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Reactions of Molybdenum Hydrides with Organochlorosilanes: Silicon–Silicon Bond Formation under Mild Conditions

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Reactions of molybdenum hydrides containing polydentate phosphinoalkylsilyl ligands with a number of chlorosilanes have been investigated; this has led to the discovery of a novel type of a dechlorinative Si–Si coupling reaction.

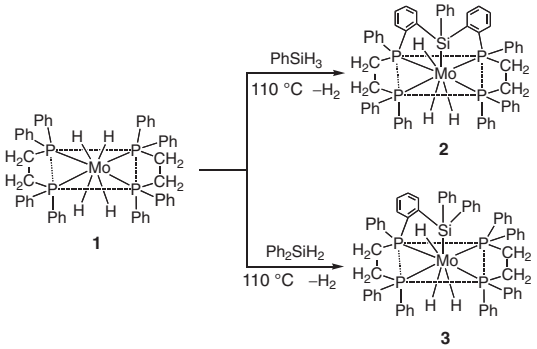
Silicon–silicon bond-forming reactions are of fundamental importance in organosilicon chemistry.[1] Interest continues to be directed toward the development of efficient reactions that provide a practical procedure for the synthesis of polysilanes.[2] The Würtz-type reaction, which involves the dechlorinative coupling of a chlorosilane using Na, represents a convenient route to high-molecular-weight polysilanes.[3] However, the synthetic usefulness of this procedure is somewhat limited because it cannot tolerate a number of functional groups that are sensitive to reduction. Recently, some alternatives to this commonly used reaction have been reported. Examples of such systems include $Mg/ZnCl_2$,[4] Sm/SmI_2,[5] low-valence titanium,[6] pyrophoric lead,[7] and yttrium metal.[7] To our knowledge, however, homogeneously promoted reactions using metal hydrides that are comparable to these heterogeneous systems have not been developed. Here, we report the ability of chlorosilanes to undergo reductive coupling to afford the corresponding disilanes using molybdenum hydrides.

Hydride complex **2** was inadvertently produced during the course of our studies on the thermal reaction of $[MoH_4(dppe)_2]$ (**1**, dppe: $Ph_2PCH_2CH_2PPh_2$) with $PhSiH_3$.[8] This novel transformation, which involves Si–H bond cleavage with concomitant selective activation of the ortho C–H bonds of phenyl groups in the dppe ligands, was shown to proceed via a silylene metal intermediate. The result prompted us to conduct an extensive study of the reactions between **1** and a variety of organosilanes. For example, with Ph_2SiH_2, complex **3** containing a tridentate ligand was additionally formed (Scheme 1).[9]

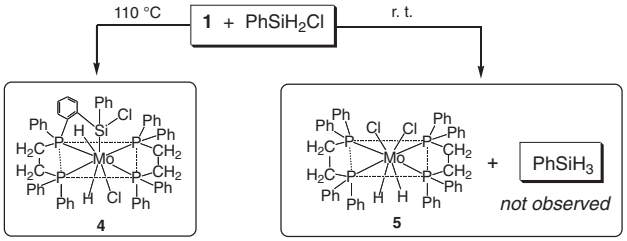
Deviating behavior was observed for $PhSiH_2Cl$, which was found to react with **1** at 110 °C in a manner similar to that described above, resulting in the formation of an analogous chloride **4**.[10] It is interesting that, unlike $PhSiH_3$, the reaction of $PhSiH_2Cl$ with **1** proceeded at room temperature, yielding the known complex, *cis*-$[MoH_2Cl_2(dppe)_2]$ (**5**, Scheme 2).[11]

This reaction might be expected to afford $PhSiH_3$ as a byproduct as simple metathesis of the chloride in $PhSiH_2Cl$ with hydride leads to its formation. Detailed ^{1}H NMR analysis of the crude products revealed several peaks in the Si–H region, indicating that a complex mixture of hydroorganosilanes was obtained. However, no significant amount of $PhSiH_3$ was detected.[12] This unexpected finding prompted us to explore the reactions between **1** and chlorosilanes at room temperature.

In order to unequivocally determine the structure of the organosilyl species resulting from this transformation, we



Scheme 1. Reaction of **1** with organosilanes.



Scheme 2. Reaction of **1** with $PhSiH_2Cl$.

conducted the reaction of **1** with the simpler chlorosilane, Me_3SiCl, at room temperature. Within 1 h, complete conversion to **5** and $Me_3SiSiMe_3$ was found to have occurred, as verified using ^{1}H and ^{29}Si NMR spectra (eq 1).[13]

$$\mathbf{1} + 4\,Me_3SiCl \xrightarrow{\text{r. t.}} 2\,Me_3SiSiMe_3 + \mathbf{5} \quad (1)$$

The yield of $Me_3SiSiMe_3$, as determined via ^{1}H NMR integration with 1,4-dioxane as the internal standard, was found to be >180% (relative to **1**); thus, complex **1** reacted with 4 equiv of Me_3SiCl to afford 2 equiv of the product.

It is interesting to speculate on the reason for the preferential formation of the Si–Si bond instead of the reduction of the Si–Cl bond in Me_3SiCl. The hydridic property of a transition-metal hydride depends on the charge, nature of the spectator ligands, and in particular, location of the metal in the periodic table.[14] The respective Pauling electronegativity values for H and Mo(IV) are 2.20 and 2.24; hence, the facile transfer of H^- from **1** to Me_3SiCl is unlikely to take place.

While the mechanistic details of the present reaction are not completely clear, it likely occurs through a series of intermediates that contain a metal–silicon σ bond. The robustness of a transition metal–silicon bond is well documented.[15] The

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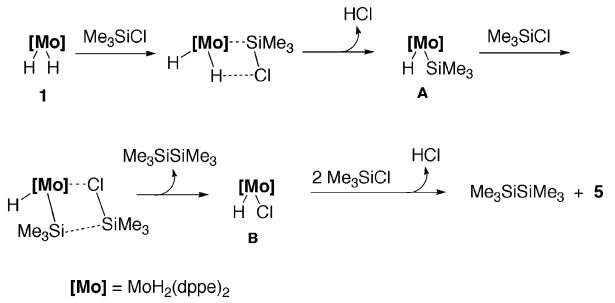

Scheme 3. Mechanistic proposal.

Table 1. Dechlorinative coupling of chlorosilanes

1 + 4 R_3SiCl $\xrightarrow{\text{r. t.}}$ 2 R_3SiSiR_3 + **5**

Entry	R_3SiCl	Time/h	Yield/%
1	Me_3SiCl	1	99[a]
2	$PhMe_2SiCl$	24	75[b]
3	$Ph_2MeSiCl$	72	NR[c]
4	Ph_3SiCl	72	NR[c]

[a]Determined by ^{1}H NMR. [b]Isolated yield. [c]NR: no discernible reaction.

Table 2. Formation of disilanes using **2** or **3**

2 R_3SiCl $\xrightarrow{\textbf{2} \text{ or } \textbf{3}}$ R_3SiSiR_3

Entry	R_3SiCl	Complex	$\tau_{1/2}$/h	Yield/%[a]
1	$PhMe_2SiCl$	**2**	0.4	92[b]
2	$PhMe_2SiCl$	**3**	0.3	96[b]
3	$Ph_2MeSiCl$	**3**	—	48[b]
4	Ph_3SiCl	**3**	—	72[c]

[a]Isolated yield. [b]The resulting disilanes were identified by comparison of their ^{1}H and ^{29}Si NMR spectra with those reported in the literatures for these compounds (see refs 5 and 20). [c]The IR, ^{1}H, and ^{29}Si NMR spectra are consistent with those of a commercial sample (Tokyo Chemical Industry).

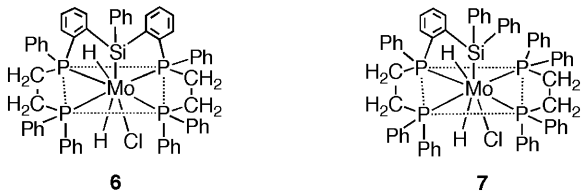

Chart 1. Possible structures of **6** and **7**.

oxidative addition of silyl chlorides to unsaturated transition metal is a typical route for the formation of metal–silicon bonds.[16] However, it is unlikely that such an active intermediate is involved in the present process, as the room temperature reaction of **1** cannot induce the liberation of H_2; therefore, the formation of the 16e intermediate, [$MoH_2(dppe)_2$], would not occur under such conditions. Accordingly, an alternative mechanism in which the Si–Cl bond in Me_3SiCl can be activated without requiring a prelude to H_2 loss from **1** is conceivable.

We assume that the reaction occurs by a σ-bond metathesis mechanism, as has been described for the dehydrocoupling of organosilanes catalyzed by group 4 metallocenes.[17] A likely mechanism for the reaction is outlined in Scheme 3. This pathway goes through a four-center transition state where the oxidation state of the metal does not change. Complex **1** reacts with 1 equiv of Me_3SiCl by the elimination of HCl to yield an intermediate **A**. ^{1}H NMR spectral monitoring of the experimental run containing **1** and Me_3SiCl did not detect any presence of **A**, suggesting that it rapidly reacted with another Me_3SiCl upon its formation. Subsequent σ-bond metathesis reaction of **A** with 1 equiv of Me_3SiCl proceeds via the formation of $Me_3SiSiMe_3$ and monochloride **B**, which further reacts with 2 equiv of Me_3SiCl by similar σ-bond metathesis reactions to yield $Me_3SiSiMe_3$ and **5**.

In order to explore the utility of this dechlorinative coupling, we decided to examine the reactivity of **1** toward several other organochlorosilanes (Table 1).[18]

As indicated above, treatment of **1** with Me_3SiCl at room temperature resulted in the rapid formation of $Me_3SiSiMe_3$. On the other hand, reaction of **1** with $PhMe_2SiCl$ proceeded sluggishly to completion; the half-life of the silane was 9.2 h. Further, $Ph_2MeSiCl$ and Ph_3SiCl were found to be highly unreactive with **1** under the reaction conditions. It is clear that the reactivity of **1** decreased as the alkyl groups became more bulky. This observation is in accordance with the mechanism shown in Scheme 3, as the rate of σ-bond metathesis should be sensitive to the size of the silane.[17]

Next, we proceeded by examining the reactions of the above complexes **2** and **3** with bulky chlorosilanes because they are indeed more reactive than **1** toward a number of substrates because of the strong trans-influencing ability of the silicon-containing fragment.[19] For comparison, the rates of the reaction of $PhMe_2SiCl$ with **2** and **3** were measured; the half-life ($\tau_{1/2}$) of the silane in each run is also presented in Table 2 (Entries 1 and 2).

As expected, reactions of both **2** and **3** with bulky chlorosilanes proceeded readily to form the corresponding disilanes, with **3** reacting 31 times faster than **1**. The products were obtained in moderate yields (48–96%, based on **2** or **3**). The relative reactivity was found to be **3** > **2**, because the reaction rate using **3** was faster than that using **2**.

A puzzling feature of the present system is the observation that unlike **1**, no further reaction ensued when 2 equiv of chlorosilane were consumed. Namely, the reaction stoichiometry indicates that both **2** and **3** react with 2 equiv of chlorosilane to afford 1 equiv of the product. It is possible that the steric constraints in the complexes are so great that the reaction of a third mole of chlorosilane is unfavorable; the P–Si ligands would prevent the approach of the incoming chlorosilane to the vicinity of the metal in **2** and **3** from the same side of the silicon atom.

By analogy of the above reactions between **1** and chlorosilanes, it is conceivable that monochloride complex **6** or **7** was concurrently formed as a by-product (Chart 1). The ^{1}H NMR spectra of the resulting reaction mixtures indeed showed completely new signals in the hydride region, suggesting the formation of novel hydrido chloride complexes.

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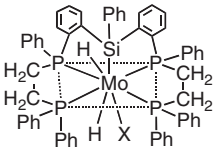
Table 3. Selected spectroscopic NMR data for **6**, **I**, and **II**



X = **Cl** (**6**), **OAc** (**I**), **OH** (**II**)

Compd	^{1}H δ (Mo–H)	^{31}P (J, Hz)
6	−8.06 (tt, J_{PH} = 17, 43 Hz)	56 (d, 122), 88 (d, 122)
I	−7.96 (tt, J_{PH} = 17, 43 Hz)	59 (d, 122), 88 (d, 122)
II	−7.25 (tt, J_{PH} = 16, 46 Hz)	54 (d, 144), 88 (d, 144)

The tentative structure of **6** was estimated by spectral comparison with two structurally related compounds **I** and **II** that had been fully characterized by spectroscopic analyses and X-ray diffraction method.[19] The ^{1}H and ^{31}P NMR data of **6**, as well as those of **I** and **II**, are given in Table 3. Undoubtedly, the spectral data closely resemble each other, in spite of the fact that these compounds incorporate quite different X ligands. These results therefore suggest that **6** is structurally analogous to complexes **I** and **II**, in which the molybdenum is eight-coordinate.

At present, the by-product from the reaction between **3** and a chlorosilane has not been isolated cleanly. Both the ^{1}H and ^{31}P NMR spectra of the reaction solution are significantly more complicated than those of **6**, and the data are insufficient for unequivocally assigning the structure of the product. More detailed studies of the structure are in progress and will be reported in due course.

In summary, the method reported herein represents a novel approach to Si–Si bond formation. Bulky chlorosilanes such as $Ph_2MeSiCl$ and Ph_3SiCl are substantially unreactive with **1**. However, it has been discovered that their reactions with **2** and **3** proceed in a clean manner to afford the coupling products, which is probably because of the strong trans-influence of the Si ligand in these complexes.[21]

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