Si−H and Si−C Bond Cleavage Reactions of Silane and Phenylsilanes with Mo(PMe₃)₆: Silyl, Hypervalent Silyl, Silane, and Disilane Complexes

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ⓈSupporting Information

ABSTRACT: Mo(PMe₃)₆ cleaves the Si−H bonds of SiH₄, PhSiH₃, and Ph₂SiH₂ to afford a variety of novel silyl, hypervalent silyl, silane, and disilane complexes, as respectively illustrated by Mo(PMe₃)₄(SiH₃)₂H₂, Mo-(PMe₃)₄(κ^2-H_2-H₂SiPh₂H)H, Mo(PMe₃)₃(σ-HSiHPh₂)-H₄, and Mo(PMe₃)₃(κ^2-H_2-H₂Si₂Ph₄)H₂. Mo(PMe₃)₄(κ^2-H_2-H₂SiPh₂H)H and Mo(PMe₃)₃(κ^2-H_2-H₂Si₂Ph₄)H₂ are respectively the first examples of complexes that feature a hypervalent κ^2-H_2-H₂SiPh₂H silyl ligand and a chelating disilane ligand, and both compounds convert to the diphenylsilane adduct, Mo(PMe₃)₃(σ-HSiHPh₂)H₄, in the presence of H₂. Mo(PMe₃)₄(SiH₃)₂H₂ undergoes isotope exchange with SiD₄, and NMR spectroscopic analysis of the SiHₓD₄₋ₓ isotopologues released indicates that the reaction does not occur via initial reductive elimination of SiH₄, but rather by a metathesis pathway.

Scheme 1

The interaction of Si−H bonds with transition metal compounds is of fundamental interest,[1] not only because it is a key step in hydrosilylation, dehydrogenative Si−H/O−H coupling, and dehydrogenative polymerization of silanes,[2] but also because it provides a model for the corresponding interactions of C−H bonds with metal centers.[3,4] By comparison to substituted silanes, however, the reactivity of SiH₄ towards transition metal compounds has received relatively little attention.[3,4a,5] Therefore, we report here the first example of the oxidative addition of 2 equiv of SiH₄ to a molybdenum center and also describe the corresponding reactivity of the series of phenylsilanes, PhₓSiH₄₋ₓ (x = 1−4), which affords silyl, hypervalent silyl, silane, and disilane complexes.

Previous studies have shown that zerovalent Mo(PMe₃)₆ is a highly reactive molecule that is subject to oxidative addition reactions with, for example, H−H, C−H, O−H, and C−S bonds.[6,7] Significantly, we now demonstrate that Mo(PMe₃)₆ also cleaves the Si−H bond of SiH₄ at room temperature to give the bis(silyl) compound Mo(PMe₃)₄(SiH₃)₂H₂ (**1**) (Scheme 1). This transformation is of particular note because related zerovalent molybdenum complexes, namely Mo-(R₂PC₂H₄PR₂)₂(CO) (R = Ph, Buⁱ), do not cleave the Si−H bond of SiH₄, but rather coordinate it to form σ-silane adducts, Mo(R₂PC₂H₄PR₂)₂(CO)(σ-SiH₄).[3] Mo(Et₂PC₂H₄PEt₂)₂(CO) reacts similarly to Mo(R₂PC₂H₄PR₂)₂(CO) (R = Ph, Buⁱ), although the silane adduct was shown to exist in equilibrium with the silyl-hydride complex Mo(Et₂PC₂H₄PEt₂)₂(CO)-
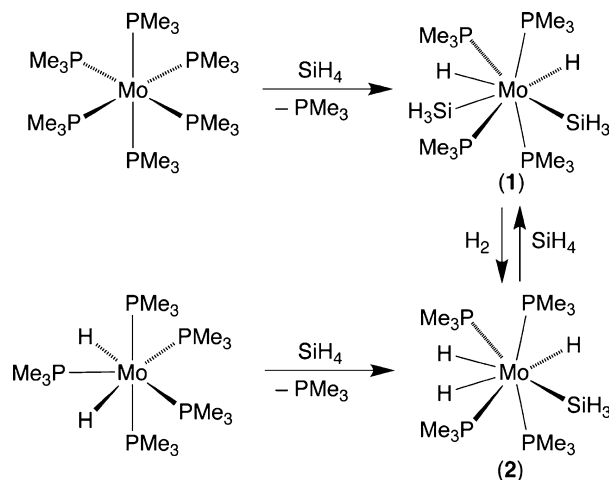
(SiH₃)H.[3] In this regard, evidence that Mo(PMe₃)₄(SiH₃)₂H₂ is a silyl-hydride and not a silane complex is provided by the observation of distinct quintet signals in the ¹H NMR spectrum at δ −4.80 and 4.02 in a 1:3 ratio, of which the former has a value of $^2J_{P-H}$ = 26 Hz and the latter $^3J_{P-H}$ = 8 Hz. In accord with the silyl-hydride assignment, the signal attributable to the SiH₃ groups exhibits coupling to silicon ($^1J_{Si-H}$ = 157 Hz), whereas no coupling is observed (i.e., $^2J_{Si-H}$ < 15 Hz) for the hydride signal.

In addition to the bis(silyl) complex, the mono(silyl) counterpart, Mo(PMe₃)₄(SiH₃)H₃ (**2**), has been obtained by both (*i*) reaction of the dihydride Mo(PMe₃)₅H₂ with SiH₄ and (*ii*) addition of H₂ to Mo(PMe₃)₄(SiH₃)₂H₂ (Scheme 1). The latter reaction is reversible, such that treatment of the mono(silyl) complex with SiH₄ regenerates the bis(silyl) compound, Mo(PMe₃)₄(SiH₃)₂H₂ (Scheme 1).[8] The molecular structures of Mo(PMe₃)₄(SiH₃)H₃ and Mo(PMe₃)₄(SiH₃)₂H₂ have been determined by X-ray diffraction, as illustrated for the latter in Figure 1a.

While a simple mechanism for formation of Mo(PMe₃)₄-(SiH₃)H₃ upon treatment of Mo(PMe₃)₄(SiH₃)₂H₂ with H₂ could involve reductive elimination of SiH₄ followed by oxidative addition of H₂, isotope labeling studies indicate that such a mechanism, which is commonly invoked for non-d⁰
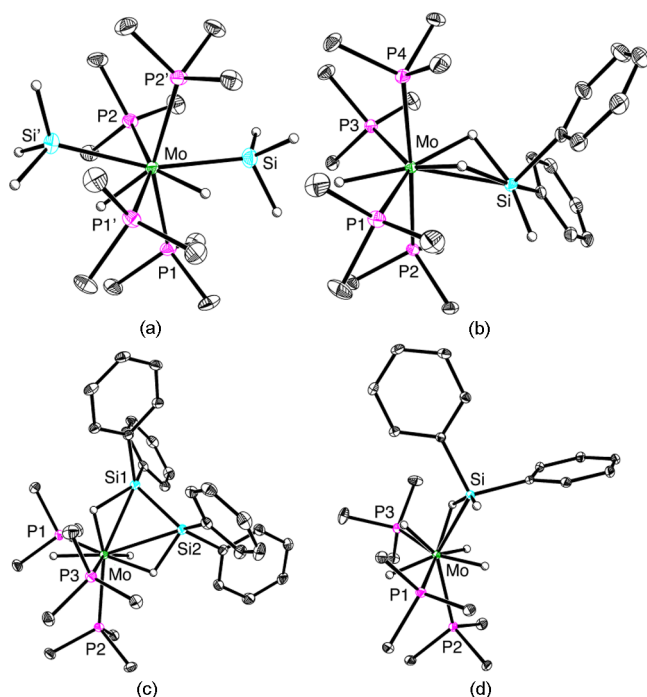
Figure 1. Molecular structures of (a) Mo(PMe₃)₄(SiH₃)₂H₂, (b) Mo(PMe₃)₄(κ^2-H_2-H₂SiPh₂H)H, (c) Mo(PMe₃)₃(κ^2-H_2-H₂Si₂Ph₄)H₂, and (d) Mo(PMe₃)₃(σ-HSiHPh₂)H₄.

metal phosphine hydride compounds, does not operate. For example, treatment of Mo(PMe₃)₄(SiH₃)₂H₂ with D₂ results primarily in the formation of SiH$_x$D$_{4-x}$ rather than SiH₄. Furthermore, treatment of Mo(PMe₃)₄(SiH₃)₂H₂ with SiD₄ demonstrates that H/D exchange involving both the silyl and hydride ligands occurs *without* reductive elimination of SiH₄ (Scheme 2). Specifically, ¹H NMR spectroscopic analysis reveals that SiHD₃, and *not* SiH₄, is the initially formed isotopologue. SiH₂D₂ and SiH₃D are also observed as the exchange reaction progresses, but negligible quantities of SiH₄

Scheme 2
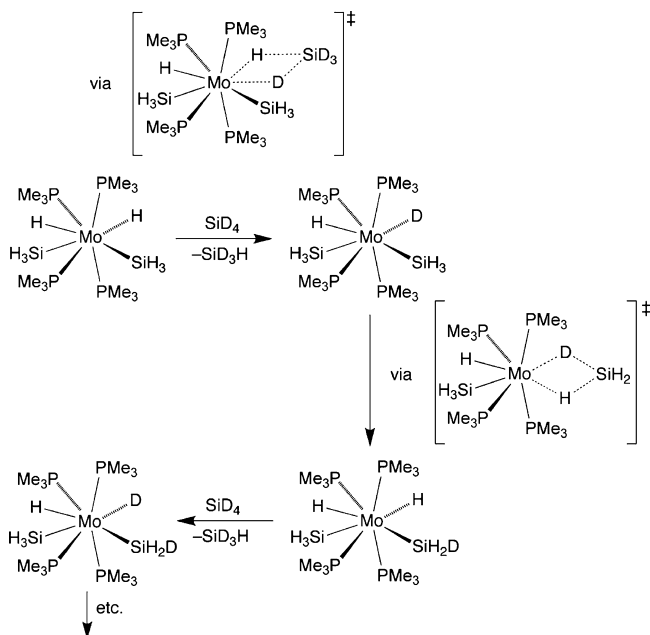
are formed during the course of the experiment. The absence of SiH₄ provides conclusive evidence that Mo(PMe₃)₄(SiH₃)₂H₂ does not undergo reductive elimination of the silyl and hydride ligands, and thus this transformation cannot be the first step in the reaction of Mo(PMe₃)₄(SiH₃)₂H₂ with H₂.[9] A plausible mechanism for the exchange is, therefore, proposed to involve metathesis between the Mo−H and D−SiD₃ bonds (possibly accompanied by reversible dissociation of PMe₃), which would form initially Mo(PMe₃)₄(SiH₃)₂HD and SiHD₃ (Scheme 2).[10] Subsequent incorporation of deuterium into the molybdenum silyl groups can be rationalized on the basis of Mo(PMe₃)₄-(SiH₃)₂HD accessing a fluxional silane adduct, Mo(PMe₃)₄-(SiH₃)(σ-SiH₃D)H, which would allow for scrambling (Scheme 2).[11]

Further evidence that Si−H reductive elimination does not operate is provided by examination of the corresponding exchange reaction between Mo(PMe₃)₄(SiD₃)₂D₂ and SiH₄. Specifically, ¹H NMR spectroscopic analysis reveals the initial formation of Mo−SiHD₂ groups rather than Mo−SiH₃ groups, with the latter being generated as the reaction progresses. Furthermore, the silane isotopologue that is released is primarily SiH₃D, which is consistent with a mechanism that involves metathesis of the Mo−D bond with the H−SiH₃ bond.

Mo(PMe₃)₆ also undergoes facile oxidative addition of Si−H bonds of PhSiH₃ at room temperature to give the bis-(phenylsilyl) compound, Mo(PMe₃)₄(SiH₂Ph)₂H₂ (**3**), which can be isolated if the reaction mixture is immediately cooled to −15 °C (Scheme 3). However, Mo(PMe₃)₄(SiH₂Ph)₂H₂

Scheme 3
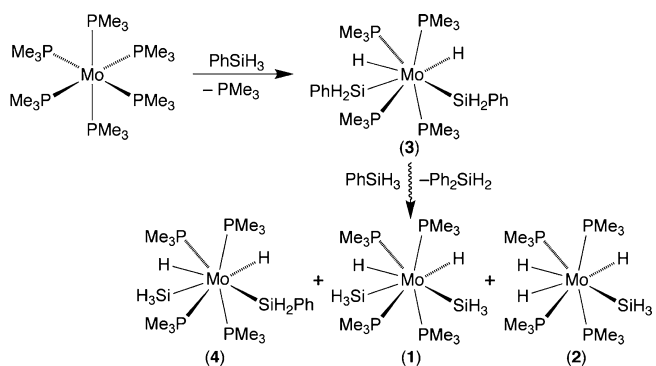

exhibits limited stability at room temperature and undergoes a series of transformations in the presence of excess PhSiH₃ to form the *silyl* (SiH₃) compounds Mo(PMe₃)₄(SiH₂Ph)(SiH₃)-H₂ (**4**), Mo(PMe₃)₄(SiH₃)₂H₂, and Mo(PMe₃)₄(SiH₃)H₃, of which the lattermost ultimately dominates (Scheme 3). The generation of these Mo−SiH₃ compounds upon treatment with PhSiH₃ is of significance not only because it requires the cleavage of Si−C bonds, but also because there is no precedent for the isolation of a metal complex with a terminal SiH₃ ligand from the reactions of PhSiH₃.[12,13]

Although the mechanistic details are unknown, formation of Mo(PMe₃)₄(SiH₂Ph)(SiH₃)H₂ from Mo(PMe₃)₄(SiH₂Ph)₂H₂ can be conceptually rationalized by an overall metathesis of Mo−SiH₂Ph and Ph−SiH₃ bonds.[14,15] In support of this suggestion, Ph₂SiH₂ is also formed during the course of the reaction. Furthermore, SiH₄ is observed, thereby making it evident that the system is capable of effecting the redistribution of PhSiH₃ into Ph₂SiH₂ and SiH₄. In this regard, the catalytic redistribution of PhSiH₃ is well-known, although it is typically

observed for d^0 transition metals[16] and lanthanides,[12a,b,17] for which σ-bond metathesis mechanisms are generally invoked.

Interestingly, the reactivity of Ph_2SiH_2 towards $Mo(PMe_3)_6$ is quite distinct from that of either $PhSiH_3$ or SiH_4. Therefore, rather than simply cleaving the Si–H bond, the reaction of $Mo(PMe_3)_6$ with Ph_2SiH_2 results in the formation of, *inter alia*, $Mo(PMe_3)_4(\kappa^2\text{-}H_2\text{-}H_2SiPh_2H)H$ (**5**) and $Mo(PMe_3)_3(\kappa^2\text{-}H_2\text{-}H_2Si_2Ph_4)H_2$ (**6**) (Scheme 4).[18] The formation of the Si–Si

Scheme 4
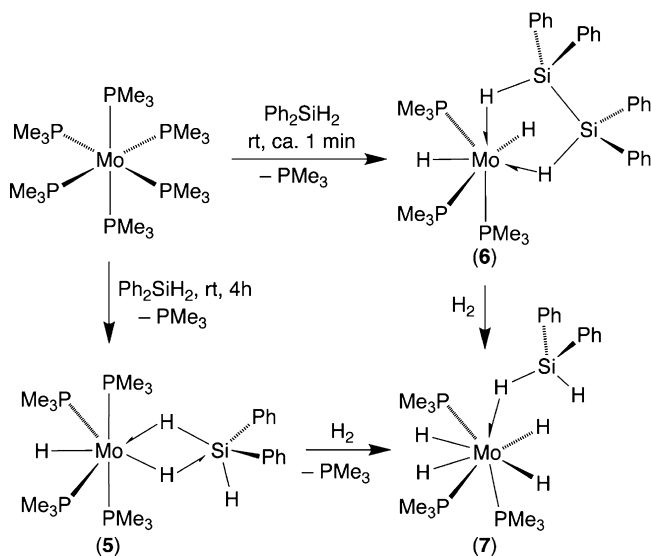
bond to yield the latter compound is, however, reversible, such that the disilane complex reacts rapidly with H_2 to give the monosilane adduct, $Mo(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$ (**7**) (Scheme 4). Furthermore, the latter compound is also formed upon treatment of $Mo(PMe_3)_4(\kappa^2\text{-}H_2\text{-}H_2SiPh_2H)H$ with H_2 (Scheme 4).[19]

The molecular structures of $Mo(PMe_3)_4(\kappa^2\text{-}H_2\text{-}H_2SiPh_2H)H$, $Mo(PMe_3)_3(\kappa^2\text{-}H_2\text{-}H_2Si_2Ph_4)H_2$, and $Mo(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$ have been determined by X-ray diffraction, as illustrated in Figure 1b–d. The three-membered [Mo,H,Si] moiety of $Mo(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$ is characterized by Mo–Si [2.500(1) Å], Mo–H [1.64(5) Å], and Si–H [1.74(4) Å] bond lengths that are in accord with its formulation as a silane adduct.[1,20,21] For example, the Si–H bond length associated with the bridging hydrogen is within the range accepted for σ-complexes (1.7–1.8 Å).[1a]

$Mo(PMe_3)_3(\kappa^2\text{-}H_2\text{-}H_2Si_2Ph_4)H_2$ is of particular note because it represents the first example of a structurally characterized metal disilane complex. Furthermore, the disilane chelates to the metal center, albeit in an asymmetric manner, with Mo–Si distances of 2.5322(8) and 2.7140(8) Å.

$Mo(PMe_3)_4(\kappa^2\text{-}H_2\text{-}H_2SiPh_2H)H$ is the first example of a structurally characterized complex with a $\kappa^2\text{-}H_2\text{-}H_2SiPh_2H$ ligand.[22] Complexes with related motifs, such as $[H_2SiPh_3]$,[23] $[H_2SiPhH_2]$,[24a] and $[H_2SiCl_3]$,[24] have also been reported,[25,26] and the bonding in these compounds has been discussed in terms of a variety of models, which include (*i*) silyl-dihydride, (*ii*) σ-silane-hydride, and (*iii*) symmetric hypervalent $[H_2SiR_3]$ formalisms.[20,25] In this regard, the Si–H [1.69(3) and 1.74(3) Å] and Mo–H [1.62(3) and 1.88(3) Å] bond lengths indicate that $Mo(PMe_3)_4(\kappa^2\text{-}H_2\text{-}H_2SiPh_2H)H$ is better described as a

hypervalent $[H_2SiPh_2H]$ silyl derivative than as a silyl-hydride complex.[27]

Finally, in contrast to the reactions of $Mo(PMe_3)_6$ with SiH_4, $PhSiH_3$, and Ph_2SiH_2, each of which involves Si–H bond cleavage, the corresponding reaction of Ph_3SiH results in the formation of the η^6-arene complex $(\eta^6\text{-}C_6H_5SiPh_2H)Mo(PMe_3)_3$ (**8**).[28] Complexes that feature Ph_3SiH as an η^6-arene ligand are rare, with there being only one other structurally characterized example, namely $(\eta^6\text{-}C_6H_5SiPh_2H)W(CO)_3$,[29] listed in the Cambridge Structural Database.

In summary, $Mo(PMe_3)_6$ exhibits diverse reactivity towards SiH_4, $PhSiH_3$, and Ph_2SiH_2 to afford a variety of novel silyl, hypervalent silyl, silane, and disilane complexes, whereas Ph_3SiH simply forms the η^6-arene complex $(\eta^6\text{-}C_6H_5SiPh_2H)Mo(PMe_3)_3$. While the reactions of non-d^0 metal phosphine hydride compounds are often interpreted in terms of sequences that involve oxidative addition and reductive elimination, NMR spectroscopic analysis of the isotope exchange reaction between $Mo(PMe_3)_4(SiH_3)_2H_2$ and SiD_4 indicates that the reaction does not occur via initial reductive elimination of SiH_4, but rather by a metathesis pathway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystallographic data for compounds **1–8** (CIFs), and Cartesian coordinates for geometry optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(8) The equilibrium constant for the reaction of $Mo(PMe_3)_4$-$(SiH_3)_2H_2$ with H_2 is 1.0(1) at room temperature, from which it may be estimated that the Mo−H BDE is *ca.* 7 kcal mol^{-1} greater than that for the Mo−SiH$_3$ bond.

(9) A mechanism that involves PMe_3 loss and α-H elimination to form a silylene species, $H_3[Mo](SiH_2)(SiH_3)$, that adds SiD_4 to form $H_3[Mo](SiH_2D)(SiH_3)(SiD_3)$, would result in a mixture of isotopologues, namely SiH_4, SiH_3D, and $SiHD_3$. However, since SiH_4 is not observed, this is not considered to be a likely mechanism.

(10) We note that the transition state for the metathesis reaction may be viewed as a hypervalent silyl derivative. Such derivatives are precedented, as illustrated by $Mo(PMe_3)_4(\kappa^2-H_2-H_2SiPh_2H)H$, described herein.

(11) A mechanism that involves α-H elimination can also be invoked to account for H/D exchange,[a] but we favor a σ-complex intermediate on the basis that it does not require a vacant coordination site and that the interconversion of silyl-hydride and σ-complexes is precedented.[b] Furthermore, H/D exchange between methyl and hydride sites has also been invoked to occur via σ-complex intermediates.[c,d] (a) Minato, M.; Zhou, D.-Y.; Zhang, L.-B.; Hirabayashi, R.; Kakeya, M.; Matsumoto, T.; Harakawa, A.; Kikutsuji, G.; Ito, T. *Organometallics* **2005**, *24*, 3434−3441. (b) References 3 and 4. (c) Parkin, G. *Acc. Chem. Res.* **2009**, *42*, 315−325. (d) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125−3146.

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(16) See, for example: (a) Sadow, A. D.; Tilley, T. D. *Organometallics* **2001**, *20*, 4457−4459. (b) Sadow, A. D.; Tilley, T. D. *Organometallics* **2003**, *22*, 3577−3585.

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(21) While the solid state structure of $Mo(PMe_3)_3(\sigma$-HSiHPh$_2)H_4$ is best described as a σ-complex, the observation of two quartets in the ^{1}H NMR spectrum at δ 6.48 ($^3J_{P-H}$ = 8 Hz) and −4.21 ($^2J_{P-H}$ = 30 Hz), attributable to a terminal silicon hydride and five hydrogen atoms attached to molybdenum, suggests that the molecule is either fluxional or exists as the silyl tautomer, $Mo(PMe_3)_3(SiHPh_2)H_5$, in solution.

(22) For comparison, there is only one other related compound listed in the Cambridge Structural Database that contains the $[H_2SiPh_2H]$ moiety, namely $Cp^*W(CO)_2(SiHPh_2)H_2$, but the much longer Si···H distances [1.92 Å and 2.00 Å] indicate that it is better classified as a silyl-dihydride. See: Sakaba, H.; Hirata, T.; Kabuto, C.; Kabuto, K. *Organometallics* **2006**, *25*, 5145−5150.

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(27) It is also pertinent to note that, as observed for $Mo(PMe_3)_3(\sigma$-HSiHPh$_2)H_4$ [2.500(1) Å], the Mo−Si distance in $Mo(PMe_3)_4(\kappa^2-H_2-H_2SiPh_2H)H$ [2.5408(7) Å] is slightly shorter than that in the silyl derivatives (2.56−2.58 Å), which indicates that a M−Si bond length does not necessarily correlate with the degree of activation of a Si−H bond.

(28) Ph_4Si does not, however, react with $Mo(PMe_3)_6$ under similar conditions.

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