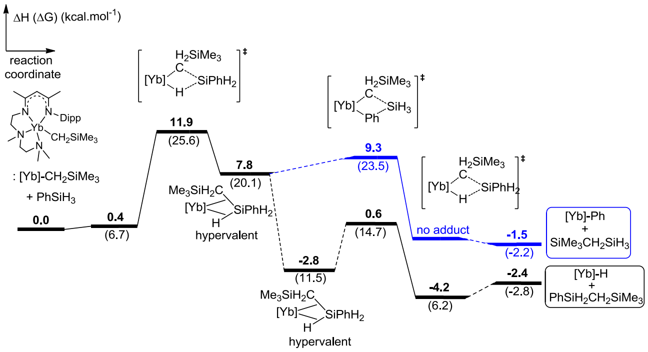


Figure 2. Computed enthalpy profile (Gibbs Free Energy between bracket) for first reaction of **2** with $PhSiH_3$.

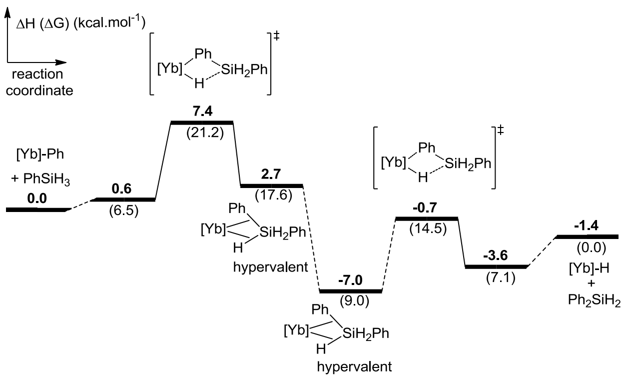


Figure 3. Computed enthalpy profile (Gibbs Free Energy between bracket) for the formation of Ph_2SiH_2 from $PhSiH_3$.

servation of $PhSiH_2CH_2SiMe_3$, but cannot catalyze the redistribution of $PhSiH_3$. DFT calculations were carried out to determine whether the reaction mechanism for the redistribution of $PhSiH_3$ catalyzed by **2** is similar to the one found for Cp^*_2SmH.[16] The first step of the reaction is the addition of the silane to the alkyl, yielding a hypervalent form of silicon with the alkyl and an hydride bonded to the metal (Figure 2). This hypervalent form can either, alike Sm(III), react directly by breaking the Si–Ph bond (and forming $H_3SiCH_2SiMe_3$) or isomerize to a more stable form with two hydrogen interacting with Yb. The latter yields a Yb(II)–H complex (and $PhSiH_2CH_2SiMe_3$). The associated barrier for these two processes are similar within the precision of the method (1.5 and 3.4 kcal/mol) so that there is a kinetic competition and both Yb(II) complexes can be formed. This is in line with the experimental observation that both $H_3SiCH_2SiMe_3$ and $PhSiH_2CH_2SiMe_3$ are readily observed. Interestingly, these barriers are lower than that found for the Sm(III) complex. The Yb(II)–Ph is the key intermediate for the formation of Ph_2SiH_2 (Figure 3). The reaction is again first involving the exothermic formation of an hypervalent silicon that further evolves by breaking a Si–H bond (barrier of 6.3 kcal/mol), yielding the Yb(II)–H complex. Interestingly, Yb(II)–H will preferentially react with $PhSiH_3$ to form another Yb(II)–Ph complex (Figure S95) that can further react as in Figure 3 rather than to form a Yb(II)–SiH_2Ph complex (Figure S96). Calculations using explicit f-electrons do not indicate any metal oxidation or radical reactivity although these two possibilities were reported in the literatures.[4] The extremely low reactivity experimentally observed for the *p*-NMe2-phenylsilane is mainly associated with the formation of a N-bonded silane adduct that disfavors the hypervalent compound formation (favorable by 11.2 kcal/mol, see the ESI)

CONCLUSIONS

In summary, the synthesis of a divalent ytterbium alkyl complex and its application for homo- and cross-metathesis of primary arylsilanes are reported. Reactions of divalent ytterbium iodide **1** with KCH_2SiMe_3 or K[$CH_2C_6H_4$-*o*-NMe_2] provide divalent ytterbium alkyl or benzyl complex, **2** or **3**. The alkyl complex **2** can efficiently catalyze the selective redistribution of primary arylsilanes as well as the cross-coupling between electron-withdrawing substituted primary arylsilanes and electron-donating substituted primary arylsilanes. DFT calculation shows that the easy (kinetically and thermodynamically) formation of both hypervalent silicon compounds and of a Yb–Ph intermediate are the key points that govern the redistribution of silane. This study shows a unique catalytic behaviour of divalent rare-earth metal complex, which may stimulate the research in organo-divalent rare-earth metal chemistry. Furthermore, the produced secondary arylsilanes can be easily transferred into other organosilicon compounds based its Si–H bond transformation, thus the protocol provides an efficient way to various arylsilanes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Experimental and computational details (PDF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interests.
CCDC 1850987 (**1**), CCDC 1850989 (**2**), CCDC 1850991 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac. uk/data request/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223336033.

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SYNOPSIS TOC (Word Style "SN_Synopsis_TOC").