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A hydrogen-bridged bis(silylene) complex as a platform for small molecule activation *via* adjacent metal–ligand cooperation†

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Effective activation of small molecules (alcohol, phenol, ketones, amine, etc.) by a hydrogen-bridged bis(silylene) complex, which has two adjacent Lewis acidic centers and a hydridic bridging hydrogen with weak Si...H bonds, is described, along with product characterization by NMR and X-ray diffraction studies.

Activation of small molecules is one of the leading topics in current chemistry. Recent extensive studies in this field have increasingly provided new strategies beyond the traditional activation that relies on coordinatively unsaturated transition-metal (TM) centres. Activation *via* frustrated Lewis acid–base pairs (FLP)^{1–3} and bifunctional low-valent main group element species^{4–8} and activation *via* metal–metal^{9,10} and metal–ligand cooperation^{11,12} have emerged as promising new strategies for molecular activation. In particular, the metal–ligand cooperative activation has been found in a variety of complexes in the past decade, from originally suggested complexes where a metal centre and the active moiety of the ligand are indirectly connected,^{11,12} to those that have a direct metal–ligand bond, *e.g.*, metal–tetryl double^{13,14} and triple^{15–17} bonds between TM and heavier group 14 elements.

In this regard, we have previously reported the synthesis and characterization of hydrogen-bridged bis(silylene) complexes, which have novel four-centre bonding interaction and can be described as two canonical forms where the Si–H is activated at the adjacent silylene ligand by coordinating its σ -bonding electrons^{18,19} (Fig. 1). These complexes have two Lewis acidic silicon centres close to each other and a hydridic bridging hydrogen atom, as suggested by detailed DFT calculations, which inspired us to investigate the reactivity toward small molecules. Here we report the reactions of Cp*W

(CO)₂{Me₂Si...H...Si(^tBu)Me} (1), which was previously synthesised,¹⁸ with several small nucleophiles (alcohol, phenol, ketones, amine, *etc.*) and product characterization including single-crystal X-ray diffraction (SC-XRD) analysis of five complexes.

Treatment of 1 with 1 equiv. of phenol at room temperature almost instantaneously led to an air-sensitive phenoxy-bridged bis(silylene) complex Cp*W(CO)₂{Me₂Si...O(Ph)...Si(^tBu)Me} (2) in 91% NMR yield, accompanied by evolution of H₂ (4.46 ppm in C₆D₆) (eqn (1)). The use of *p*-cresol instead of phenol led to an analogous complex Cp*W(CO)₂{Me₂Si...O(*p*-tol)...Si(^tBu)Me} (3). Complexes 2 and 3 were isolated in 68% and 65% yields, respectively, after recrystallisation and characterised by ¹H, ¹³C and ²⁹Si NMR, IR spectroscopy and elemental analysis. The appearance of moderately downfield-shifted ²⁹Si NMR resonances (108.0 and 121.8 ppm) of 2 is indicative of the formation of base-stabilised silylene ligands,^{20–25} and these resonances are comparable to those of the methoxy-bridged bis(silylene) complex Cp*W(CO)₂{Me₂Si...O(Me)...Si(^tBu)Me} (A) (97.5 ppm for SiMe₂ and 111.4 ppm for SiMe^tBu).¹⁸ Thus, as expected, 1 reacted with weak protic acids at the bridging hydrogen moiety, in line with its hydridic nature previously reported, resulting in the replacement of the bridging hydrogen atom with the aryloxy group by releasing dihydrogen. Complex 1 also reacted with ^tPrOH just as MeOH¹⁸ despite being bulkier, to afford a similar complex Cp*W(CO)₂{Me₂Si...O(^tPr)...Si(^tBu)Me} (4). The extremely easy



Fig. 1 Description of hydrogen-bridged bis(silylene) complexes: charge distribution and the Si–H bond activation form on the adjacent silylene ligand. R = alkyl groups.

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and clean occurrence of the reaction and concomitant dihydrogen evolution can be notable features.



Remarkably, the exactly same complex **4** was formed in an excellent yield of 75% by the treatment of **1** with acetone at room temperature (Scheme 1). This reaction is viewed as one-pot hydro-bis(silylation) of the carbonyl compound, which is unprecedented, to the best of our knowledge. This reaction



Scheme 1 Reactions of **1** with ketones.



Fig. 2 Crystal structure of $Cp^*W(CO)_2\{Me_2Si\cdots O(Ad)\cdots Si^tBuMe\}$ (**5**). Selected interatomic distances (Å): W–Si1 2.535(3), W–Si2 2.500(3), Si1–O3 1.871(8), Si2–O3 1.817(8). Hydrogen atoms have been omitted for clarity.

can also be viewed as the insertion of the carbonyl compound into the Si–H–Si moiety in the WSiHSi ring, demonstrating a new pattern of insertion: the two ligand moieties located next to each other acted as a cooperative multi-site activation platform toward the substrate, enabling the one-pot hydro-bis(silylation) reaction. During the reaction, the bridging hydrogen atom of **1** was efficiently and rapidly transferred onto the carbonyl carbon atom, implying a concerted process. It should be noted here that there are several examples of insertion of olefins^{26–28} and carbonyl compounds^{29,30} into the Si–H bond of hydrosilylene complexes with a $Si(sp^2)$ –H bond. In the former cases, a concerted mechanism based on direct addition of the olefin C=C bond to the $Si(sp^2)$ –H bond is proposed, while several mechanisms are discussed for the latter cases.

A similar reaction occurred on using adamantanone with the quantitative formation of $Cp^*W(CO)_2\{Me_2Si\cdots O(Ad)\cdots Si^tBuMe\}$ (**5**) (Ad = adamantyl). Complexes **4** and **5** were characterized based on multiple spectroscopic data and the structure of **5** was confirmed by SC-XRD analysis. The molecular structure of **5** is illustrated in Fig. 2, which clearly reveals the WSiOSi four-membered-ring structure with the O(Ad) group bridging over the two silicon moieties. The W–Si bond lengths [2.535(3), 2.500(3) Å] are slightly longer than those of a previously reported methoxy-bridged tungsten complex $Cp^*W(CO)_2\{Me_2Si\cdots O(Me)\cdots SiMe_2\}$ [2.490(3), 2.490(3) Å],³¹ but are very close to those of complex **A** [2.537(3), 2.509(3) Å] (see Fig. S26 in the ESI†), which has exactly the same bis(silylene) moieties as those of **5**. The Si–O bond lengths [1.871(8), 1.816(8) Å] at the bridging moiety of **5** are significantly longer than those of usual Si–O single bonds (1.63–1.65 Å),³² evidently indicating their coordination character. In the ^{29}Si NMR spectrum of **5**, two resonances were observed at 99.3 and 110.2 ppm, accompanied by clear satellite J_{Wsi} couplings of 83 and 117 Hz, respectively (Table 1). The chemical shift values of **5** are close to those of **A** and **2**. The spin–spin coupling constants J_{Wsi} , which reflect the s-character of the nuclei involved in the bond, are nearly intermediate between those of the silyl (sp^3 Si) and silylene (sp^2 Si) ligands: for instance, 30.5 Hz for WSiMe₃ and 154.9 Hz for W = SiMe₂ in $Cp^*W(CO)_2(=SiMe_2)$ (SiMe₃).³³ All these features are characteristics of base-stabilised bis(silylene) complexes.²⁴

To further examine the reactivity, we also tested the reactions of **1** with carbonyl compounds bearing functional groups, *i.e.* a vinyl group or an ethynyl group. Although there are two possible products that can be formed *via* 1,2-addition

Table 1 $^{29}Si\{^1H\}$ NMR (C_6D_6) data of complexes **A** and **2–10**

Complex	$^{29}Si\{^1H\}$ NMR (J_{Wsi}) ^b	Complex	$^{29}Si\{^1H\}$ NMR (J_{Wsi}) ^b
A ^a	97.5 (87.1) SiMe ₂ , 111.4 (94.1) SiMe ^t Bu	6	102.6, 115.3
2	108.0, 121.8	7	— ^c
3	106.9 (93), 126.4 (116)	8	100.8, 117.7
4	99.3, 110.2	9	22.9 (118) SiHMe ^t Bu, 101.4 SiMe ₂
5	99.1 (82.9), 120.8 (116.9)	10	26.9 (70.4) SiHMe ^t Bu, 86.7 (114.5) SiMe ₂ ←DMAP

^a From ref. 18. ^b ppm (Hz). ^c Not obtained due to thermal instability.

or 1,4-addition, both reactions of **1** with methyl vinyl ketone and ethyl vinyl ketone selectively gave rise to $\text{Cp}^*\text{W}(\text{CO})_2\{\text{Me}_2\text{Si}\cdots\text{O}[\text{CHR}'(\text{CH}=\text{CH}_2)]\cdots\text{Si}(\text{tBu})\text{Me}\}$ (**6**: $\text{R}' = \text{Et}$, **7**: $\text{R}' = \text{Me}$) in nearly quantitative yields. Thus, the 1,2-addition type of reaction solely occurred. In the case of **6**, there were two diastereomeric isomers in the solution, and one of them was crystallised and structurally confirmed by SC-XRD analysis. The molecular structure of the crystal is depicted in Fig. 3(a), which clearly reveals its alkoxy-bridged bis(silylene) backbone with a four-membered ring. The main bond distances and angles quite resemble those of **5** (Table S2 in the ESI†). The presence of a vinyl group on the alkoxy bridging ligand is evidenced by the C21–C22 bond distance of 1.292(8) Å, which is considerably shorter than the normal C–C single bond distance of the ethyl group [C23–C24 [1.435(8) Å]]. In the ^1H NMR spectrum, two sets of resonances for the major and minor diastereomers appeared. For instance, two resonances of Cp^* were observed at 1.93 and 1.94 ppm with a 5 : 3 intensity. The H_a proton of the vinyl group ($-\text{CH}_a=\text{CH}_b\text{H}_c$) appeared with a pattern of ddd (doublet of doublet of doublet) at 5.66 ppm (major) and at 5.66 ppm (minor) with a good separation (see Fig. S13–2†). The other signals were rationally assigned using multiple techniques such as ^1H – ^1H COSY and ^1H – $^{29}\text{Si}\{^1\text{H}\}$ COSY measurements (Fig. S14 and S16†). Complex **7** was extremely thermally unstable to decompose but its structure was supported by HRMS (high-resolution mass spectrum) and the similarity of the resonances in the ^1H NMR (Fig. S18†) and IR (νCO) bands of **7** to those of **6** (see the ESI†).

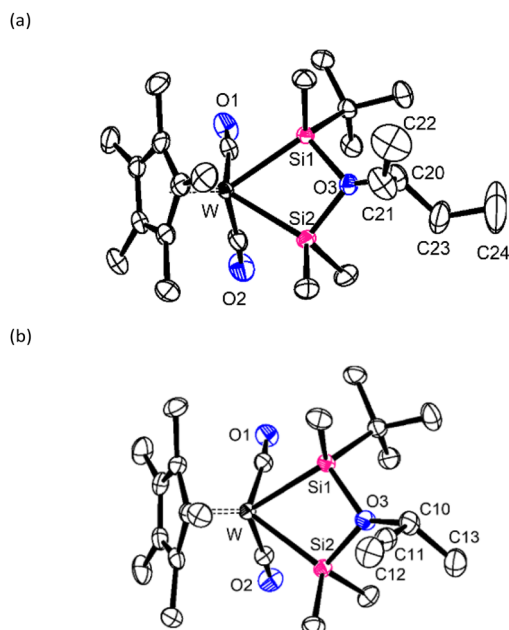


Fig. 3 Crystal structures of (a) $\text{Cp}^*\text{W}(\text{CO})_2\{\text{Me}_2\text{Si}\cdots\text{O}[\text{CHEt}(\text{CH}=\text{CH}_2)]\cdots\text{Si}(\text{tBu})\text{Me}\}$ (**6**) and (b) $\text{Cp}^*\text{W}(\text{CO})_2\{\text{Me}_2\text{Si}\cdots\text{O}[\text{CHMe}(\text{C}\equiv\text{CH})]\cdots\text{Si}(\text{tBu})\text{Me}\}$ (**8**). Selected interatomic distances (Å): W–Si1 2.5188(9), W–Si2 2.5037(9), Si1–O3 1.828(3), Si2–O3 1.813(3), C21–C22 1.292(8), C23–C24 1.435(8) for **6**; W–Si1 2.5236(13), W–Si2 2.5049(13), Si1–O3 1.829(4), Si2–O3 1.818(4), C11–C12 1.174(8) for **8**. Hydrogen atoms have been omitted for clarity.

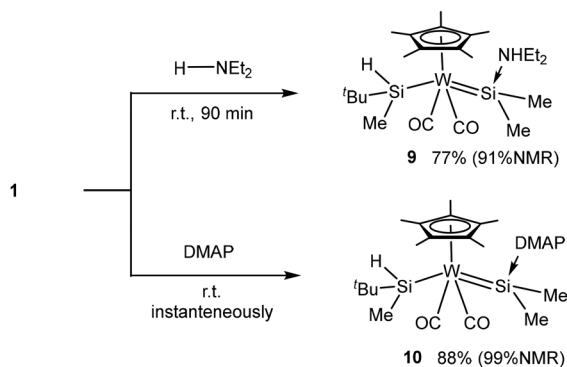
Previously, Sakaba *et al.* demonstrated that an alkynyl moiety can be coordinated to the silylene ligand by its $\text{C}\equiv\text{C}$ triple bond in the formation of $\text{Cp}^*(\text{OC})_2\text{W}(\text{SiPh}_2)(\text{C}\equiv\text{C}^t\text{Bu})$.³⁴ If a similar coordination of the alkynyl moiety of 3-buten-2-one to a silylene ligand is possible, we could expect the formation of a cyclic base-stabilized silyl(silylene) complex **a** (Scheme 2) by the reaction with **1**. However, instead of the expected complex **a**, exclusive 1,2-addition at the $\text{C}=\text{O}$ bond occurred to form the four-membered-ring complex $\text{Cp}^*\text{W}(\text{CO})_2\{\text{Me}_2\text{Si}\cdots\text{O}[\text{CHMe}(\text{C}\equiv\text{CH})]\cdots\text{Si}(\text{tBu})\text{Me}\}$ (**8**). SC-XRD analysis [Fig. 3(b)] confirmed the structure of **8** possessing an ethynyl group on the alkoxy bridging ligand, as indicated by the very short C11–C12 distance [1.174(8) Å]. The ^{29}Si NMR resonances that resemble those of **2–6** are consistent with its structure (Table 1).

Furthermore, we tested the reaction with a secondary amine to clarify whether the N–H bond can be activated or not in this system. No N–H bond activation of the amine occurred in the reaction with **1** unlike the O–H bond of alcohol and phenol. Instead, coordination of the N lone pair to the silylene moiety led to a base-stabilized silyl(silylene) complex without a ring structure, $\text{Cp}^*(\text{OC})_2\text{W}(\text{SiHMe}^t\text{Bu})(=\text{SiMe}_2\leftarrow\text{NHMe}_2)$ (**9**). A similar simple coordination occurred on using a more basic substrate, dimethyl aminopyridine (DMAP), to afford $\text{Cp}^*(\text{OC})_2\text{W}(\text{SiHMe}^t\text{Bu})(=\text{SiMe}_2\leftarrow\text{DMAP})$ (**10**), whose structure was also confirmed by SC-XRD (Fig. S27 and Table S2†). Both complexes exhibited clearly two ^{29}Si NMR resonances in very different fields at around 20–30 and 86–100 ppm for silyl and base-coordinated silylene ligands, respectively (Table 1). These examples indicate the convertibility of the bridging form of the SiHSi moiety of **1** into the open form, *i.e.* the hydrosilyl-silylene complex (Scheme 3).

The mechanisms for these unique reactions of **1** with ROH and $\text{O}=\text{CR}_2$ are not clear yet at present but the main route can be considered as follows: it starts from the nucleophilic approach of the substrates to the silicon centre through their oxygen atoms. Then, the O–H bond of ROH or the $\text{O}=\text{C}$ bond of $\text{O}=\text{CR}_2$ interacts with the activated $\text{Si}\cdots\text{H}$ bond, followed by evolution of H_2 (for the former case) or H-migration to the carbonyl carbon (for the latter case). As another possible H-migration process for carbonyl compounds, the approach of the substrate to the silicon centre gives rise to a hydrosilyl ($\text{R}_2\text{C}=\text{O}\rightarrow\text{silylene}$) complex, from which H-migration occurs



Scheme 2 Reactions of **1** with conjugated molecules.



Scheme 3 Reactions of **1** with diethylamine and DMAP.

through a 6-membered-ring transition state to form an (alkoxy-silyl)silylene complex. Finally, the alkoxy group on the silyl ligand bridges over the silylene ligand to afford the four-membered-ring products. During the processes, it seems that the two adjacent Lewis acidic unsaturated silicon centres and a hydridic hydrogen atom function cooperatively in transforming the substrates.

In summary, complex **1** bearing a hydrogen-bridged bis(silylene) moiety displayed remarkable reactivity toward various small molecules (phenol, alcohol, carbonyl compounds, amine, DMAP). All reactions proceeded almost instantaneously and quantitatively at room temperature. Carbonyl compounds were hydro-bis-silylated selectively at the $\text{C}=\text{O}$ bond. These results demonstrate that the hydrogen-bridged bis(silylene) complex can provide a new platform for the efficient activation of small molecules *via* a new type of adjacent multi-site metal-ligand cooperation. Further investigations on the detailed reaction mechanism and dynamic behaviour of **1** by theoretical calculations are in progress.

Data availability

Electronic supplementary information (ESI) available: synthetic and experimental procedures, characterisation data, details of X-ray crystallographic analysis and NMR spectra. CCDC 2403405 (for **A**), 2403406 (for **5**), 2403407 (for **6**), 2403408 (for **8**) and 2403409 (for **10**) can be obtained from CCDC (<https://www.ccdc.cam.ac.uk/structures/>).

The data supporting this article have been included in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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