Table 1: NMR spectral data for salinosporamide A (**1**).

C no.	δ_C	δ_H, mult., int., J [Hz]	COSY correlations	HMBC correlations
1	176.4 C			
2	46.2 CH	3.17, t, 1 H, 7.0	H-12	C-1, 3, 12, 13, 14
3	86.1 C			
4	80.2 C			
5	70.9 CH	4.24, d, 1 H, 9.0	H-6	C-3, 6, 7
6	39.2 CH	2.85, m, 1H	H-5, H-11a/b	
7	128.4 CH	6.42, d, 1 H, 9.6	H-6, 8, 9	C-9
8	128.8 CH	5.88, m, 1H	H-7, 9	
9	25.3 CH_2	1.91, m, 2H	H-8, 10b	C-11
10	21.7 CH_2	a 1.66, m, 1 H	H-9, 10b	C-6, 8, 9
		b 1.38, m, 1 H	H-9, 10a	
11	26.5 CH_2	a 2.37, m, 1 H	H-6, 11b	C-6, 7, 9, 10
		b 1.66, m, 1 H	H-6, 10b	C-5, 6
12	29.0 CH_2	a 2.48, m, 1 H	H-2, 12b, 13	C-1, 2, 3, 13
		b 2.32, m, 1 H	H-2, 12a, 13	C-1, 2, 3, 13, 14
13	43.2 CH_2	a 4.14, m, 1 H	H-12a/b, 13b	C-2, 12
		b 4.01, m, 1 H	H-12a/b, 13a	C-2, 12
14	20.0 CH_3	2.07, s, 3 H		C-2, 3, 4, 15
15	169.0 C			
NH		10.60, br s		C-2, 3, 4
OH		4.99, br s		

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[4] Crystal Data for **1**: $C_{15}H_{21}ClNO_4$, $M_r = 313.11$, monoclinic space group, $P21$, $a = 10.4805(6)$, $b = 24.2085(13)$, $c = 12.5163(7)$ Å, $\beta = 108.603(10)°$, $V = 3009.7(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.385$ g cm^{-3}; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.269$ mm^{-1}, $T = -100$ K. 25 627 data (13 056 unique, $R_{int} = 0.0146$, $\theta < 27.52°$) were collected on a Bruker SMART APEX CCD X-ray diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, SHELXTL Manual) to give $wR2 = 0.0824$, conventional $R = 0.0313$ for F values of 12 747 reflections, $S = 1.037$ and 773 parameters. Residual electron density max/min 0.448/ -0.232 e Å^{-3}. CCDC-183413 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Molybdenum–Silicon Multiple Bonds

Multiple Bonding Between Silicon and Molybdenum: A Transition-Metal Complex with Considerable Silylyne Character[**]

*Benjamin V. Mork and T. Don Tilley**

The 2p elements carbon, nitrogen, and oxygen readily form multiple bonds to many other elements, and such bonds contribute strongly to the chemical behavior of organic compounds. In contrast, the heavier main-group elements (with principal quantum numbers of three or greater) reluctantly participate in multiple bonding,[1] and this aspect of main-group chemistry has been the focus of considerable fundamental research. A number of stable compounds with

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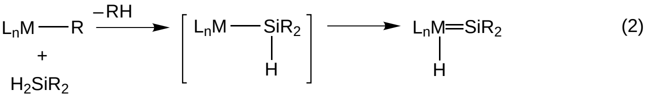
double bonds to p-block elements have been isolated,[2] but examples of the corresponding triply bonded compounds are quite rare. The first compounds containing triple bonds to a Group 14 element (germanium) were the transition-metal complexes $[Cp(CO)_2M{\equiv}Ge(C_6H_3\text{-}2,6\text{-}Ar_2)]$ ($Cp = \eta^5$-cyclopentadienyl; M = Cr, Mo, W; Ar = Mes, Trip; Mes = 2,4,6-trimethylphenyl; Trip = 2,4,6-triisopropylphenyl), reported by Power and co-workers.[3] Recently, Filippou et al. described another class of complexes featuring triple-bonding to germanium, $[X(dppe)_2M{\equiv}Ge(\eta^1\text{-}Cp^*)]$ (X = Cl, Br, I; M = Mo, W; Cp* = pentamethylcyclopentadienyl; dppe = 1,2-bis(diphenylphosphanyl)ethane).[4] In addition, Power has recently reported the heavy Group 14-element analogues of alkynes, $[(2,6\text{-}Ar_2H_3C_6)EE(C_6H_3\text{-}2,6\text{-}Ar_2)]$ (E = Ge, Sn, Pb; Ar = Trip, Dipp; Dipp = 2,6-diisopropylphenyl).[5] The lead dimer is described as having primarily metal–metal single-bond character with lone pairs of electrons localized at each lead center; the germanium and tin species are postulated to have electronic structures intermediate between the singly- and triply-bonded extremes.

Efforts to prepare stable triple bonds to silicon have not yet been successful, although results from the work of Wiberg suggest that the disilyne $[tBu_3SiSi{\equiv}SiSitBu_3]$ may be an unobserved intermediate in a reaction which forms its dimer, the tetrasilatetrahedrane $[(tBu_3SiSi)_4]$.[6] West's research group has also proposed the intermediacy of the disilyne species $[(2,6\text{-}Mes_2H_3C_6)Si{\equiv}Si(C_6H_3\text{-}2,6\text{-}Mes_2)]$, which decomposes through the cleavage of two C–C bonds in the terphenyl groups.[7] Thus, the synthesis of the first stable compound with a formal triple bond to silicon remains a key synthetic challenge. Here we report the isolation and characterization of $[\{Cp^*(dmpe)(H)MoSiMes\}\{B(C_6F_5)_4\}]$ (dmpe = 1,2-bis(dimethylphosphanyl)ethane), a complex that possesses considerable silylyne character.

Routes that have been developed to prepare silylene complexes include the abstraction of a group bound to silicon,[8] [Eq. (1)] and the activation of two Si–H bonds of a hydrosilane by oxidative addition and subsequent α-hydrogen elimination (silylene extrusion; [Eq. (2)]).[9] The availability of these different methods for the generation of metal–silicon multiple bonds suggested the possibility of combining them in the synthesis of a silylyne complex. This approach involves silylene extrusion to produce a silylene complex with a potential leaving group, followed by abstraction of the leaving group from silicon. Ideally, the silylene-extrusion step in this scheme would produce a neutral silylene complex, since the subsequent abstraction necessarily produces a cation.

$$L_nM{-}SiR_2X \xrightarrow{-X^-} \left[L_nM{=}SiR_2\right]^+ \qquad (1)$$



$$\begin{matrix} L_nM{-}R \\ + \\ H_2SiR_2 \end{matrix} \xrightarrow{-RH} \left[\begin{matrix} L_nM{-}SiR_2 \\ | \\ H \end{matrix}\right] \longrightarrow \begin{matrix} L_nM{=}SiR_2 \\ | \\ H \end{matrix} \qquad (2)$$

A suitable system for the application of this strategy was discovered in studies of the interactions of silanes with $[Cp^*(dmpe)Mo(\eta^3\text{-}CH_2Ph)]$ (**2**), prepared by the reaction of $[Cp^*(dmpe)(PMe_3)MoCl]$ (**1**)[10] with one equivalent of $PhCH_2MgCl$ in benzene. Complex **2**, which appears to be in equilibrium with its more reactive $[Cp^*(dmpe)Mo(\eta^1\text{-}benzyl)]$ form, reacts with chloromesitylsilane to produce the neutral silylene complex $[Cp^*(dmpe)(H)Mo{=}Si(Cl)Mes]$ (**3**). This reaction proceeds with the elimination of toluene, and presumably an α-hydrogen migration in the putative 16-electron intermediate $[Cp^*(dmpe)MoSi(H)(Cl)Mes]$. Benzyl complex **2** reacts with a variety of hydrosilanes to eliminate toluene, and these reactions are currently being investigated.

Silylene complex **3** was isolated as dark-red crystals in 88 % yield. ^1H NMR spectroscopy shows that the complex has mirror symmetry, with a hydride resonance at $\delta = -12.50$ ppm ($J_{H\text{-}P} = 19$ Hz, $J_{H\text{-}Si} = 38$ Hz). The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits a single resonance at $\delta = 64.9$ ppm, and the silylene silicon center resonates at $\delta = 182$ ppm in the $^{29}Si\{^1H\}$ NMR spectrum. The molecular structure of **3**, as determined by X-ray crystallography (Figure 1),[11] features a very short Mo–Si separation of 2.288(2) Å, and the sum of the angles about the silicon center is 359.8(3)°. These values are consistent with what is expected for base-free silylene complexes and sp^2 hybridization at silicon centers. The Mo–Si separation may be reduced somewhat by the presence of the chloride substituent, as has been observed in chloro-substituted silyl complexes.[12] The location of the hydride ligand was not determined, however, the spectroscopic data is consistent with a position *trans* to the centroid of the Cp* ring.

The conversion of **3** to a cationic silylyne–hydride complex required exchange of the chloride ion for an inert, noncoordinating anion, such as $[B(C_6F_5)_4]^-$. The reaction of **3** with $[Li(OEt_2)_3B(C_6F_5)_4]$ occurred immediately upon mixing the reagents in fluorobenzene, and the reaction solution changed from dark red to dark green/amber. The ^1H NMR spectrum of the resultant mixture in fluorobenzene/$[D_6]$benzene (10:1) revealed the quantitative conversion of **3** to a new product that has a hydride resonance at $\delta = -9.78$ ppm ($J_{H\text{-}P} = 20$ Hz). The new complex also exhibits a downfield-shifted resonance in the $^{29}Si\{^1H\}$ NMR spectrum at $\delta = 289$ ppm. The downfield-shifted ^{29}Si resonance, coupled with the very low $J_{Si\text{-}H}$ value of 15 Hz suggested the formulation of the new product as the silylyne complex, $[\{Cp^*(dmpe)(H)MoSiMes\}\{B(C_6F_5)_4\}]$ (**4**, [Eq. (3)]). The extent to which the

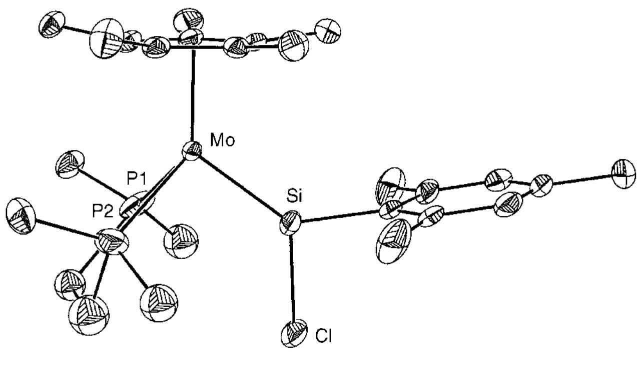


Figure 1. ORTEP diagram of the chloromesityl silylene complex **3**.

$$[\mathrm{Cp^*(dmpe)(H)Mo{=}Si(Cl)Mes}] \xrightarrow[\substack{\mathrm{PhF} \\ -\mathrm{LiCl}}]{\mathrm{LiB(C_6F_5)_4}} [\{\mathrm{Cp^*(dmpe)(H)MoSiMes}\}\{\mathrm{B(C_6F_5)_4}\}] \qquad (3)$$

hydride ligand interacts with the silicon center in this complex is difficult to determine, although the low $J_{\text{Si-H}}$ value suggests that the interaction is minimal.[12]

Amber crystals of **4**, suitable for X-ray crystallography, were grown by layering a solution of the compound in fluorobenzene with pentane in a glass tube stored under nitrogen. The structure of the complex, determined by X-ray diffraction techniques, was found to exhibit an Mo–Si bond, which at 2.219(2) Å is the shortest bond of this type reported to date. An ORTEP diagram of the cation in **4** is shown in Figure 2. The Mo-Si-C angle of 170.9(2)° is approximately linear and in the range of M-C-C bond angles observed in carbyne complexes.[13] Additional geometric parameters of interest are the P-Mo-Si angles (99.66(6) and 87.14(6)°) for P1 and P2, respectively. The significantly wider P1-Mo-Si angle suggests that the hydride ligand adopts a position as the fourth leg of the "piano stool"-type structure (**A**, Scheme 1). This limiting case, suggested by the relatively low $J_{\text{Si-H}}$ coupling constant, bears no Si–H interaction. However, a peak in the Fourier-difference electron-density map could be refined as a hydride ligand in a bridging position between the molybdenum and silicon atoms. The H–Mo and H–Si bond lengths of 1.85(5) and 1.39(5) Å, respectively, represent reasonable separations for bonds of these types. Although X-ray diffraction is not a reliable method for determining hydride positions in the vicinity of a heavy metal, the refined position for the hydride ligand of **4** suggests that in the solid state an H···Si interaction may be present (**B**, Scheme 1). A third possible structure bears a hydride ligand that caps the P-Si-P face below the piano stool (**C**, Scheme 1). This structure is in agreement with the mirror symmetry observed for **4** by NMR spectroscopy.

In principle, it should be possible to differentiate between the mirror-symmetric structure **C** and structures **A** and **B** by NMR spectroscopy. Although the solid-state structure of **4** does not possess mirror symmetry, in solution at room temperature the cation of **4** exhibits C_s symmetry on the NMR timescale. However, an asymmetric structure is observed at −30 °C (in fluorobenzene) by NMR spectroscopy. For example, **4** exhibits a single resonance at $\delta = 47.9$ ppm in its ^{31}P{^{1}H} NMR spectrum at room temperature, while at low temperature, two doublets at $\delta = 49.5$ and 46.3 ppm are observed ($J_{\text{P-P'}} = 20$ Hz). Additionally, the ^{1}H NMR spectrum of **4** at −30 °C exhibits four peaks for the inequivalent dmpe methyl groups at $\delta = 1.48$, 1.31, 1.05, and 0.87 ppm. The resonance for the hydride ligand at $\delta = -10.03$ ppm is a multiplet resulting from coupling to inequivalent phosphorous nuclei. Thus, it appears that **4** adopts structure **A** or **B** and undergoes a rapid dynamic process that exchanges the phosphorous atoms of the dmpe ligand. This process could involve migration of the hydride ligand to the silicon center, followed by rotation about the Mo–Si bond, or a pseudorotation (for **A**).

Preliminary computational studies on the cation of **4** using DFT methods (at the B3LYP/LACVP** level of theory) resulted in an energy-minimized structure that closely resembles the crystallographically determined one. Most importantly, the calculated structure features the hydride ligand in a bridging position across the Mo–Si bond. This is further evidence that the complex bears a nonclassical Si–H interaction, as in structure-type **B** (Scheme 1). Studies are in progress to locate energy minima which correspond to structure-type **A.** If such a minimum is found, a comparison of the energies of these two structures will be informative.

Initial reactivity studies of complex **4** show that its silicon center is electrophilic. Reaction of the complex with $\mathrm{Me_3SiCH_2Li}$ in fluorobenzene resulted in an immediate color change of the solution to purple/red. A new product formed

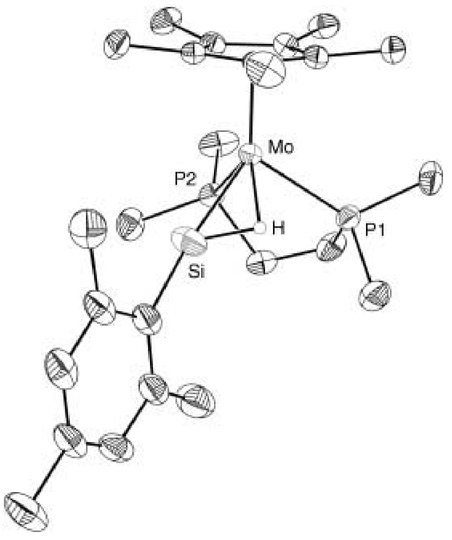
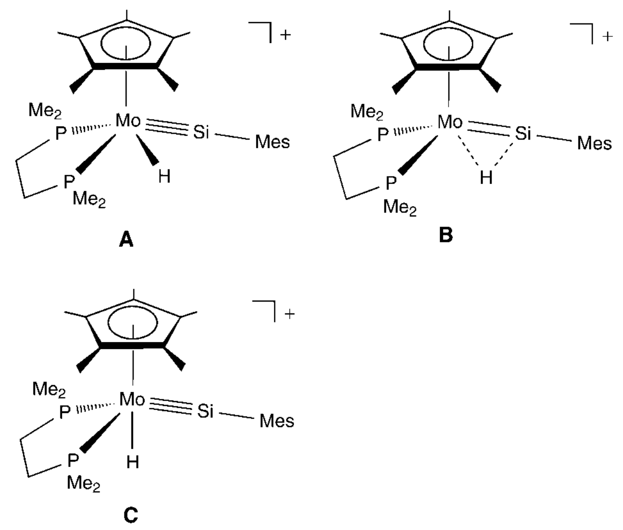


Figure 2. ORTEP diagram of the cation in **4**.



Scheme 1. Structural models discussed for the cation in **4**.

cleanly (as given by ^{1}H, ^{31}P{^{1}H}, and ^{29}Si{^{1}H} NMR spectroscopy), and was identified as the neutral silylene complex [Cp*(dmpe)(H)Mo=Si(CH$_2$SiMe$_3$)Mes] (**5**). The silylene and trimethylsilyl silicon centers resonate at $\delta = 243$ and -2 ppm in the ^{29}Si{^{1}H} NMR spectrum, respectively. Preliminary experiments have shown that weaker nucleophiles such as pyridine and bipyridine will also coordinate to the silicon center of **4** (as shown by ^{1}H NMR spectroscopy). The electrophilicity observed for the silylyne center is consistent with what has been observed for silylene complexes of transition metals.[8,9]

Complex **4** is the first example of an isolable compound that has silylyne (M≡Si) character.[14] The electrophilic silicon center in this complex may be stabilized by an interaction with the molybdenum hydride, although this interaction is likely to be weak considering the very low $J_{\text{H-Si}}$ coupling constant, and the exact location of the hydride ligand has not been firmly established. The metal–silicon bond order in this complex is difficult to ascertain, and the models used to describe bonding in second-row-element species often break down in heavy-element systems. However, it is interesting to make comparisons with [{Cp(P(OMe)$_3$)$_2$(H)Mo≡C-CH$_2$CMe$_3$}{BF$_4$}], prepared by Green and co-workers,[15] which was reported to have strictly carbyne hydride character. Future efforts are planned to probe the bonding in **4** and in related compounds.

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[10] The preparative procedures and data for compounds **1**–**5** are explained in detail in the Supporting Information.

[11] CCDC-194946 (**3**) and -194947 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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