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Si–H and Si–C Bond Cleavage Reactions of Silane and Phenylsilanes with Mo(PMe$_3$)$_6$: Silyl, Hypervalent Silyl, Silane, and Disilane Complexes

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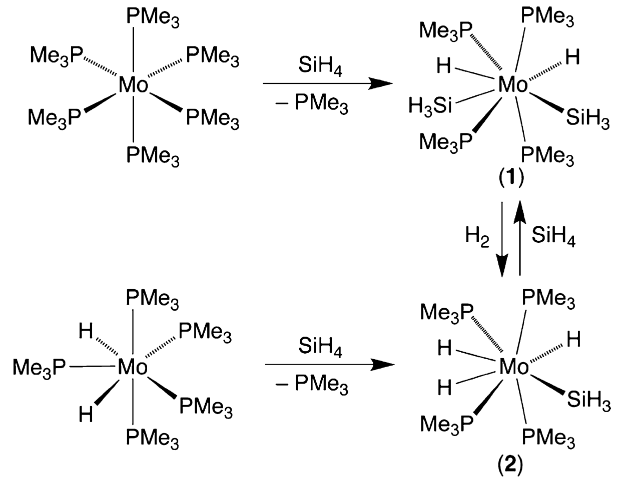
Supporting Information

ABSTRACT: Mo(PMe$_3$)$_6$ cleaves the Si–H bonds of SiH$_4$, PhSiH$_3$, and Ph$_2$SiH$_2$ to afford a variety of novel silyl, hypervalent silyl, silane, and disilane complexes, as respectively illustrated by Mo(PMe$_3$)$_4$(SiH$_3$)$_2$H$_2$, Mo(PMe$_3$)$_4$(κ^2-H_2-H$_2$SiPh$_2$H)H, Mo(PMe$_3$)$_3$(σ-HSiHPh$_2$)H$_4$, and Mo(PMe$_3$)$_3$(κ^2-H_2-H$_2$Si$_2$Ph$_4$)H$_2$. Mo(PMe$_3$)$_4$(κ^2-H_2-H$_2$SiPh$_2$H)H and Mo(PMe$_3$)$_3$(κ^2-H_2-H$_2$Si$_2$Ph$_4$)H$_2$ are respectively the first examples of complexes that feature a hypervalent κ^2-H_2-H$_2$SiPh$_2$H silyl ligand and a chelating disilane ligand, and both compounds convert to the diphenylsilane adduct, Mo(PMe$_3$)$_3$(σ-HSiHPh$_2$)H$_4$, in the presence of H$_2$. Mo(PMe$_3$)$_4$(SiH$_3$)$_2$H$_2$ undergoes isotope exchange with SiD$_4$, and NMR spectroscopic analysis of the SiH$_x$D$_{4-x}$ isotopologues released indicates that the reaction does not occur via initial reductive elimination of SiH$_4$, but rather by a metathesis pathway.

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 SiH$_4$ 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 SiH$_4$ to a molybdenum center and also describe the corresponding reactivity of the series of phenylsilanes, Ph$_x$SiH$_{4-x}$ (x = 1–4), which affords silyl, hypervalent silyl, silane, and disilane complexes.

Previous studies have shown that zerovalent Mo(PMe$_3$)$_6$ 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(PMe$_3$)$_6$ also cleaves the Si–H bond of SiH$_4$ at room temperature to give the bis(silyl) compound Mo(PMe$_3$)$_4$(SiH$_3$)$_2$H$_2$ (**1**) (Scheme 1). This transformation is of particular note because related zerovalent molybdenum complexes, namely Mo(R$_2$PC$_2$H$_4$PR$_2$)$_2$(CO) (R = Ph, Bu^i), do not cleave the Si–H bond of SiH$_4$, but rather coordinate it to form σ-silane adducts, Mo(R$_2$PC$_2$H$_4$PR$_2$)$_2$(CO)(σ-SiH$_4$).[3] Mo(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$(CO) reacts similarly to Mo(R$_2$PC$_2$H$_4$PR$_2$)$_2$(CO) (R = Ph, Bu^i), although the silane adduct was shown to exist in equilibrium with the silyl-hydride complex Mo(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$(CO)(SiH$_3$)H.[3] In this regard, evidence that Mo(PMe$_3$)$_4$(SiH$_3$)$_2$H$_2$ is a silyl-hydride and not a silane complex is provided by the observation of distinct quintet signals in the ^{1}H NMR spectrum at δ −4.80 and 4.02 in a 1:3 ratio, of which the former has a value of $^2J_{\text{P-H}}$ = 26 Hz and the latter $^3J_{\text{P-H}}$ = 8 Hz. In accord with the silyl-hydride assignment, the signal attributable to the SiH$_3$ groups exhibits coupling to silicon ($^1J_{\text{Si-H}}$ = 157 Hz), whereas no coupling is observed (i.e., $^2J_{\text{Si-H}}$ < 15 Hz) for the hydride signal.

Scheme 1



In addition to the bis(silyl) complex, the mono(silyl) counterpart, Mo(PMe$_3$)$_4$(SiH$_3$)H$_3$ (**2**), has been obtained by both (i) reaction of the dihydride Mo(PMe$_3$)$_5$H$_2$ with SiH$_4$ and (ii) addition of H$_2$ to Mo(PMe$_3$)$_4$(SiH$_3$)$_2$H$_2$ (Scheme 1). The latter reaction is reversible, such that treatment of the mono(silyl) complex with SiH$_4$ regenerates the bis(silyl) compound, Mo(PMe$_3$)$_4$(SiH$_3$)$_2$H$_2$ (Scheme 1).[8] The molecular structures of Mo(PMe$_3$)$_4$(SiH$_3$)H$_3$ and Mo(PMe$_3$)$_4$(SiH$_3$)$_2$H$_2$ have been determined by X-ray diffraction, as illustrated for the latter in Figure 1a.

While a simple mechanism for formation of Mo(PMe$_3$)$_4$(SiH$_3$)H$_3$ upon treatment of Mo(PMe$_3$)$_4$(SiH$_3$)$_2$H$_2$ with H$_2$ could involve reductive elimination of SiH$_4$ followed by oxidative addition of H$_2$, isotope labeling studies indicate that such a mechanism, which is commonly invoked for non-d^0

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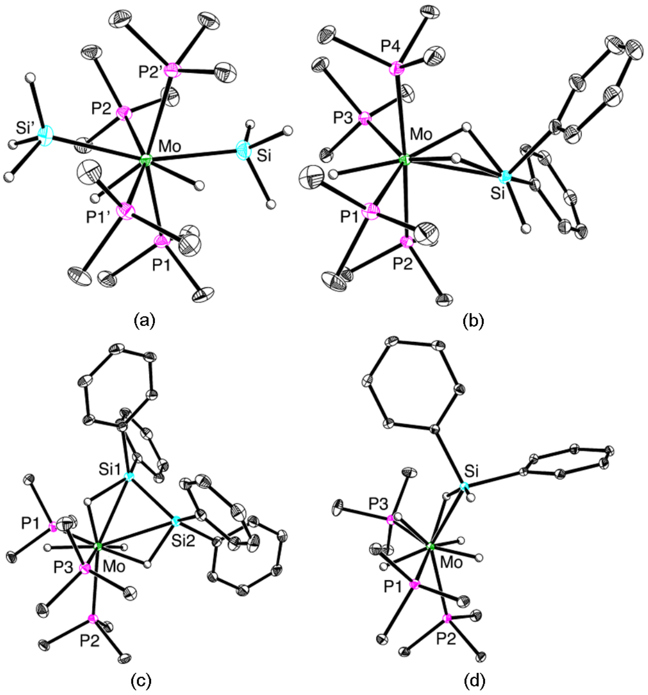
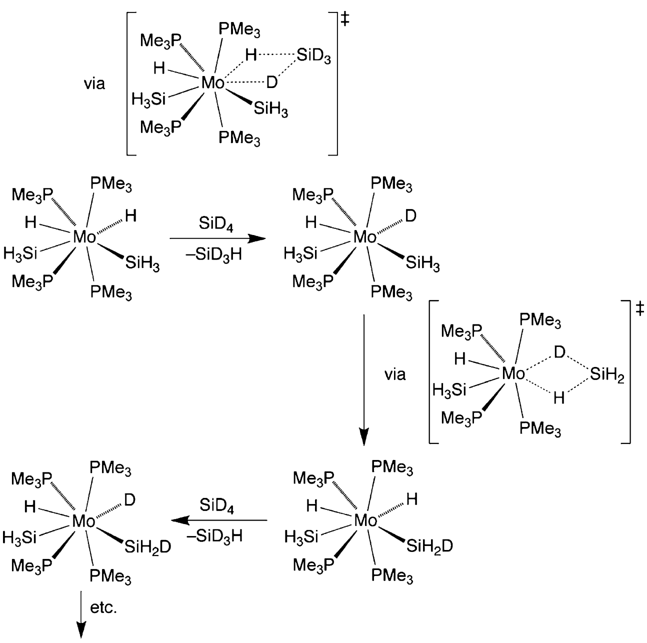


Figure 1. Molecular structures of (a) $Mo(PMe_3)_4(SiH_3)_2H_2$, (b) $Mo(PMe_3)_4(\kappa^2\text{-}H_2\text{-}H_2SiPh_2H)H$, (c) $Mo(PMe_3)_3(\kappa^2\text{-}H_2\text{-}H_2Si_2Ph_4)H_2$, and (d) $Mo(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$.

metal phosphine hydride compounds, does not operate. For example, treatment of $Mo(PMe_3)_4(SiH_3)_2H_2$ with D_2 results primarily in the formation of SiH_xD_{4-x} rather than SiH_4. Furthermore, treatment of $Mo(PMe_3)_4(SiH_3)_2H_2$ with SiD_4 demonstrates that H/D exchange involving both the silyl and hydride ligands occurs *without* reductive elimination of SiH_4 (Scheme 2). Specifically, ^1H NMR spectroscopic analysis reveals that $SiHD_3$, and *not* SiH_4, is the initially formed isotopologue. SiH_2D_2 and SiH_3D are also observed as the exchange reaction progresses, but negligible quantities of SiH_4 are formed during the course of the experiment. The absence of SiH_4 provides conclusive evidence that $Mo(PMe_3)_4(SiH_3)_2H_2$ does not undergo reductive elimination of the silyl and hydride ligands, and thus this transformation cannot be the first step in the reaction of $Mo(PMe_3)_4(SiH_3)_2H_2$ with H_2.[9] A plausible mechanism for the exchange is, therefore, proposed to involve metathesis between the Mo−H and $D{-}SiD_3$ bonds (possibly accompanied by reversible dissociation of PMe_3), which would form initially $Mo(PMe_3)_4(SiH_3)_2HD$ and $SiHD_3$ (Scheme 2).[10] Subsequent incorporation of deuterium into the molybdenum silyl groups can be rationalized on the basis of $Mo(PMe_3)_4(SiH_3)_2HD$ accessing a fluxional silane adduct, $Mo(PMe_3)_4(SiH_3)(\sigma\text{-}SiH_3D)H$, which would allow for scrambling (Scheme 2).[11]

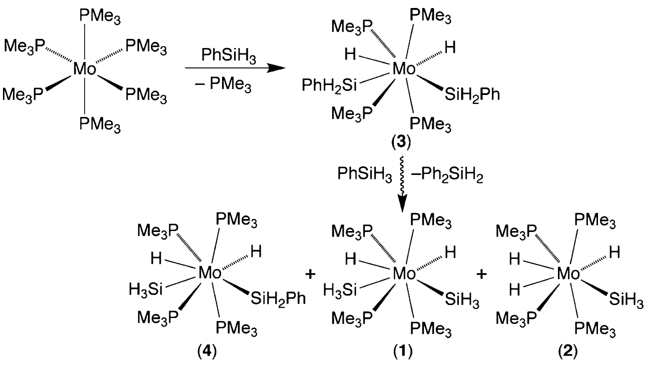
Scheme 2



Further evidence that Si−H reductive elimination does not operate is provided by examination of the corresponding exchange reaction between $Mo(PMe_3)_4(SiD_3)_2D_2$ and SiH_4. Specifically, ^1H NMR spectroscopic analysis reveals the initial formation of $Mo{-}SiHD_2$ groups rather than $Mo{-}SiH_3$ groups, with the latter being generated as the reaction progresses. Furthermore, the silane isotopologue that is released is primarily SiH_3D, which is consistent with a mechanism that involves metathesis of the Mo−D bond with the $H{-}SiH_3$ bond.

$Mo(PMe_3)_6$ also undergoes facile oxidative addition of Si−H bonds of $PhSiH_3$ at room temperature to give the bis(phenylsilyl) compound, $Mo(PMe_3)_4(SiH_2Ph)_2H_2$ (**3**), which can be isolated if the reaction mixture is immediately cooled to −15 °C (Scheme 3). However, $Mo(PMe_3)_4(SiH_2Ph)_2H_2$ exhibits limited stability at room temperature and undergoes a series of transformations in the presence of excess $PhSiH_3$ to form the *silyl* (SiH_3) compounds $Mo(PMe_3)_4(SiH_2Ph)(SiH_3)H_2$ (**4**), $Mo(PMe_3)_4(SiH_3)_2H_2$, and $Mo(PMe_3)_4(SiH_3)H_3$, of which the lattermost ultimately dominates (Scheme 3). The generation of these $Mo{-}SiH_3$ compounds upon treatment with $PhSiH_3$ 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 SiH_3 ligand from the reactions of $PhSiH_3$.[12,13]

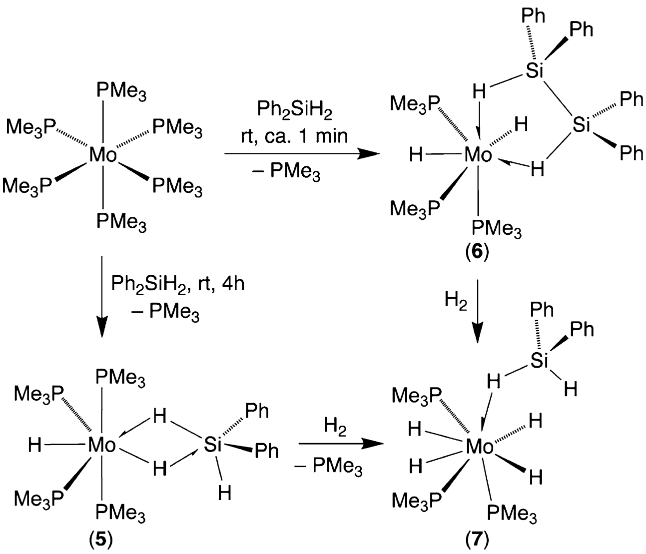
Scheme 3



Although the mechanistic details are unknown, formation of $Mo(PMe_3)_4(SiH_2Ph)(SiH_3)H_2$ from $Mo(PMe_3)_4(SiH_2Ph)_2H_2$ can be conceptually rationalized by an overall metathesis of $Mo{-}SiH_2Ph$ and $Ph{-}SiH_3$ bonds.[14,15] In support of this suggestion, Ph_2SiH_2 is also formed during the course of the reaction. Furthermore, SiH_4 is observed, thereby making it evident that the system is capable of effecting the redistribution of $PhSiH_3$ into Ph_2SiH_2 and SiH_4. In this regard, the catalytic redistribution of $PhSiH_3$ 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 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]

Scheme 4



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 $Mo(PMe_3)_4(\kappa^2\text{-}H_2\text{-}H_2SiPh_2H)H$, 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.

(12) There are, however, a few examples of the formation of bridging μ-SiH_3 compounds from $PhSiH_3$ for the f-block metals. See, for example: (a) Castillo, I.; Tilley, T. D. *Organometallics* **2000**, *19*, 4733−4739. (b) Radu, N. S.; Hollander, F. J.; Tilley, T. D.; Rheingold, A. L. *Chem. Commun.* **1996**, 2459−2460. (c) Korobkov, I.; Gambarotta, S. *Organometallics* **2009**, *28*, 5560−5567.

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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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(18) The κ^x notation refers to the number of Si−H hydrogen atoms attached to the metal. See: Green, J. C.; Green, M. L. H.; Parkin, G. *Chem. Commun.* **2012**, *48*, 11481−11503.

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(21) While the solid state structure of $Mo(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$ is best described as a σ-complex, the observation of two quartets in the ^1H 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 $Mo(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$ [2.500(1) Å], the Mo−Si distance in $Mo(PMe_3)_4(\kappa^2\text{-}H_2\text{-}H_2SiPh_2H)H$ [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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