σ-Silane, Disilanyl, and [W(μ-H)Si(μ-H)W] Bridging Silylene Complexes via the Reactions of W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H with Phenylsilanes

Ashley A. Zuzek, Michelle C. Neary, and Gerard Parkin*

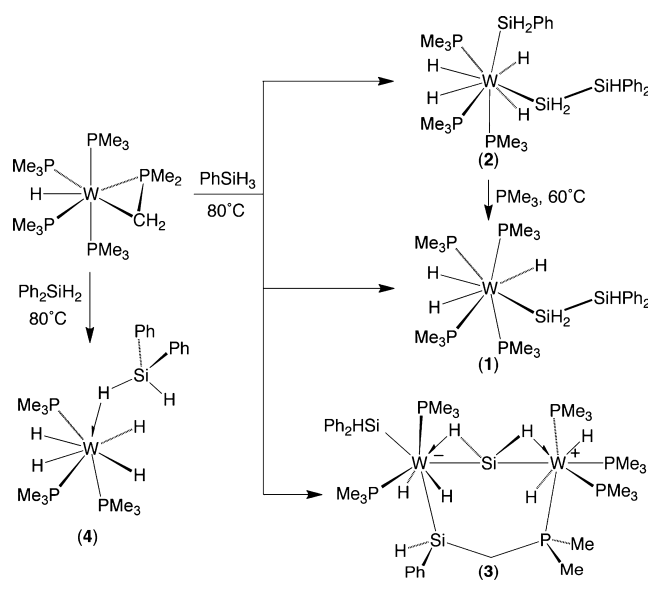Department of Chemistry, Columbia University, New York, New York 10027, United States

Ⓢ Supporting Information

ABSTRACT: W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H reacts with PhSiH$_3$ to give the first examples of diphenyldisilanyl compounds, W(PMe$_3$)$_4$(SiH$_2$SiHPh$_2$)H$_3$ and W(PMe$_3$)$_3$-(SiH$_2$Ph)(SiH$_2$SiHPh$_2$)H$_4$, via a mechanism that is proposed to involve migration of a SiHPh$_2$ group to a silylene ligand. In addition to the formation of the aforementioned mononuclear compounds, the reaction of W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H with PhSiH$_3$ also yields a novel dinuclear compound, [W(PMe$_3$)$_2$(SiHPh$_2$)H$_2$]-(μ-Si,P-SiHPhCH$_2$PMe$_2$)(μ-SiH$_2$)[W(PMe$_3$)$_3$H$_2$], which features a bridging silylene ligand that participates in 3-center-2-electron interactions with both tungsten centers. The bonding within the [W(μ-H)Si(μ-H)W] core can be described by a variety of resonance structures, some of which possess multiple bond character between tungsten and silicon. In this regard, [W(PMe$_3$)$_2$(SiHPh$_2$)H$_2$]-(μ-Si,P-SiHPhCH$_2$PMe$_2$)(μ-SiH$_2$)[W(PMe$_3$)$_3$H$_2$] possesses the shortest W–Si bond length reported. The corresponding reaction of W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H with Ph$_2$SiH$_2$ yields the σ-silane compound, W(PMe$_3$)$_3$-(σ-HSiHPh$_2$)H$_4$.

Scheme 1

The reactivity of transition metal compounds towards silanes is of considerable interest[1] in view of the fact that such compounds provide a means of catalyzing a variety of transformations of silanes, such as hydrosilylation and dehydrogenative polymerization.[2] Furthermore, the interaction of silanes with transition metal centers has been invoked as a model for the corresponding interactions of C–H bonds.[3] In this regard, we recently demonstrated that the electron-rich molybdenum complex, 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.[4] Here we describe the corresponding reactivity of a related tungsten complex, thereby demonstrating the existence of reaction pathways that afford classes of compounds that are not observed for the molybdenum system.

W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H,[5] a cyclometalated derivative of W(PMe$_3$)$_6$,[6] is a highly reactive molecule that is capable of cleaving a variety of X–Y bonds.[6b,7] As such, it is not surprising that W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H is also reactive towards PhSiH$_3$; however, it is most interesting that the reaction follows a very different course from that of Mo(PMe$_3$)$_6$. For example, while Mo(PMe$_3$)$_6$ undergoes facile oxidative-addition of the Si–H bonds of PhSiH$_3$ to give the bis(phenylsilyl) compound, Mo(PMe$_3$)$_4$(SiH$_2$Ph)$_2$H$_2$,[4] the corresponding re-

action of W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H does not yield W(PMe$_3$)$_4$(SiH$_2$Ph)$_2$H$_2$, but rather the isomeric disilanyl compound, W(PMe$_3$)$_4$(SiH$_2$SiHPh$_2$)H$_3$ (**1**) (Scheme 1), which features a Si–Si bond. Furthermore, whereas the reaction of Mo(PMe$_3$)$_6$ with excess PhSiH$_3$ yields the silyl (SiH$_3$) compounds Mo(PMe$_3$)$_4$(SiH$_2$Ph)(SiH$_3$)H$_2$, Mo(PMe$_3$)$_4$(SiH$_3$)$_2$H$_2$, and Mo(PMe$_3$)$_4$(SiH$_3$)H$_3$, the reaction between W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H and excess PhSiH$_3$ yields W(PMe$_3$)$_3$(SiH$_2$Ph)(SiH$_2$SiHPh$_2$)H$_4$ (**2**). Oxidative-addition of PhSiH$_3$ to form the latter compound is, however, reversible since W(PMe$_3$)$_3$(SiH$_2$Ph)(SiH$_2$SiHPh$_2$)H$_4$ may be converted to W(PMe$_3$)$_4$(SiH$_2$SiHPh$_2$)H$_3$ by treatment with PMe$_3$.

The molecular structures of W(PMe$_3$)$_4$(SiH$_2$SiHPh$_2$)H$_3$ (**1**) (Figure 1) and W(PMe$_3$)$_3$(SiH$_2$Ph)(SiH$_2$SiHPh$_2$)H$_4$ (**2**) (Figure 2) have been determined by X-ray diffraction and are of interest because there are no other structurally characterized M(SiH$_2$SiHPh$_2$) disilanyl compounds listed in the Cambridge Structural Database (CSD).[8] Furthermore, there are only three structurally characterized compounds of the type M(SiH$_2$SiR$_3$) (R = H, Ph), namely Cp*Os(PPr$^i_3$)(H)(Br)SiH$_2$SiPh$_3$,[9a] Cp*$_2$ScSiH$_2$SiPh$_3$,[9b] and Cp*Fe(CO)$_2$SiH$_2$SiH$_3$,[9c] and none of these were synthesized by a reaction involving Si–Si bond formation. Specifically, Cp*Os(PPr$^i_3$)(H)(Br)SiH$_2$SiPh$_3$[9a] and
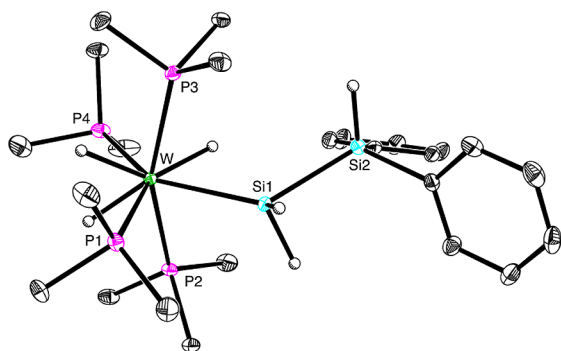
Figure 1. Molecular structure of $W(PMe_3)_4(SiH_2SiHPh_2)H_3$ (**1**).
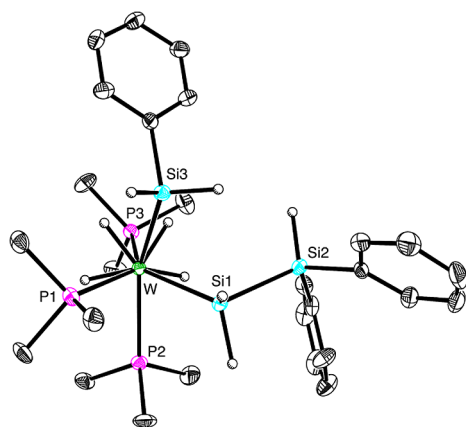

Figure 2. Molecular structure of $W(PMe_3)_3(SiH_2Ph)(SiH_2SiHPh_2)H_4$ (**2**).

$Cp*_2ScSiH_2SiPh_3$,[9b] were obtained by reactions with the disilane, Ph_3SiSiH_3, while $Cp*Fe(CO)_2SiH_2SiH_3$ was obtained by treatment of the chloride derivative $Cp*Fe(CO)_2SiCl_2SiCl_3$ with $LiAlH_4$.[9c]

$W(PMe_3)_4(SiH_2SiHPh_2)H_3$ (**1**) exhibits a distinct 1:2 set of hydride signals in the ^{1}H NMR spectrum, in accord with the solid state structure. In contrast, $W(PMe_3)_3(SiH_2Ph)$-$(SiH_2SiHPh_2)H_4$ (**2**) is fluxional at room temperature, exhibiting a single broad signal for the hydride ligands. A static structure that exhibits independent signals for each of the four hydride ligands of $W(PMe_3)_3(SiH_2Ph)(SiH_2SiHPh_2)H_4$ (**2**) is, nevertheless, observed at 193 K.

The mechanism of the formation of the disilanyl ligand is of interest in view of the relevance of Si–Si bond formation to the production of polysilanes. In this regard, the mechanism for formation of the SiH_2SiHPh_2 ligand is proposed to involve sequential (i) α-H elimination of a bis(silyl) species, $[W](SiH_2Ph)_2$,[10] to form a silylene intermediate of the type $[W](=SiHPh)(SiH_2Ph)H$, (ii) 1,3-migration of a phenyl group to produce an isomeric silylene complex, $[W](SiHPh_2)(=SiH_2)H$, and (iii) 1,2-migration of the newly generated $SiHPh_2$ group to form $[W](SiH_2SiHPh_2)H$. Similar 1,2-silyl and 1,3-alkyl and aryl migrations have also been proposed in other systems.[11,12] For example, treatment of $Cp^RFe(CO)(=SiMes_2)(SiMe_3)$ (Cp^R = Cp, Cp*) with Bu^tNC yields the disilanyl compound $Cp*Fe(CO)(CNBu^t)(SiMesMe-SiMesMe_2)$, which was rationalized by a series of 1,3-migrations of the methyl and mesityl groups, followed by 1,2-silyl migration.[12a]

Density Functional Theory (DFT) calculations also support the viability of the proposed mechanism. Specifically, not only is the disilanyl compound $W(PMe_3)_4H_3(SiH_2SiHPh_2)$ (**1**) calculated to be significantly more thermodynamically stable than the bis(silyl) derivative, $W(PMe_3)_4H_2(SiH_2Ph)_2$, by 8.7 kcal mol^{-1}, but the proposed silylene intermediates are also thermodynamically accessible.

In addition to the formation of the above mononuclear compounds, the reaction of $W(PMe_3)_4(\eta^2-CH_2PMe_2)H$ with $PhSiH_3$ also produces a low yield of a novel dinuclear compound, $[W(PMe_3)_2(SiHPh_2)H_2](\mu-Si,P-SiHPhCH_2PMe_2)$-$(\mu-SiH_2)[W(PMe_3)_3H_2]$, "[WSiW]" (**3**), which features a bridging silylene ligand.[13,14] The molecular structure of the silylene complex has been determined by X-ray diffraction (Figure 3), thereby demonstrating that the SiH_2 moiety
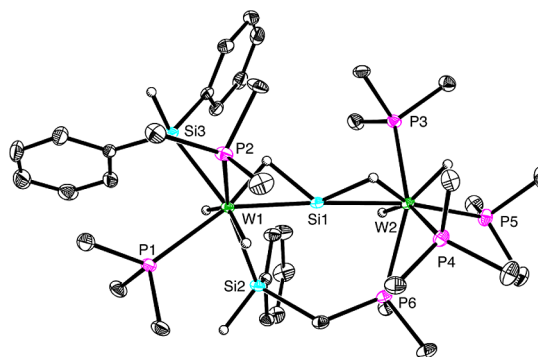

Figure 3. Molecular structure of $[W(PMe_3)_2(SiHPh_2)H_2](\mu-Si,P-SiHPhCH_2PMe_2)(\mu-SiH_2)[W(PMe_3)_3H_2]$ (**3**).

coordinates to the two tungsten centers in a manner that is quite distinct from other $\mu-SiH_2$ compounds. For example, (i) the W–Si–W bond angle is close to linear [176.16(6)°], whereas other $\mu-SiH_2$ compounds are significantly bent, as illustrated by the M–Si–M bond angles in $[CpFe(CO)_2]_2$-$(\mu-SiH_2)$ [123.48(6)°],[15a] $(Cp_2Ti)_2(\mu-SiH_2)$ [102.8°],[15b] and $[CpMn(CO)_2H]_2(\mu-SiH_2)$ [124.4(3)°],[15c] and (ii) the $\mu-SiH_2$ moiety is not orthogonal to the W···W vector, such that the angle between the SiH_2 and SiW_2 planes is 31.1° rather than 90°. This displacement from orthogonality is a consequence of the fact that the hydrogen atoms attached to silicon also participate in 3-center-2-electron interactions with the tungsten centers,[16,17] with the result that the $[W(\mu-H)Si(\mu-H)W]$ core is characterized by Si–H distances of 1.68(4) Å and 1.68(5) Å, W–H distances of 1.59(4) Å and 1.58(5) Å, and W–Si distances of 2.2813(13) Å and 2.3651(13) Å. DFT calculations reproduce well the overall features of the experimental structure of [WSiW], including the asymmetry of the W–Si interactions (2.300 Å and 2.424 Å). The bonding within this core can be described by a variety of resonance structures, some of which emphasize multiple bond character between tungsten and silicon (Figure 4). In this regard, both W–Si distances are significantly shorter than the average W–Si bond length (2.55 Å) for compounds listed in the CSD.[8] Furthermore, the W–Si bond length of 2.2813(13) Å is shorter than the values for compounds listed in the CSD.[8,18]

Dinuclear [WSiW] is fluxional in solution at room temperature, such that the ^{1}H NMR spectrum consists of two broad signals in a 1:1 ratio for the six hydrogen atoms associated with the $[H_2W(SiH_2)WH_2]$ component. However, at low temperature (210 K), the six hydrogen atoms associated
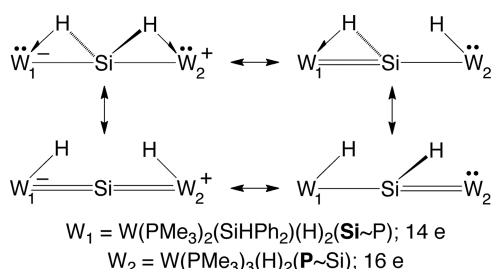
$W_1 = W(PMe_3)_2(SiHPh_2)(H)_2(\textbf{Si}{\sim}P)$; 14 e
$W_2 = W(PMe_3)_3(H)_2(\textbf{P}{\sim}Si)$; 16 e

Figure 4. Resonance structures for [WSiW]. In the absence of the bridging SiH_2 group, the W_1 and W_2 tungsten centers respectively possess 14- and 16-electron configurations, such that the W−Si interactions are necessarily asymmetric.

with the $[H_2W(SiH_2)WH_2]$ component can be distinguished in the $^1H\{^{31}P\}$ NMR spectrum. These observations suggest that the two terminal hydride ligands on each tungsten center are in rapid exchange with the respective bridging hydride ligand at room temperature, and that exchange of hydride ligands between the metals is not facile.

The synthesis of [WSiW] is of particular interest, not only because it is the first example of a silylene compound that features a $[M(\mu\text{-}H)Si(\mu\text{-}H)M]$ coordination mode of this type, but also because compounds that feature $\mu\text{-}SiH_x$ ligands are rare, with there being few structurally characterized compounds that possess $\mu\text{-}SiH_2$,[15] $\mu\text{-}SiH_3$,[19] $\mu\text{-}SiH_4$[20] and $\mu\text{-}SiH_6$[21] ligands.

Whereas the products isolated from the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with $PhSiH_3$ are very different from those observed for the corresponding reaction of $Mo(PMe_3)_6$, the reactions with Ph_2SiH_2 bear similarities for the two systems. Specifically, $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ reacts with Ph_2SiH_2 to give, *inter alia*, the σ-silane compound, $W(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$ (4) (Scheme 1),[22,23] which is analogous to the formation of the molybdenum complex, $Mo(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$, from $Mo(PMe_3)_6$. As observed for the molybdenum system, the yield of $W(PMe_3)_3$-$(\sigma\text{-}HSiHPh_2)H_4$ (4) is improved in the presence of H_2. In contrast to the molybdenum system, however, counterparts to the hypervalent silyl compound, $Mo(PMe_3)_4(\kappa^2\text{-}H_2\text{-}H_2SiPh_2H)H$,[24] and the disilane adduct, $Mo(PMe_3)_3(\kappa^2\text{-}H_2\text{-}H_2Si_2Ph_4)H_2$, are yet to be isolated for the tungsten system.

The molecular structure of $W(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$ (4) has been determined by X-ray diffraction (Figure 5), and the three-membered [W,H,Si] moiety is characterized by W−Si

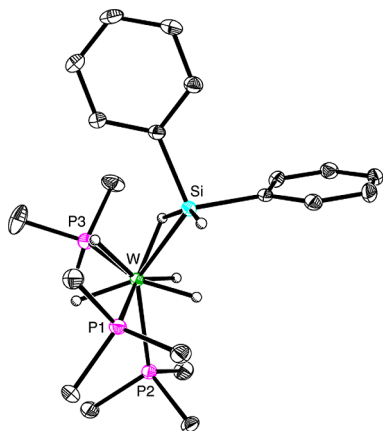**Figure 5.** Molecular structure of $W(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$ (4).

[2.5110(10) Å], W−H [1.65(4) Å], and Si−H [1.87(4) Å] bond lengths that are consistent with its formulation as a silane adduct[25,26] rather than a silyl derivative. Significantly, $W(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$ (4) is the first structurally characterized σ-silane compound of tungsten, although such species have been observed spectroscopically.[27] Also of note, the W−Si bond length [2.5110(10) Å] is considerably longer than the aforementioned distances in [WSiW] [2.2813(13) Å and 2.3651(13) Å], which provides further support for W−Si multiple bond character in the latter.

In summary, the reactivity of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ towards $PhSiH_3$ results in the formation of diphenyldisilanyl compounds, $W(PMe_3)_4(SiH_2SiHPh_2)H_3$ (1) and $W(PMe_3)_3$-$(SiH_2Ph)(SiH_2SiHPh_2)H_4$ (2), and a novel dinuclear bridging silylene complex, [WSiW] (3), while the σ-silane compound $W(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$ (4) is obtained from Ph_2SiH_2. Interestingly, none of the compounds derived from $PhSiH_3$ have counterparts in the corresponding molybdenum system, thereby highlighting a significant difference in the chemistry of these otherwise often similar elements. The bonding within [WSiW] is also particularly interesting because the $[W(\mu\text{-}H)Si(\mu\text{-}H)W]$ core possesses very short W−Si bonds, W−H−Si hydride bridges, and an almost linear W−Si−W arrangement, each of which is in marked contrast to other compounds with $\mu\text{-}SiH_2$ ligands.

■ ASSOCIATED CONTENT

⑤ Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author
parkin@columbia.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Corey, J. Y. *Chem. Rev.* **2011**, *111*, 863−1071. (b) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175−292.

(2) (a) Kim, B.-H.; Woo, H.-G. *Adv. Organomet. Chem.* **2005**, *52*, 143−174. (b) Roy, A. K. *Adv. Organomet. Chem.* **2008**, *55*, 1−59. (c) Troegel, D.; Stohrer, J. *Coord. Chem. Rev.* **2011**, *255*, 1440−1459. (d) Corey, J. Y. *Adv. Organomet. Chem.* **2004**, *51*, 1−52. (e) Waterman, R. *Chem. Soc. Rev.* **2013**, *42*, 5629−5641. (f) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363−405. (g) Hartwig, J. F. *Acc. Chem. Res.* **2011**, *45*, 864−873.

(3) (a) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 1159−1160. (b) Vincent, J. L.; Luo, S.; Scott, B. L.; Butcher, R.; Unkefer, C. J.; Burns, C. J.; Kubas, G. J.; Lledós, A.; Maseras, F.; Tomàs, J. *Organometallics* **2003**, *22*, 5307−5323.

(4) Zuzek, A. A.; Parkin, G. *J. Am. Chem. Soc.* **2014**, *136*, 8177−8180.

(5) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Bandy, J. A.; Grebenik, P. D.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 2025−2035.

(6) (a) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1990**, *112*, 5381−5383. (b) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1992**, *114*, 4611−4621.

(7) See, for example: (a) Green, M. L. H.; Parkin, G.; Chen, M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1986**, 2227−2236. (b) Sattler, A.; Parkin, G. *J. Am. Chem. Soc.* **2011**, *133*, 3748−3751. (c) Buccella, D.; Parkin, G. *Chem. Commun.* **2009**, 289−291.

(8) Cambridge Structural Database (Version 5.35). Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8*, 31−37.

(9) (a) Glaser, P. B.; Tilley, T. D. *Organometallics* **2004**, *23*, 5799−5812. (b) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 643−656. (c) Malisch, W.; Jehle, H.; Möller, S.; Thum, G.; Reising, J.; Gbureck, A.; Nagel, V.; Fickert, C.; Kiefer, W.; Nieger, M. *Eur. J. Inorg. Chem.* **1999**, 1597−1605.

(10) The suggestion of $W(PMe_3)_4H_2(SiH_2Ph)_2$ as a proposed intermediate is based on the observation that $W(PMe_3)_4H_2(SiH_3)_2$ is obtained upon reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with SiH_4, and that the molybdenum counterpart $Mo(PMe_3)_4H_2(SiH_2Ph)_2$ is obtained upon addition of $PhSiH_3$ to $Mo(PMe_3)_6$. See refs 4 and 7a.

(11) (a) Ogino, H. *Chem. Rec.* **2002**, *2*, 291−306. (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351−1374. (c) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493−506.

(12) (a) Tobita, H.; Matsuda, A.; Hashimoto, H.; Ueno, K.; Ogino, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 221−224. (b) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056−1057. (c) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777−1780.

(13) Various other descriptions can be used to refer to the $[W(\mu\text{-}H)Si(\mu\text{-}H)W]$ core, of which an extreme example would be a silicide−hydride that features interligand hypervalent interactions. For brevity, we simply refer to the bridging moiety as a silylene.

(14) While the mechanism for formation of [WSiW] is obviously complex, one possibility involves the intermediacy of a mononuclear terminal silylene species, $[W](=SiH_2)(SiHPh_2)H$, of the type that was invoked in the formation of $W(PMe_3)_4(SiH_2SiHPh_2)H_3$.

(15) (a) Malisch, W.; Vögler, M.; Käb, H.; Wekel, H.-U. *Organometallics* **2002**, *21*, 2830−2832. (b) Hencken, G.; Weiss, E. *Chem. Ber. Recl.* **1973**, *106*, 1747−1751. (c) Herrmann, W. A.; Voss, E.; Guggolz, E.; Ziegler, M. L. *J. Organomet. Chem.* **1985**, *284*, 47−57.

(16) Green, J. C.; Green, M. L. H.; Parkin, G. *Chem. Commun.* **2012**, *48*, 11481−11503.

(17) For some tungsten silyl compounds with 3-center-2-electron interactions, see: Pandey, K. K. *Polyhedron* **2013**, *55*, 241−248.

(18) For W=SiR_2 compounds with short W−Si bond lengths, see: (a) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 9702−9703. (b) Ueno, K.; Asami, S.; Watanabe, N.; Ogino, H. *Organometallics* **2002**, *21*, 1326−1328. (c) Watanabe, T.; Hashimoto, H.; Tobita, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 218−221.

(19) (a) Radu, N. S.; Hollander, F. J.; Tilley, T. D.; Rheingold, A. L. *Chem. Commun.* **1996**, 2459−2460. (b) Hou, Z. M.; Zhang, Y.; Nishiura, M.; Wakatsuki, Y. *Organometallics* **2003**, *22*, 129−135. (c) Castillo, I.; Tilley, T. D. *Organometallics* **2000**, *19*, 4733−4739. (d) Korobkov, I.; Gambarotta, S. *Organometallics* **2009**, *28*, 5560−5567.

(20) (a) Atheaux, I.; Donnadieu, B.; Rodriguez, V.; Sabo-Etienne, S.; Chaudret, B.; Hussein, K.; Barthelat, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 5664−5665. (b) Ben Said, R.; Hussein, K.; Barthelat, J. C.; Atheaux, I.; Sabo-Etienne, S.; Grellier, M.; Donnadieu, B.; Chaudret, B. *Dalton Trans.* **2003**, 4139−4146.

(21) Lipke, M. C.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2012**, *51*, 11115−11121.

(22) $W(PMe_3)_3(\sigma\text{-}HSiHPh_2)H_4$ is depicted in Scheme 1 using the half-arrow structure bonding representation discussed in ref 16, while the structure shown in Figure 4 merely indicates connectivity. The bonding in σ-silane compounds is highly variable and ranges from an almost linear angle at hydrogen, with little M···Si interaction, to much smaller angles which are indicative of significant M···Si interactions. See, for example: (a) Yang, J.; White, P. S.; Schauer, C. K.; Brookhart, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4141−4143. (b) Komuro, T.; Okawara, S.; Furuyama, K.; Tobita, H. *Chem. Lett.* **2012**, *41*, 774−776.

(23) For other types of silane adducts, see: (a) Lipke, M. C.; Tilley, T. D. *J. Am. Chem. Soc.* **2011**, *133*, 16374−16377. (b) Reference 21.

(24) The κ^x notation refers to the number of Si−H hydrogen atoms attached to the metal (see ref 16). In terms of the η^x notation, the κ^2-H_2-H_2SiPh_2H ligand would be described as η^3-H_2SiPh_2H.

(25) (a) Lin, Z. *Chem. Soc. Rev.* **2002**, *31*, 239−245. (b) Nikonov, G. I. *Adv. Organomet. Chem.* **2005**, *53*, 217−309. (c) Lachaize, S.; Sabo-Etienne, S. *Eur. J. Inorg. Chem.* **2006**, 2115−2127. (d) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151−187.

(26) These values compare favorably with DFT calculations: W−Si (2.596 Å), W−H (1.732 Å), and Si−H (1.862 Å).

(27) See, for example: (a) Gadek, A.; Kochel, A.; Szymanska-Buzar, T. *J. Organomet. Chem.* **2007**, *692*, 3765−3777. (b) Matthews, S. L.; Pons, V.; Heinekey, D. M. *Inorg. Chem.* **2006**, *45*, 6453−6459.