Unexpected Formation of NHC-Stabilized Hydrosilylyne Complexes via Alkane Elimination from NHC-Stabilized Hydrido(alkylsilylene) Complexes

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S *Supporting Information*

ABSTRACT: N-heterocyclic carbene (NHC)-stabilized hydrosilylyne complex $Cp^*(CO)_2WSiH(^{Me}IMe)_2$ (**3a**) (^{Me}IMe = 1,3,4,5-tetramethylimidazole-2-ylidene) was formed by the reaction of an NHC-stabilized silylene complex $Cp^*(CO)_2(H)WSiH(^{Me}IMe)\{C(SiMe_3)_3\}$ (**2a**) with 1 equiv of ^{Me}IMe at 70 °C. In this reaction, $HC(SiMe_3)_3$ was unexpectedly eliminated from **2a**. A C_5Me_4Et analogue of **3a**, $(C_5Me_4Et)(CO)_2WSiH(^{Me}IMe)_2$ (**3b**), was also synthesized by the same method, and the structure of **3b** was confirmed by X-ray crystallography. Although the silicon center of **3b** is coordinated by two NHCs, the length of the W–Si bond of **3b** [2.363(4) Å] is as short as that of the shortest W=Si double bond (∼2.36 Å). These complexes, **3a** and **3b**, are the first examples of a base-stabilized silylyne complex having only a hydrogen on the silicon atom.

Chart 1. Examples of Structurally Determined Silylyne Complexes
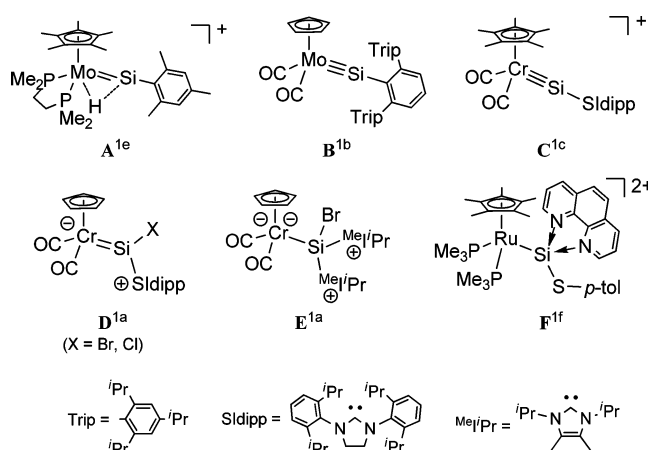
Transition-metal complexes having a M≡E bond (E = Si,[1] Ge,[2] Sn,[3] and Pb[4]) are attracting considerable attention in the chemistry of heavier main-group elements. Isolation of these complexes has been achieved by kinetic stabilization with bulky substituents or electronic stabilization with coordination of Lewis base(s). Among them, the silylyne complex has been the most challenging synthetic target because of its highly reactive M≡Si triple bond. In 2003, Tilley's group reported the synthesis of a cationic molybdenum complex $[Cp^*(dmpe)(H)MoSiMes]-[B(C_6F_5)_4]$ ($Cp^* = \eta^5-C_5Me_5$, dmpe = $PMe_2CH_2CH_2PMe_2$, Chart 1A)[1e] that has a strong Mo≡Si triple bond character with a weak bonding interaction between the hydrido ligand and the silicon atom. In 2010, Filippou's group succeeded in isolating a genuine Mo≡Si triple-bonded complex $Cp(CO)_2Mo≡Si-(C_6H_3-2,6-Trip_2)$ ($Cp = \eta^5-C_5H_5$, Trip = $C_6H_2-1,3,5-^iPr_3$, Chart 1B)[1b] by introducing a very bulky aryl group on the silicon atom. This complex was soon succeeded by two more examples, $[Cp^*(P^iPr_3)(H)Os≡SiTrip]^+$[1d] and $[Cp^*-(CO)_2Cr≡Si-SIdipp]^+$ (SIdipp = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene), Chart 1C).[1c] In addition to these examples, syntheses of base-stabilized silylyne complexes have been reported by several groups. For example, Filippou's group reported the synthesis of an NHC-stabilized halosilylyne complex $Cp(CO)_2CrSiBr(SIdipp)$ (Chart 1D) by the reaction of an NHC-stabilized dihalosilylene $SiBr_2(SIdipp)$ with a metal complex anion $Li[CpCr(CO)_3]$.[1a] Tilley's dicationic complex $[Cp^*(PMe_3)_2RuSi\{S(p-C_6H_4Me)\}(phen)](OTf)_2$ (Chart 1F) was synthesized by replacement of two OTf groups

on a silyl complex $Cp^*Ru(PMe_3)_2Si\{S(p-C_6H_4Me)\}(OTf)_2$ with phenanthroline.[1f] However, until now, there are no reports on the silylyne complex having a hydrogen on the silylyne silicon. Here, we report an unexpected formation of this type of silylyne complexes, namely, NHC-stabilized hydrosilylyne complexes[5] $(C_5Me_4R)(CO)_2WSiH(^{Me}IMe)_2$ (R = Me: **3a**, R = Et: **3b**) (^{Me}IMe = 1,3,4,5-tetramethylimidazole-2-ylidene) from $(C_5Me_4R)(CO)_2(H)WSiH(^{Me}IMe)(Tsi)$ (Tsi = $C(SiMe_3)_3$, R = Me: **2a**, R = Et: **2b**) via novel alkane elimination reaction. The crystal structure of **3b** and theoretical calculations on a model complex of **3a,b** are also presented.

Recently, we found that isolation and handling of the pyridine adducts of silylene complexes $(C_5Me_4R)(CO)_2(H)W=SiH(Tsi)$ (R = Me: **1a**, R = Et: **1b**),[6] i.e., **1a-py** and **1b-py**, are easier than those of highly reactive base-free complexes **1a** and **1b**. Therefore, we used **1a-py** and **1b-py** instead of **1a** and **1b** for the synthesis of NHC-stabilized silylene complexes **2a** and **2b**. Complex **1a-py**[7] was synthesized by the reaction of $Cp^*-(CO)_2(py)W(Me)$ with 1 equiv of H_3SiTsi and was isolated as an orange powder in 65% yield (Scheme 1). ^1H and ^{13}C NMR spectra of **1a-py** in C_6D_6 only showed somewhat broadened signals assignable to base-free silylene complex **1a** and free pyridine, which indicates that the pyridine of **1a-py** almost completely dissociates in solution at room temperature.[8]

Scheme 1. Synthesis of NHC-Stabilized Hydrosilylyne Complexes 3a and 3b
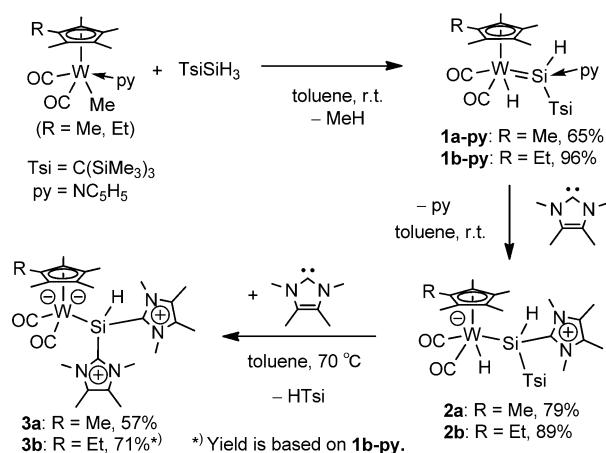
Treatment of **1a-py** with 1 equiv of ^{Me}IMe at room temperature instantaneously afforded the NHC-stabilized silylene complex **2a** via exchange of the coordinating base (Scheme 1). In contrast to **1a-py**, dissociation of ^{Me}IMe from **2a** was not observed in C_6D_6 even at 70 °C. Complex **2a** was isolated as a light-yellow powder in 79% yield. Complex **2b**, a C_5Me_4Et analogue of **2a**, was also synthesized by the same method. Complexes **2a** and **2b** were characterized by NMR and IR spectroscopy as well as elemental analysis.[8] The crystal structure of **2a** was determined by X-ray diffraction study (Figure 1). The W−Si bond length of **2a** (2.5206(8) Å) is much longer
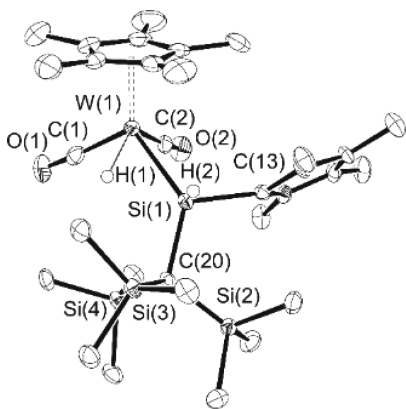

Figure 1. ORTEP drawing of **2a**. The thermal ellipsoids represent 50% probability. Hydrogen atoms except for H(1) and H(2) are omitted for clarity. Selected bond lengths (Å) and angles (deg): W(1)−Si(1) 2.5206(8); W(1)−C(1) 1.951(4); W(1)−C(2) 1.933(4); W(1)−H(1) 1.64(3); Si(1)−H(2) 1.40(3); Si(1)···H(1) 2.06(3); Si(1)−C(13) 1.989(3); Si(1)−C(20) 1.984(3); C(20)−Si(2) 1.908(3); C(20)−Si(3) 1.937(3); C(20)−Si(4) 1.917(3); C(1)−W(1)−C(2) 77.67(13); W(1)−Si(1)−C(13) 110.84(9); W(1)−Si(1)−C(20) 129.07(9); C(13)−Si(1)−H(2) 93.3(11); C(20)−Si(1)−H(2) 97.6(11); H(2)−Si(1)−W(1) 108.5(11).

than that of base-free silylene complex **1b** [2.3703(11) Å][6] and is in the ranges of those for base-stabilized silylene complexes (2.44−2.58 Å) and silyl complexes (2.47−2.69 Å).[9]

In the ^{1}H NMR spectrum of **2a** (C_6D_6, r.t.), the signal of SiH (5.50 ppm) is shifted substantially upfield compared with that of base-free silylene complex **1a** (10.39 ppm) (see Table 1 for comparison), and this chemical shift of **2a** is within the range of

those for tungsten-hydrosilyl complexes (4.4−7.3 ppm).[7,10] The signal of WH is observed at −6.37 ppm with satellite couplings (J_{WSi} = 54.6 Hz, J_{SiH} = 27.0 Hz). The J_{SiH} value is larger than 20 Hz, which implies that a weak Si···H bonding interaction analogous to that in **1a** exists.[6] In the ^{29}Si NMR spectrum, the signal of WSi (−16.7 ppm) is observed at the field much higher than those of normal base-stabilized tungsten−silylene complexes (58−145 ppm)[11,12] and is in the range of those for tungsten−hydrosilyl complexes (−51 to +61 ppm).[7,10] In the IR spectrum of **2a**, the wavenumbers of ν_{CO} bands (1871 and 1780 cm^{-1}) are considerably lower than those of base-free silylene complex **1a** (1928 and 1853 cm^{-1}),[6] indicating that the W center of **2a** is more electron-rich than that of **1a**.

When **1a-py** was treated with 2 equiv of ^{Me}IMe in C_6D_6, instantaneous and quantitative formation of **2a** was observed by ^{1}H NMR. The resulting reaction mixture was then heated at 50 °C for 78 h to accelerate the reaction of excess ^{Me}IMe with **2a**, and we unexpectedly observed the formation of $HC(SiMe_3)_3$ in 88% NMR yield.[8] After this heating, the ^{Me}IMe-stabilized hydrosilylyne complex $Cp^*(CO)_2WSiH(^{Me}IMe)_2$ (**3a**) was precipitated out of the reaction mixture as red crystals. Complex **3a** was isolated in 57% yield as very air-sensitive red thin crystals from a large-scale reaction at 70 °C for 1 day in which isolated **2a** and 1.2 equiv of ^{Me}IMe were employed. Complex **3b**, a C_5Me_4Et analogue of **3a**, was also synthesized by the same method.

Complexes **3a** and **3b** were characterized by NMR and IR spectroscopy as well as elemental analysis.[8] Once **3a** and **3b** were crystallized from organic solvents, **3a** and **3b** showed extremely poor solubility in various organic solvents (toluene, ether, THF, and fluorobenzene). ^{1}H and ^{29}Si{^{1}H} NMR spectral data of **3a** were therefore collected from a reaction mixture containing **3a**, **2a**, ^{Me}IMe, and $HC(SiMe_3)_3$ obtained by the reaction of **2a** with 1 equiv of ^{Me}IMe in THF-d_8 at 60 °C (see Figures S25 and S26).

The ^{1}H NMR spectrum of **3a** indicates that the two ^{Me}IMe moieties are chemically equivalent in solution. The ^{1}H NMR signal of SiH is observed at 5.83 ppm with satellite signals ($^1J_{SiH}$ = 136.6 Hz), which is upfield shifted compared with that of $Cp^*(CO)_2(H)W=Si(H)(Tsi)$ (**1a**) (10.39 ppm)[6] and is in the region for those of hydrosilyl complexes (4.4−7.3 ppm).[7,10] The satellite coupling $^1J_{SiH}$ of 136.6 Hz is much smaller than that of **2a** (156.4 Hz), indicating an increased p character of an Si orbital used for the formation of the Si−H bond in **3a**. In the ^{29}Si{^{1}H} NMR spectrum, the signal of WSi for **3a** appears at −25.3 ppm accompanied by satellite signals ($^1J_{WSi}$ = 247.0 Hz): The solid-state ^{29}Si NMR spectrum of isolated **3a**[8] also shows the WSi signal in the same region (−21.8 ppm). This ^{29}Si NMR chemical shift of **3a** is close to that of analogous NHC-stabilized chromium−silylyne complex $Cp(CO)_2CrSiBr(^{Me}I^iPr)_2$ (Chart 1E) (17.3 ppm).[1a] The difference between **3a** and **E**, i.e., the upfield shift of the signal of **3a**, is attributable to the shielding effect of the H atom on the Si atom. An electronic shielding effect by a H atom at Si was reported for silyl complexes $Cp^*(CO)_2(PMe_3)WSi(H)(Me)X$ (X = H, Cl).[10] The most remarkable spectroscopic feature is the satellite coupling $^1J_{WSi}$ of 247.0 Hz, which is much larger than those of **1a** (109.9 Hz) and **2a** (114.2 Hz). This value is also significantly larger than those of usual silyl (5−64 Hz)[6,7,10] and silylene (91−155 Hz)[6,12,13] complexes, suggesting a very large s character of the W and Si orbitals used for formation of the W−Si bond in **3a**. This is further supported by NBO analysis (vide infra).

Two ν_{CO} bands of **3a** (1741 and 1658 cm^{-1}) in the IR spectrum appear at much lower wavenumber region compared with those of **2a** (1871 and 1780 cm^{-1}) in which the silicon is

Table 1. Comparison of Some Important Spectroscopic Data and Bond Lengths of the Products

	^{1}H NMR		^{29}Si NMR		IR	X-ray	
	SiH (ppm)	$^1J_{SiH}$ (Hz)	WSi (ppm)	$^1J_{WSi}$ (Hz)	ν_{CO} (cm^{-1})	d(W−Si) (Å)	d(W−CO) (Å)
1a[6]	10.39	154.9	275.3	109.9	1928, 1853	2.3703(11)[a]	1.950(5), 1.964(5)[a]
1a-py	9.78 (br)	−	−	−	1871, 1782	2.4807(7)	1.932(3), 1.945(3)
2a	5.50	156.4	−16.7	114.2	1871, 1780	2.5206(8)	1.933(4), 1.951(4)
3a	5.83	136.6	−25.4	247.0	1741, 1658	2.363(4)[b]	1.900(5), 1.904(5)[b]

[a]Data of **1b**. [b]Data of **3b**.

coordinated by only one ^{Me}IMe. Obviously, π back-donation from the W center to the CO ligands in **3a** is much stronger than that in **2a** due to the strong electron-donation from two NHCs to the W center through Si. Exactly the same spectroscopic features are also observed for **3b**.

The X-ray crystal structure analysis[8] of **3b** confirmed its three-legged piano-stool structure consisting of a C$_5$Me$_4$Et, two COs, and a hydrosilylyne ligand [SiH] coordinated by two NHCs. The two W−C(CO) bond lengths [1.904(5), 1.900(5) Å] are shorter than the corresponding lengths in ^{Me}IMe-stabilized silylene complex **2a** [1.952(4), 1.933(4) Å], supporting a very strong π back-donation from the W center to the CO ligands in **3b**. The W−Si bond length of **3b** [2.363(4) Å], Figure 2, is significantly shorter than that of **2a** [2.5206(8) Å] and is comparable to the shortest known value for the W=Si double bonds of base-free silylene complexes (2.36−2.47 Å).[9]
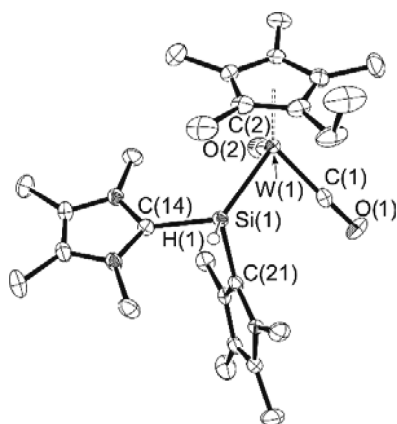

Figure 2. ORTEP drawing of **3b**. The thermal ellipsoids represent 50% probability. Hydrogen atoms except for H(1) are omitted for clarity. Selected bond lengths (Å) and angles (deg): W(1)−Si(1) 2.363(4); W(1)−C(1) 1.904(5); W(1)−C(2) 1.900(5); Si(1)−H(1) 1.43(4); Si(1)−C(14) 1.968(5); Si(1)−C(21) 1.913(5); C(1)−W(1)−C(2) 88.8(2); C(1)−W(1)−Si(1) 81.65(16); C(2)−W(1)−Si(1) 94.86(17); W(1)−Si(1)−H(1) 118.5(16); W(1)−Si(1)−C(14) 129.17(13); W(1)−Si(1)−C(21) 121.88(18); H(1)−Si(1)−C(14) 89.9(14); H(1)−Si(1)−C(21) 96.1(17); C(14)−Si(1)−C(21) 92.7(2).

A related NHC-stabilized chromium silylyne complex Cp-(CO)$_2$CrSiBr(^{Me}I^{i}Pr)$_2$ (**E**)[1a] reported by Filippou et al. also has a metal−silicon bond [Cr−Si = 2.2515(7) Å] that is considerably shorter than Cr−Si single bonds (2.361−2.660 Å). The authors suggested that this shortening of the Cr−Si bond in **E** was ascribable to a strong d$_\pi$(Cr) → σ*(Si−Br) hyperconjugation because complex **E** has an elongated Si−Br bond [2.4340(6) Å] compared with those of metal bromosilyl complexes (~2.314 Å).[1a]

To get further information on the bonding nature of the W−Si bond of **3b**, theoretical calculations (DFT/B3LYP) were performed on a model complex Cp(CO)$_2$WSiH(IMe)$_2$ (**3′**) (IMe = 1,3-dimethylimidazol-2-ylidene) using Gaussian 09 program.[8] For comparison, we also carried out the calculations on Cp(CO)$_2$WSiMe$_3$ (**G**) as a model of a silyl complex, which has a three-legged piano-stool geometry as in **3b** and **3′**. The W−Si bond length of **3′** [2.388 Å] is in the double-bond range (2.36−2.47 Å), while that of **G** [2.589 Å] is within the range of usual W−Si single bonds [2.48−2.68 Å].[9] Wiberg bond index[8] of the W−Si bond in **3′** [1.05] is much larger than that in **G** [0.85], implying that the W−Si bond of **3′** has some multiple bond character. NBO analysis[8] shows that the Si atom in **3′** uses the orbital having a very high s character to form the W−Si bond (Si: 47.7% s, 52.3% p), while it uses the orbitals bearing a high p character (Si: 15−19% s, 80−84% p) to form the Si−H and Si−C$_{NHC}$ bonds (see Table S9), in accord with the above-mentioned NMR data (large $^1J_{WSi}$ and small $^1J_{SiH}$) and also with the X-ray data of **3b** [the bond angles around the Si atom are close to 90°: H(1)−Si(1)−C(14) 89.9(14); H(1)−Si(1)−C(21) 96.1(17); C(14)−Si(1)−C(21) 92.7(2) °]. This is in sharp contrast with the bonding situation in the silyl complex **G** where the Si atom uses typical sp^3-hybrid orbitals for formation of the W−Si bond and the Si−C(Me) bonds (see Table S11). NBO analysis also suggests the existence of hyperconjugation similar to that reported for **E**. In the case of **3′**, there are two types of hyperconjugation, d$_\pi$(W) → σ*(Si−H) and d$_\pi$(W) → σ*(Si−C$_{NHC}$), judging from the occupancy coefficients for two σ* Si−C$_{NHC}$ bonds (0.14, 0.10) and a σ* Si−H bond (0.07) (Table S9): These values are significantly larger than those of three σ* Si−C$_{Me}$ bonds (0.03 each) of **G** (Table S11). These two types of hyperconjugation can be seen in the HOMO and HOMO−1 of **3′** (Figure S41). On the other hand, we estimate that these interactions are rather small, because there is no lengthening of the Si−C(substituent) bonds of real complex **3b** [1.968(5); 1.913(5) Å] compared with those of **2a** [Si−C$_{NHC}$ bond: 1.989(3) Å, Si−C$_{TSi}$ bond: 1.984(3) Å].[14] Considering these data, the shortening of the W−Si bond in **3b** is mainly ascribable to the high s character of the Si orbital that is used for formation of the W−Si bond.

Scheme 2 shows two possible reaction mechanisms for the formation of **3**. As mentioned above, **2** is thermally stable in the absence of ^{Me}IMe even at 70 °C, and the elimination of HC(SiMe$_3$)$_3$ does not proceed without additional ^{Me}IMe. Thus, the first step is probably the nucleophilic attack of ^{Me}IMe on the Si center of **2** that generates a sterically crowded transiton state **a**. After that, in path A, the steric crowding around the Si center in **a** pushes the C(SiMe$_3$)$_3$ group toward the hydrogen on the W center to induce 1,2-elimination of HC(SiMe$_3$)$_3$ to form **3**. In path B, it induces 1,1-elimination of HC(SiMe$_3$)$_3$ to generate ^{Me}IMe-stabilized metallosilylene **b** and subsequent 1,2-H migration from W to Si gives **3**. Although we have no strong evidence to rule out one of them, 1,1-elimination in path B could

Scheme 2. Possible Reaction Mechanisms for Formation of 3
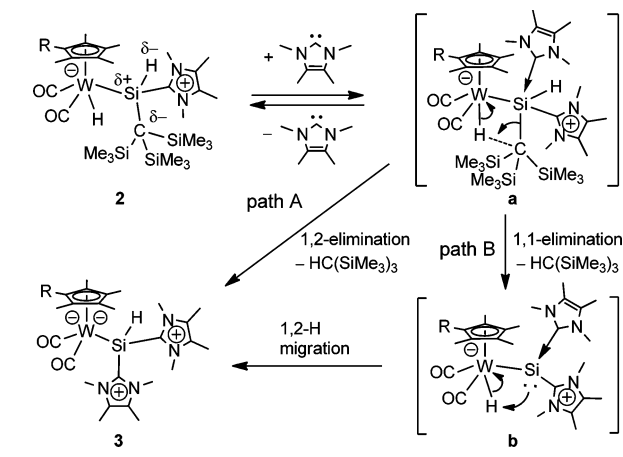
be more feasible, in consideration of Hoffman's theoretical calculations on dinuclear systems where 1,2-reductive elimination is suggested to be fundamentally unfavorable.[15]

In conclusion, we synthesized unprecedented NHC-stabilized hydrosilylyne complexes **3a** and **3b** from NHC-stabilized hydrido(alkylsilylene) complexes via unexpected alkane elimination. Complexes **3a** and **3b** are the first examples of base-stabilized mononuclear hydrosilylyne (SiH) complexes. The crystal structure of **3b** features a remarkably short W−Si bond length. Based on DFT calculations, we proposed two reasons for the shortening of the W−Si bond; (1) high s character of the W and Si orbitals used for the W−Si bond and (2) $d_\pi(W) \rightarrow \sigma^*(Si-H)$ and $d_\pi(W) \rightarrow \sigma^*(Si-C_{NHC})$ hyperconjugation. Importantly, synthesis of a silylyne complex from a silylene complex via alkane elimination has never been reported before, and this reaction therefore will develop a new general approach to the synthesis of base-stabilized silylyne complexes.

■ **ASSOCIATED CONTENT**

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06366.

> Detailed experimental procedures, characterization data, and X-ray crystallographic data (PDF)
> (CIF)
> (CIF)
> (CIF)

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Notes

The authors declare no competing financial interest.

■ **ACKNOWLEDGMENTS**

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(5) Although we describe **3a/3b** using a structure that has a W−Si single bond due to the lack of usual π-bonds, we use the term "base-stabilized silylyne complexes" for them rather than alternative description of "bis(imidazolium)-substituted silyl complexes," because **3a/3b** are fundamentally different from the usual silyl complexes as explained in the text.

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(14) Probably, the Si−C(substituent) bonds in **2a** have already been lengthened by steric repulsion between bulky ^{Me}IMe and Tsi groups at the Si atom. In sterically less hindered model complexes **3′** vs **G**, there is a slight lengthening in the Si−C(substituent) bond lengths from **G** (1.920, 1.904 Å) to **3′** (2.037, 1.985 Å). Similarly, the calculated Si−H bond length in **3′** (1.53 Å) is slightly longer than that in a typical tetrahedral silicon compound (SiH_4 1.48 Å).

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