**Silylene Complexes**

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# Stabilization of a Silaaldehyde by its $\eta^2$ Coordination to Tungsten

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**Abstract:** *Treatment of pyridine-stabilized silylene complexes* $[(\eta^5\text{-}C_5Me_4R)(CO)_2(H)W{=}SiH(py)(Tsi)]$ *(R = Me, Et; py = pyridine; Tsi = $C(SiMe_3)_3$) with an N-heterocyclic carbene* $^{Me}I^iPr$ *(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) caused deprotonation to afford anionic silylene complexes* $[(\eta^5\text{-}C_5Me_4R)(CO)_2W{=}SiH(Tsi)][H^{Me}I^iPr]$ *(R = Me (**1-Me**); R = Et (**1-Et**)). Subsequent oxidation of **1-Me** and **1-Et** with pyridine-N-oxide (1 equiv) gave anionic $\eta^2$-silaaldehyde-tungsten complexes* $[(\eta^5\text{-}C_5Me_4R)(CO)_2W\{\eta^2\text{-}O{=}SiH(Tsi)\}][H^{Me}I^iPr]$ *(R = Me (**2-Me**); R = Et (**2-Et**)). The formation of an unprecedented W-Si-O three-membered ring was confirmed by X-ray crystal structure analysis.*

Compounds containing Si=O double bonds have long been one of the most important synthetic targets in the chemistry of heavier main-group elements. These compounds are highly reactive because of a weak and strongly polarized Si–O π bond[1] (Figure 1, structures I and I′), which causes rapid and facile polymerization of monomeric $O{=}SiR_2$ species to give stable polysiloxanes $(R_2SiO)_n$.[1,2] Some specific stabilization is therefore essential for isolation of monomeric $O{=}SiR_2$ species. The first example of such compounds[3a] was synthesized by Driess and co-workers using donor–acceptor stabilization (Figure 1, type II).[3] Type III compounds (Figure 1) have also been prepared,[4] which demonstrated that isolation of $O{=}SiR_2$ species is possible only by stabilization with a donor group on the Si atom. As a notable achievement in the chemistry of Si=O compounds, Filippou and co-workers very recently successfully synthesized a cationic base-free silanone $[Cp^*(CO)_3CrSi({=}O)SIdipp][B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4]$ (SIdipp = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene; Cp* = $\eta^5$-$C_5Me_5$) in which one of the substituents on the silicon center was a metal fragment (Figure 1, I).[5]

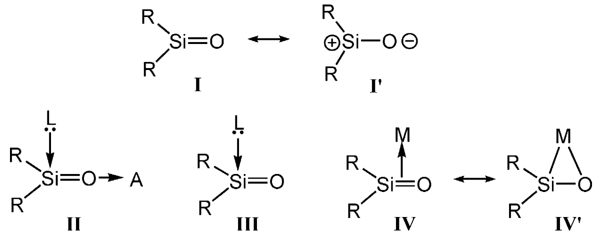

***Figure 1.*** Reported compounds containing Si=O double bonds. Structures I and I′: Silanone $O{=}SiR_2$ and its zwitterionic structure. II: silanone stabilized by a donor–acceptor interaction. III: silanone stabilized by coordination of a base. Structures IV and IV′: $\eta^2$-silanone complex. L: = Lewis base, A = Lewis acid or metal, M = transition metal.

Although, as mentioned above, the synthesis of several different types of Si=O compounds have been reported, transition-metal-coordinated Si=O compounds are still rare. A base-stabilized $\eta^1$-silanone complex $[Cp^*(CO)_2W(SiMe_3)\text{-}\{O{=}SiMes_2(DMAP)\}]$ (DMAP = 4-(dimethylamino)pyridine; Figure 1, type II) was reported by Ueno and co-workers.[3d] However, to our knowledge, there have been no reports on the isolation of a transition-metal complex in which the Si=O double bond is coordinated to a transition metal in a $\eta^2$ fashion (Figure 1, structures IV and IV′), although the generation of $\eta^2$-silanone complexes has been hypothesized in some reactions.[6]

Herein we report the first synthesis of $\eta^2$-silaaldehyde complexes $[(\eta^5\text{-}C_5Me_4R)(CO)_2W\{\eta^2\text{-}O{=}SiH(Tsi)\}][H^{Me}I^iPr]$ (R = Me (**2-Me**), R = Et (**2-Et**); Tsi = $C(SiMe_3)_3$, $^{Me}I^iPr$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) obtained through development of a new synthetic route to anionic silylene complexes $[(\eta^5\text{-}C_5Me_4R)(CO)_2W{=}SiH(Tsi)][H^{Me}I^iPr]$ (R = Me (**1-Me**); R = Et (**1-Et**)) as the precursor complexes.

An anionic silylene complex **1-Me** was synthesized by proton abstraction from a base-stabilized silylene complex $[Cp^*(CO)_2W(H){=}SiH(py)(Tsi)]$[7] with $^{Me}I^iPr$ (1 equiv) in toluene/THF solution (Scheme 1). Complex **1-Me** was isolated as red crystals in 79% yield after recrystallization. Complex **1-Et**, a $C_5Me_4Et$ analogue of **1-Me**, was also synthesized by the same procedure. Complexes **1-Me** and **1-Et** were characterized by NMR and IR spectroscopy as well as elemental analysis.[8] It should be noted here that anionic silylene complexes, such as **1-Me** and **1-Et**, have been rarely reported.[9]

In the $^1$H NMR spectrum of **1-Me** in [D$_8$]THF, no signal for the W-H fragment is detected but a new C2 proton signal for the imidazolium counter cation appears at $\delta = 8.75$ ppm instead. The $^1$H chemical shift of SiH and the $^{29}$Si chemical shift of WSi for **1-Me** (SiH: $\delta_H = 9.99$ ppm; WSi: $\delta_{Si} = 286.1$ ppm) are close to those of a base-free, neutral silylene complex $[Cp^*(CO)_2W(H){=}SiH(Tsi)]$ (**A**; SiH: $\delta_H = 10.39$ ppm; WSi: $\delta_{Si} = 275.3$ ppm),[10a] which is consistent with the "silylene complex" nature of **1-Me**. Notably, the coupling constant between tungsten and silicon for **1-Me** ($^1J_{W-Si} = 281.3$ Hz) is much larger than those of neutral

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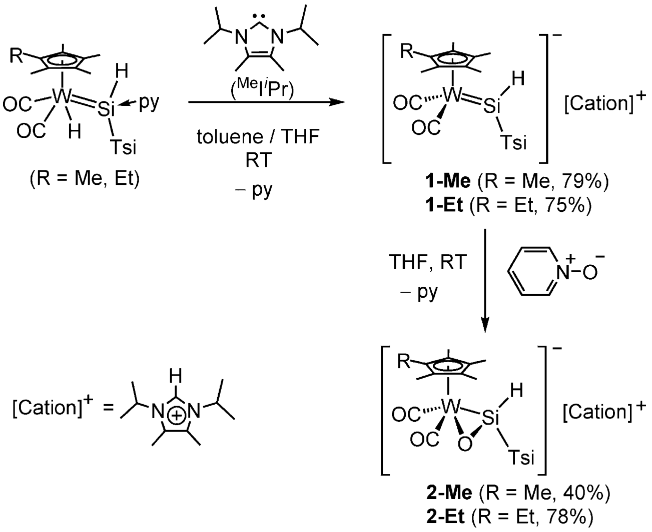


*Scheme 1.* Synthesis of $\eta^2$-silaaldehyde complexes **2-Me** and **2-Et** from anionic silylene complexes **1-Me** and **1-Et**. py = $NC_5H_5$, Tsi = $C(SiMe_3)_3$.

tungsten–silylene complexes (91–155 Hz).[10] The $^{13}C\{^1H\}$ NMR spectrum of **1-Me** shows a single resonance signal for two CO ligands at $\delta = 243.6$ ppm, suggesting this molecule is $C_s$-symmetric in solution. In the IR spectrum, the CO stretching bands for **1-Me** are considerably shifted to lower wavenumbers (1801 and 1716 $cm^{-1}$) compared with those of neutral silylene complex **A** (1928 and 1853 $cm^{-1}$),[10a] obviously as a result of the strong back donation from the highly electron-rich W center of the anionic component of **1-Me**.

The structure of **1-Me** was determined by X-ray crystal structure analysis (Figure 2).[8] The W–Si bond length (2.3367(17) Å) is considerably shorter than that of neutral silylene complex **A** (2.3703(11) Å),[10a] and the two W–C(carbonyl) bond lengths (1.958(7) and 1.924(6) Å) are also shorter than those of **A** (1.964(5) and 1.950(5) Å).[10a] The shortening of these W–Si and W–C(carbonyl) bonds is attributable to the increased back-donation from the highly electron-rich W center to the silylene and CO ligands. The C23–H23 vector of the counter cation is directed toward the O2 atom and the distance between C23 and O2 (3.13 Å) is close to the shortest C···O distance of a C–H···O hydrogen bond (circa 3.0 Å) reported to date,[11] indicating the existence of a C–H···O hydrogen bond in the crystal.

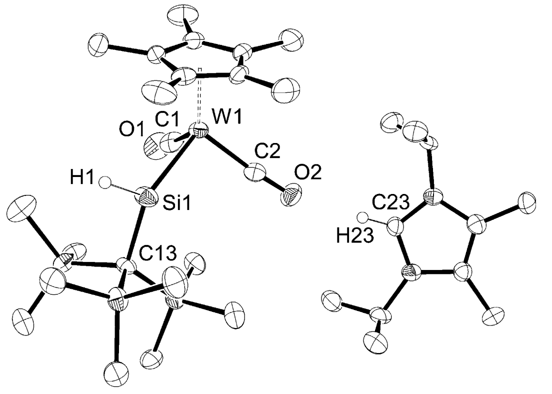


*Figure 2.* ORTEP drawing of **1-Me**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms, except H1 and H23, are omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–Si1 2.3367(17), W1–C1 1.958(7), W1–C2 1.924(6), O2···C23 3.13, Si1–H1 1.50(6), Si1–C13 1.918(5), C23–H23 0.94(5); C1-W1-C2 89.5(2), C2-W1-Si1 95.43(17), Si1-W1-C1 87.91(19), W1-Si1-C13 144.32(18), C13-Si1-H1 100(2), H1-Si1-W1 115(2).

Treatment of anionic complex **1-Me** with pyridine-*N*-oxide ($C_5H_5N^+$-$O^-$) in THF at room temperature resulted in the instantaneous formation of $\eta^2$-silaaldehyde complex **2-Me** (Scheme 1). Complex **2-Me** was isolated as highly air-sensitive red crystals in 40% yield after recrystallization from an $Et_2O$ solution of **2-Me** layered with *n*-hexane. Similarly, the $C_5Me_4Et$ analogue **2-Et** was isolated in 78% yield. Complex **2-Me** is unstable in organic solvents (THF, benzene, and toluene) at room temperature (half-life $t_{1/2} \approx 12$ h in $C_6D_6$).[8]

In the $^1H$ NMR spectrum of **2-Me** in $C_6D_6$, the signal for the SiH moiety appears at $\delta = 4.29$ ppm with satellite signals coupled with $^{29}Si$ ($^1J_{Si-H} = 190.6$ Hz). The large $J_{Si-H}$ coupling constant supports the structure with the H atom directly bonded to the Si atom. The signal for the aromatic ring proton in the imidazolium cation is detected at $\delta = 10.05$ ppm, with the value being shifted downfield compared with that of **1-Me** ($\delta = 8.75$ ppm).[11f] Additionally, the $^{13}C\{^1H\}$ NMR spectrum of **2-Me** in $[D_8]$THF at 250 K displays a broad resonance signal at $\delta = 133.7$ ppm. This signal can be assigned to the C2 carbon of the imidazolium cation $[H^{Me}I^iPr]^+$ because its chemical shift is nearly identical to that of the corresponding signal for $[H^{Me}I^iPr][PF_6]$[12] in $[D_8]$THF ($\delta = 130.4$ ppm).[11e,f] These results confirm that **2-Me** exists as an ion pair in solution, that is, an ion pair between the anionic complex $[Cp^*(CO)_2W\{\eta^2\text{-}O{=}SiH(Tsi)\}]^-$ and the imidazolium cation $[H^{Me}I^iPr]^+$. The two CO signals detected at $\delta = 246.7$ and 246.8 ppm in the $^{13}C$ NMR spectrum indicate the presence of a chiral center at the W atom, which is consistent with the structure of **2-Me** shown in Scheme 1. The $^{29}Si\{^1H\}$ NMR spectrum of **2-Me** ($[D_8]$THF at 250 K) exhibits two signals for WSi ($\delta = -21.8$ ppm, $^1J_{W-Si} = 42.1$ Hz) and SiMe (−1.7 ppm). Although the chemical shift ($\delta_{Si}$) and coupling constant ($^1J_{W-Si}$) for the WSi fragment are both much smaller than those for the anionic silylene complex **1-Me** ($\delta_{Si} = 286$ ppm, $^1J_{W-Si} = 281$ Hz), they are within the ranges typical for tungsten–hydrosilyl complexes ($\delta_{Si}$ from −51 to +61 ppm, $^1J_{W-Si} = 5$–$64$ Hz),[13] suggesting that the Si moiety on the W center of **2-Me** takes on considerable character of a silyl ligand. In the IR spectrum (KBr), the two $\nu$(CO) bands of **2-Me** (1830 and 1736 $cm^{-1}$) appear in approximately the same region as those of anionic complex **1-Me** (1801 and 1716 $cm^{-1}$), supporting the conclusion that complex **2-Me** is anionic. In addition, the $\nu$(SiH) band is detected at 2038 $cm^{-1}$. The same spectroscopic features are detected for **2-Et**.[8]

The structure of silaaldehyde complex **2-Et** was unambiguously confirmed by X-ray crystal structure analysis.[8] One of three independent molecules in the unit cell is depicted in Figure 3 (molecule A),[14] which clearly shows that the introduced O(3) atom bridges the W and Si atoms to form a W-Si-O three-membered ring. Complex **2-Et** is the first isolated and structurally determined $\eta^2$-silaaldehyde complex.

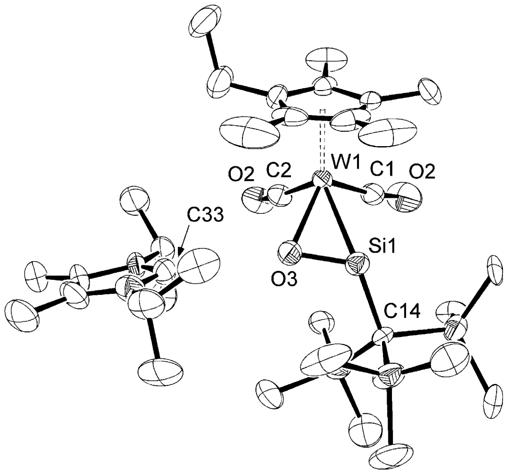
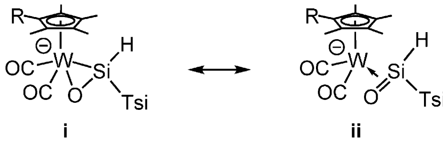


*Figure 3.* ORTEP drawing of one of the three independent molecules of **2-Et** (molecule A). Thermal ellipsoids are set at 50% probability. The hydrogen atom on Si1 was not found. Other hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: W1−Si1 2.475(3), W1−O3 2.242(6), Si1−O3 1.637(7), W1−C1 1.872(10), W1−C2 1.935(10), O3···C33 3.11; Si1-W1-O3 40.2(2), W1-O3-Si1 77.6(3), O3-Si1-W1 62.2(1), C1-W1-C2 76.8(4).

Though the position of the H atom on the Si center could not be determined, the existence of the SiH moiety is strongly supported by the detection of both a $^{1}$H NMR signal and a $\nu$(SiH) band attributable to it (see above). The W−Si bond length (2.475(3) Å) is close in value to the shortest reported W−Si bond lengths, which normally fall within the range 2.48–2.68 Å.[15] The Si−O bond length (1.637(7) Å) is also a value typical of normal Si−O single bond lengths (1.61–1.67 Å),[16] and is longer than those of previously reported base-stabilized Si=O compounds (1.54–1.58 Å).[3,4] The W−O bond length (2.242(6) Å) is longer than typical W−O single bond lengths (1.87–1.93 Å)[17] and is also longer than those of $\eta^2$-aldehyde and $\eta^2$-ketone complexes (1.95–2.16 Å),[18] but falls within the range of standard W←O coordinate bond lengths (2.14–2.39 Å).[19] The short contact between O3 and the imidazolium ring carbon C33 (3.11 Å) implies the existence of a C−H···O hydrogen bond, which is analogous to that in the anionic silylene complex **1-Me**. However, importantly, the oxygen atom that forms the hydrogen bond changes from the carbonyl oxygen in **1-Me** to the bridging oxygen in **2-Et**, which implies that the O3 atom in **2-Et** is highly electronegative.

It is suggested that the hydrogen bond found in the crystal structure of **2-Et** is also maintained in solution, based on the chemical shift of the aromatic ring proton of the imidazolium cation ($\delta = 9.70$ ppm).[11f] However, the bond is relatively weak and a cation exchange occurs easily. Thus, treatment of **2-Me** with 2 equiv of [PPh$_4$]Br in [D$_8$]THF resulted in 72% replacement of the imidazolium cation [H$^{\mathrm{Me}}$I$^{i}$Pr]$^+$ with the [PPh$_4$]$^+$ cation. After this partial replacement, an upfield shift of all resonance signals attributable to fragments of the anionic part of **2-Me**, that is, SiMe, Cp*, and SiH, was detected. This upfield shift can be rationalized by a partial loss of the hydrogen bond between the bridging O atom and the imidazolium C−H moiety ($\Delta\delta_{\mathrm{H}}$/ppm: −0.03 (SiMe), −0.06 (Cp*), −0.07 (SiH); see Figure S20 in the Supporting Information for details).

The structures of $\eta^2$-silaaldehyde complexes **2-Me** and **2-Et** can be described in terms of resonance between two canonical forms (Scheme 2). Considering the following spectroscopic and structural features of **2-Me** and **2-Et**: 1) the low chemical shift of the $^{29}$Si NMR signal of the coordinating Si atom, 2) the shift towards lower wavenumbers of the $\nu$(CO) bands, and 3) the bond lengths in the W-Si-O three-membered-ring framework (particularly the Si−O bond length corresponding to the single bond), it would be expected that canonical form i is the more dominant form.



*Scheme 2.* Possible canonical forms for the anionic components of **2-Me** and **2-Et**.

To better understand the bonding and electronic structure of silaaldehyde complex **2**, DFT calculations were performed on a model complex for the anionic part of **2**, namely [($\eta^5$-C$_5$H$_5$)W(CO)$_2${$\eta^2$-O=SiH[C(SiH$_3$)$_3$]}]$^-$ (**2′**), together with a model complex for **1**, namely [($\eta^5$-C$_5$H$_5$)W(CO)$_2$=SiH{C(SiH$_3$)$_3$}]$^-$ (**1′**), at the B3LYP/6-31+G(d,p) level.[8,20] The optimized structure of **2′** (Figure 4, left) corresponded well to the molecular structure of the anionic part of **2-Et** determined by X-ray crystal structure analysis (Table S9).[21] The calculated position of the H atom on the coordinating Si atom allows us to estimate the hybridization of the Si atom of **2′**. Namely, the sum of the angles between the three bonds around the coordinating Si atom except the W−Si bond is 330.7°, which is close to that around an atom with ideal sp$^3$ hybridization (328.5°). A Kohn–Sham orbital corresponding to d$_{zx}$(W)→$\pi^*$(Si=O) back donation is found in HOMO-2 (Figure 4, middle). This orbital mainly contributes to the formation of the W−Si σ bond. On the other hand, HOMO-6

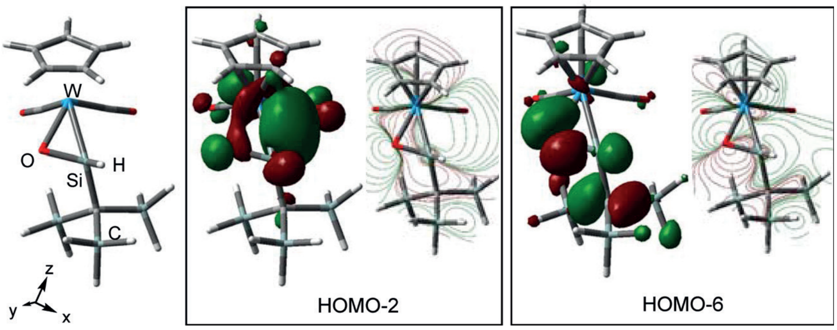


*Figure 4.* Optimized structure (left) and important Kohn–Sham orbitals of **2′** (middle and right).

(Figure 4, right) shows a σ donation from the π(Si=O) orbital to the vacant $d_{z^2}$ orbital of the W center, according to detailed analysis (see page S27 in the Supporting Information). The existence of these orbitals indicates that the W−Si−O ring is formed by synergistic σ-donation/π-back-donation interactions between the d orbitals of the W center and the π(Si=O) bonding and π*(Si=O) antibonding orbitals of the silaaldehyde. The π back donation is very strong as a result of the anionic W center (see below), and the resulting complex shows a pronounced metallacycle character. The HOMO and HOMO-1 mainly consist of $d_{yz}$(W) and $d_{x^2-y^2}$(W) contributions, respectively (Figure S26-1). In these HOMO and HOMO-1 orbitals, we find weak but non-negligible antibonding interactions between the d orbitals of the W center and the lone pairs of the O atom, which cause the elongation of the W−O bond.

The Wiberg bond indices (WBIs) indicate that both the W−Si and Si−O bonds in **2′** have strong single-bond character. The WBI for the W−Si bond in **2′** (0.74) is nearly half of that for the W=Si bond in silylene complex **1′** (1.50). The WBI for the Si−O bond in **2′** (0.75) is also roughly half of that for the Si=O double bond in the model silaaldehyde $O{=}SiHC(SiH_3)_3$ (1.36; Tables S8, S10, and S11). The double-bond character of the Si−O bond is nearly lost because of the strong back donation from the anionic W center to the π*(Si=O) orbital. Indeed, the negative NPA (natural population analysis) charge of the W in **2′** ($-0.69\,e$) is greatly decreased compared with that of anionic silylene complex **1′** ($-1.24\,e$), while the bridging O atom of **2′** (Si*O*: $-1.03\,e$) is highly negatively charged (Figure S29). As a result, the Si−O bond of **2′** is strongly polarized as $Si^{\delta+}(+1.52\,e)$–$O^{\delta-}(-1.03\,e)$. This accumulated negative charge on the O atom and the W atom would produce strong repulsion between them, which is also responsible for the elongation of the W−O bond. These results from WBI analysis and charge distribution also suggest the dominant contribution of canonical form i in Scheme 2 for complexes **2-Me** and **2-Et**.

In conclusion, we have successfully synthesized the first examples of silaaldehyde stabilized by $\eta^2$ coordination of the Si=O bond to an anionic W center. The spectral data, molecular structures, and DFT calculations strongly indicate that these silaaldehyde complexes can be regarded as M-Si-O three-membered metallacycles rather than Si=O π complexes. This distinctive structural feature is clearly as a result of very strong metal-to-ligand π back donation. Research on the reactivity of **2** is in progress.

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[8] See the Supporting Information for details. Synthetic procedures, crystallographic data, and theoretical calculations are included in the Supporting Information. CCDC 1401273 (**1-Me**) and 1401274 (**2-Et**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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[15] W–Si single bond lengths were taken from the Cambridge Structural Database, CSD version 5.35 (November **2014**).

[16] For Si–O single bond lengths in compounds with tetracoordinated silicon and dicoordinated oxygen atoms, see: M. Kaftory, M. Kapon, M. Botoshansky in *The Chemistry of Organic Silicon Compounds*, *Vol. 2*, Part 1 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, Chapter 5, pp. 181 – 265.

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[19] W–O coordinate bond lengths in ether complexes [W←OR$_2$] (R = H or alkyl) were taken from the Cambridge Structural Database, CSD version 5.35 (November **2014**).

[20] Some theoretical calculations on $\eta^2$-silanone complexes have been reported. See: a) O. Uzan, Y. Gozin, J. M. L. Martin, *Chem. Phys. Lett.* **1998**, *288*, 356 – 362; b) S. Sakaki, T. Takayama, M. Sugimoto, *Organometallics* **2001**, *20*, 3896 – 3905.

[21] Optimization of the real complex **2-Me** that contains a counter cation was also performed (**2-Me**-opt). The structural parameters of the anionic part of **2-Me**-opt were close to those of **2′** (Figure S25 and Table S9). Therefore, here we discuss, for simplicity, the molecular orbitals of **2′**.

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