

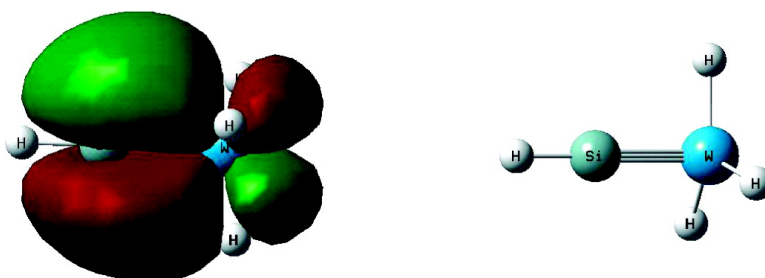
Article

## Silylidyne, HSi#MoH and HSi#WH, and Silyl Metal Hydride, SiH#CrH, Products in Silane Reactions

Xuefeng Wang, and Lester Andrews

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# Silyldiyne, $\text{HSi}\equiv\text{MoH}_3$ and $\text{HSi}\equiv\text{WH}_3$ , and Silyl Metal Hydride, $\text{SiH}_3\text{—CrH}$ , Products in Silane Reactions

Xuefeng Wang and Lester Andrews\*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904-4319

Received December 4, 2007; E-mail: isa@virginia.edu

**Abstract:** Laser-ablated group 6 metal atoms react with silane to form inserted  $\text{SiH}_3\text{—MH}$  hydride intermediates, which are identified from M—H and Si—H stretching modes. Following two successive  $\alpha\text{-H}$ -transfers, the  $\text{HSi}\equiv\text{MH}_3$  (M = Mo, W) silyldiyne molecules are produced. These silicon—metal triple-bonded species are identified as major products from the strong M—H stretching modes through deuterium substitution and comparison with frequencies and intensities from density functional calculations and from the analogous methylidyne. The silyldynes have calculated  $C_{3v}$  structures and longer Si—H bonds than silane, but the  $C_{3v}$  methylidyne analogues have shorter C—H bonds than methane. The  $\text{Si}\equiv\text{Mo}$  and  $\text{Si}\equiv\text{W}$  bonds are polarized differently and have slightly lower effective bond orders than their carbon analogues. In addition, calculations for the group 6 silylidene molecules reveal  $C_s$  structures with no evidence of agostic distortion, in contrast to the corresponding methylidene molecules.

## Introduction

Carbon, nitrogen, and oxygen form multiple bonds with their 2p valence orbitals, and these bonds are responsible for the chemical properties of many organic compounds. However, heavier main group elements from the third, fourth, and fifth rows of the periodic table are much less inclined to form multiple bonds, and their synthesis has provided a research challenge.<sup>1</sup> Although the heavier p-block elements are involved in double bonds, such triple bonds are seldom found. The only known example of a silicon—transition metal complex with silicon—metal triple bond character is  $[\{\text{Cp}^*(\text{dmpe})(\text{H})\text{MoSiMes}\}\{\text{B}(\text{C}_6\text{F}_5)_4\}]$ .<sup>2</sup> However, numerous organometallic complexes containing carbon—transition metal triple bonds have been investigated extensively for their varied chemistry and catalytic metathesis of alkynes.<sup>3–6</sup> The related chloromesityl molybdenum silylidene precursor complex has also been characterized,<sup>2</sup> and it will be interesting to compare the structures calculated here for the simple group 6 silylidene complexes with their agostic methylidene analogues.<sup>7–9</sup>

The simplest group 6 methylidyne molecules,  $\text{HC}\equiv\text{MoH}_3$  and  $\text{HC}\equiv\text{WH}_3$ , have been prepared recently in our laboratory by reactions of laser-ablated Mo and W atoms with methane during condensation in excess argon.<sup>7–9</sup> Density functional calculations found  $C_{3v}$  structures and  $\text{C}\equiv\text{M}$  bond lengths comparable to those measured in larger ligand-stabilized organometallic complexes.<sup>5</sup> These reactions proceeded through C—H insertion to form  $\text{CH}_3\text{—MH}$  methyl metal hydrides, followed by  $\alpha\text{-H}$ -transfer to the  $\text{CH}_2\equiv\text{MH}_2$  methylidene dihydrides and then another  $\alpha\text{-H}$ -transfer to the methylidyne trihydride molecules  $\text{HC}\equiv\text{MH}_3$ . In the case of W, the methylidyne is the lowest energy product; however, with Cr, the initial insertion product is the most stable, and  $\text{CH}_3\text{—CrH}$  is the only product formed.<sup>8</sup>

In contrast to methane,<sup>9</sup> metal reactions with silane have received limited attention. Group 12 and 13 metal atom reactions with silane have provided evidence for silyl metal hydride molecules,<sup>10–13</sup> which are analogous to the methyl metal hydride C—H insertion products.<sup>9</sup>

We report here an investigation of group 6 metal atom reactions with silane. The reaction proceeds through the silyl metal hydride intermediate. Energy trends analogous to those found with methane<sup>8</sup> govern the formation of the simple silyldiyne product molecules. However, the H—Si $\equiv$ M functional groups exhibit different polarization from the analogous H—C $\equiv$ M subunits, and the Si—H bond hybridization in silyldynes differs from that of the C—H bond in methylidyne.

## Experimental and Computational Methods

Laser-ablated Cr, Mo, and W atoms (Johnson-Matthey) were reacted with  $\text{SiH}_4$  (Matheson) and  $\text{SiD}_4$  (MSD Isotopes) in excess

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argon or neon during condensation at 4 K using a closed-cycle refrigerator (Sumitomo Heavy Industries Model RDK 205D). These methods have been described in detail elsewhere.<sup>14,15</sup> Reagent gas mixtures were typically 0.5 or 1% in neon or argon. After reaction, infrared spectra were recorded at a resolution of 0.5 cm<sup>-1</sup> using a Nicolet 750 spectrometer with an Hg–Cd–Te B range detector. Samples were later irradiated for 15 min periods by a mercury arc street lamp (175 W) with the globe removed using a combination of optical filters, and then samples were annealed to allow reagent diffusion and further reaction.

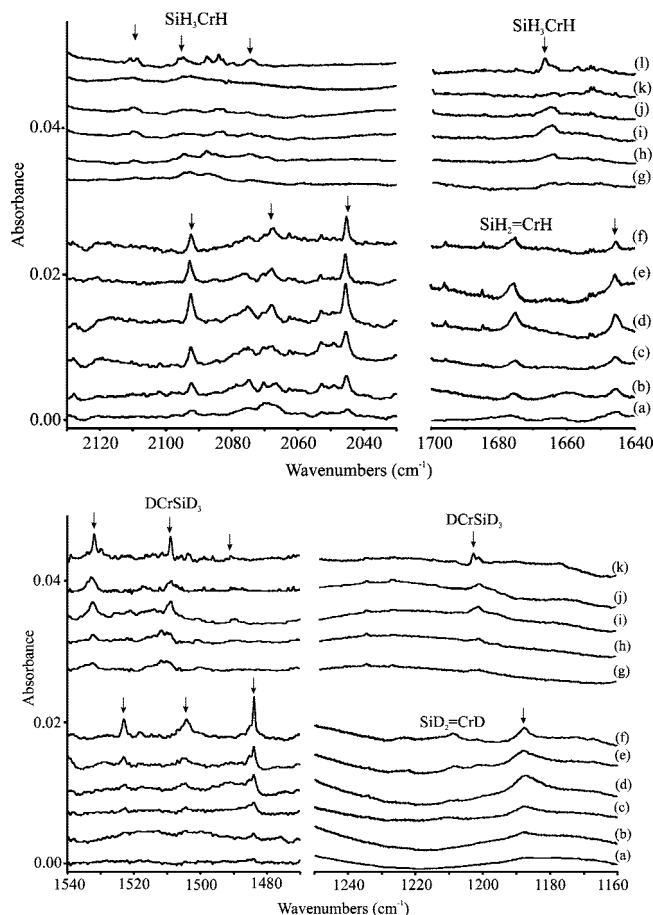
Complementary density functional theory (DFT) calculations were carried out using the Gaussian 03 package,<sup>16</sup> the hybrid B3LYP density functional,<sup>17</sup> the 6-311++G(3df,3pd) basis sets for Si and H,<sup>18</sup> and the SDD pseudopotential and basis set<sup>19</sup> for the metal atoms in order to provide a consistent set of vibrational frequencies for the reaction products. Different spin states were computed to locate the ground-state product molecule. Geometries were fully relaxed during optimization, and the optimized geometry was confirmed by vibrational analysis. All of the vibrational frequencies were calculated analytically with zero-point energy included for the determination of reaction energies. Natural bond order (NBO)<sup>16,20</sup> analysis was also done to explore the bonding in new silyldiyne molecules.

## Results and Discussion

The reaction products of Cr, Mo, and W atoms with silane will be characterized by matrix infrared spectra and density functional theory calculations and comparison to results from the analogous methane reactions.<sup>7–9</sup> These experiments also produce common absorptions due to precursor fragment and reactive species such as SiH, SiH<sub>2</sub>, and Si<sub>2</sub>H<sub>2</sub> that have been reported previously.<sup>21</sup>

**Cr.** Infrared spectra of the laser-ablated Cr and SiH<sub>4</sub> reaction products are illustrated in Figure 1. Two product absorptions with slightly different behaviors were observed at 1675.3 and 1645.7 cm<sup>-1</sup>, and these bands increased on annealing and more so on ultraviolet irradiation, where >380 nm favored the 1645.7 cm<sup>-1</sup> band and >290 nm irradiation decreased it more than the 1675.3 cm<sup>-1</sup> band. The SiD<sub>4</sub> counterparts were found at 1208.9 and 1187.7 cm<sup>-1</sup>, and the latter band was favored substantially over the former with >380 nm irradiation. New bands at 2092.4, 2074.8, 2067.5, 2053.0, 2045.5, and 849.1 cm<sup>-1</sup> and at 1522.8, 1504.1, and 1483.7 cm<sup>-1</sup> are associated on ultraviolet irradiation.

The neon matrix experiment with silane gave only the lower band at 1664.6 cm<sup>-1</sup> with associated bands at 855.6 cm<sup>-1</sup> and at 2111.2, 2084.7, and 2059.0 cm<sup>-1</sup>. Investigation with silane-*d*<sub>4</sub> found these bands at 1201.8 cm<sup>-1</sup> and at 1532.2, 1508.8, and 1490.3 cm<sup>-1</sup>. The grouping of three bands at 2092.4, 2067.5, and 2045.5 cm<sup>-1</sup> in the Si–H and one band at 1645.7 cm<sup>-1</sup> in the Cr–H stretching region<sup>22</sup> suggests the silyl



**Figure 1.** Infrared spectra for Cr atom reaction products with silane in the 2130–2030 and 1700–1640 cm<sup>-1</sup> regions and silane-*d*<sub>4</sub> in the 1540–1460 and 1260–1160 cm<sup>-1</sup> regions. (a) Spectrum after co-deposition of laser-ablated Cr and SiH<sub>4</sub> (top) or SiD<sub>4</sub> (bottom) at 1% in argon at 4 K for 60 min, (b) after annealing to 25 K, (c) after >470 nm irradiation, (d) after >380 nm irradiation, (e) after 290 nm irradiation, (f) after annealing to 30 K, (g) after co-deposition of Cr and silane at 0.5% in neon at 4 K for 60 min, (h) after annealing to 10 K, (i) after >470 nm irradiation, (j) after >380 nm irradiation, (k) after 290 nm irradiation, and (l) after annealing to 12 K. Arrows denote SiH<sub>3</sub>CrH or SiD<sub>3</sub>CrD products.

chromium hydride assignment, and comparison with the calculated frequencies in Table 1 attests to that point. The H/D isotopic frequency ratios for the 2092.4, 2067.5, and 2045.5 cm<sup>-1</sup> argon matrix bands are 1.3740, 1.3746, and 1.3786 and for the lower band, 1.3856, which are appropriate for H vibrating against Si and Cr centers, respectively.<sup>21,22</sup> Similar H/D ratios of 1.3779, 1.3814, 1.3816, and 1.3851 were determined for the neon matrix counterparts. The additional band at 855.6 cm<sup>-1</sup> in neon and 849.1 cm<sup>-1</sup> in argon corresponds to the strong SiH<sub>3</sub> umbrella deformation mode calculated at 850 cm<sup>-1</sup>. The argon-to-neon matrix shifts are 6–29 cm<sup>-1</sup> and typical of differences for metal hydrides in these two matrix media of different polarizabilities.<sup>15</sup>

It is interesting to compare the SiH<sub>3</sub>–CrH and CH<sub>3</sub>–CrH hydride molecules. We find that the Cr–H stretching mode is blue-shifted 22 cm<sup>-1</sup> in the silyl species, and our calculations using the same basis sets predict a 28 cm<sup>-1</sup> blue shift and a 0.008 Å shorter Cr–H bond for the silyl chromium hydride. We find that the computed atomic charges on CrH in the silyl species reveal higher electron density, which results in a stronger Cr–H bond. A similar 38 cm<sup>-1</sup> blue shift is found for the Al–H stretching modes on going from the methyl to the silyl aluminum hydrides.<sup>10</sup>

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(21) Andrews, L.; Wang, X. *J. Phys. Chem. A* **2002**, *106*, 7696. and references therein (Si + H<sub>2</sub>)

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**Table 1.** Observed and Calculated Fundamental Frequencies of the SiH<sub>3</sub>–CrH and SiH<sub>3</sub>–MoH Silyl Metal Hydrides in Ground <sup>5</sup>A' Electronic States with the C<sub>s</sub> Structures<sup>a</sup>

approximate description	SiH <sub>3</sub> –CrH			SiD <sub>3</sub> –CrD			SiH <sub>3</sub> –MoH			SiD <sub>3</sub> –MoD		
	obs	calc	int	obs	calc	int	obs	calc	int	obs	calc	int
Si–H str, a''	2092.4 <sup>b</sup>	2179	107	1522.8 <sup>b</sup>	1574	45	2094.5 <sup>c</sup>	2175	96	1524.5 <sup>c</sup>	1571	50
Si–H str, a'	2067.5	2173	99	1504.1	1564	46	2051.9	2171	96	1492.5	1559	57
Si–H str, a'	2045.5	2150	113	1483.7	1536	85	2044.2	2140	115	1484.2	1531	59
M–H str, a''	1645.7	1711	226	1187.7	1222	115	1747.7	1834	189	1254.3	1304	97
SiH <sub>2</sub> bend, a'		950	44		680	48		947	40		679	19
SiH <sub>2</sub> bend, a'		945	44		677	41		941	38		674	18
SiH <sub>3</sub> def, a'	849.1	851	391		629	42		864	400		639	208
HMSi bend, a''		459	82		349	11		426	43		324	25
SiH <sub>2</sub> rock, a''		367	0		271	16		383	0		282	0
HM,SiH <sub>3</sub> rock, a'		299	22		265	13		293	23		266	0
Si–M str, a'		265	16		202	4		273	29		200	27
HMSi def, a''		88	77		63	3		123	46		88	24

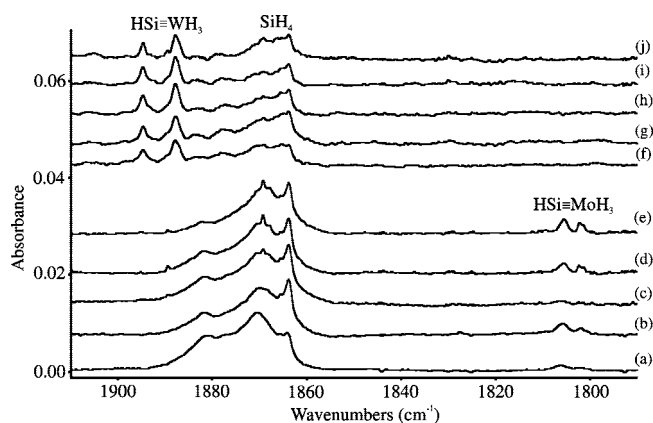
<sup>a</sup>Frequencies and intensities are in cm<sup>-1</sup> and km/mol. Observed in an argon matrix. Frequencies and intensities computed with B3LYP/6-311++G(3df,3pd) in the harmonic approximation using the SDD core potential and basis set for Mo and W. Symmetry notations are based on the C<sub>s</sub> structure. <sup>b</sup>Neon matrix values 2111.1, 2084.2, 2074.7, 1664.6, and 855.6 cm<sup>-1</sup> and 1532.2, 1508.8, 1490.3 and 1201.8 cm<sup>-1</sup>. <sup>c</sup>Neon matrix values 2113.2, 2084.7, 2076.7, and 1768.3 cm<sup>-1</sup> and 1533.6, 1510.3, 1501.7, and 1270.0 cm<sup>-1</sup>.

The 1675.3 cm<sup>-1</sup> absorption in solid argon is also favored by >290 nm irradiation and exhibits an appropriate H/D ratio, 1.3858, for the Cr–H vibration in another molecule that is apparently not formed in solid neon. The deuterium counterpart at 1208.9 cm<sup>-1</sup> is much weaker, and apparently this isotopic molecule is more difficult to produce. The known stability of the III oxidation state for Cr prompted a calculation for SiH<sub>2</sub>=CrH, the silylidene chromium monohydride, which has essentially the same structure as SiH<sub>2</sub>=CrH<sub>2</sub> without one hydride. The single Cr–H frequency is calculated 24 cm<sup>-1</sup> higher than this mode for SiH<sub>3</sub>–CrH (Tables 1 and S1), and the 1675.3 cm<sup>-1</sup> band is 30 cm<sup>-1</sup> higher than the mode assigned above. On this basis, the 1675.3 cm<sup>-1</sup> band is assigned to the strongest absorption, the Cr–H stretching mode, of SiH<sub>2</sub>=CrH. The next strongest mode, the SiH<sub>2</sub> bend, is masked by this mode for SiH<sub>4</sub>. The weaker 2074.8 and 2053.0 cm<sup>-1</sup> bands can be assigned to the two Si–H stretching modes for the SiH<sub>2</sub>=CrH species.

The Cr reaction with silane proceeds though Si–H insertion, and analogous to the methane reaction,<sup>7</sup> only the insertion product has low enough energy to be formed in these experiments, although at the B3LYP level of theory, reaction 1a is endothermic by 2 kcal/mol. In addition, the SiH<sub>3</sub>–CrH product increased on annealing, so reaction 1a is spontaneous, but the yield was also increased substantially on >380 nm irradiation. One can envision a favorable interaction between the Cr atom with six unpaired electrons and the empty 3d orbitals on silicon. There is an abundance of SiH<sub>2</sub> and SiH produced in these experiments, so H atoms are also a byproduct of co-deposition with laser-ablated metal atoms. The SiH<sub>2</sub>=CrH molecule is most likely formed by H atom reaction 1b on annealing, which is exothermic by 31 kcal/mol. Such a reaction would be less effective for the deuterium isotopic molecule.



**Mo.** Initial experiments employed argon as the matrix material, and new bands at 1806.2 and 1802.1 cm<sup>-1</sup> increased on annealing, decreased on >470 nm irradiation, but returned on >290 nm irradiation, as shown in Figure 2. A weak 1747.7 cm<sup>-1</sup> band increased on annealing and increased markedly on >470 nm irradiation, along with bands at 2094.5, 2051.9, and 2044.2 cm<sup>-1</sup>. Deuterium counterparts were observed at 1292.8



**Figure 2.** Infrared spectra for Mo and W atom reaction products with silane in excess argon. (a) Spectrum after co-deposition of laser-ablated Mo and 1% SiH<sub>4</sub> in argon at 4 K for 60 min, (b) after annealing to 25 K, (c) after irradiation at >470 nm for 15 min, (d) after irradiation at >290 nm for 15 min, (e) after annealing to 30 K, (f) after co-deposition of laser-ablated W and 1% SiH<sub>4</sub> in argon at 4 K for 60 min, (g) after annealing to 25 K, (h) after irradiation at >470 nm for 15 min, (i) after irradiation at >290 nm for 15 min, and (j) after annealing to 30 K.

and 1286.4 cm<sup>-1</sup> for the bands that decreased on visible irradiation and at 1254.3, 1524.5, 1492.5, and 1484.2 cm<sup>-1</sup> for the bands that increased.

The leading absorption at 1806.2 cm<sup>-1</sup> falls just below the strong Mo–H stretching mode observed for HC≡MoH<sub>3</sub> at 1830 cm<sup>-1</sup> and invites consideration for the silicon analogue HSi≡MoH<sub>3</sub>, and to this end calculated frequencies are listed in Table 2. The strongest calculated frequency for the silylidene is the degenerate antisymmetric Mo–H stretching mode. This mode is 19 cm<sup>-1</sup> below the calculated mode for the methylidyne, and the 1806.2 cm<sup>-1</sup> band is 24 cm<sup>-1</sup> below that mode observed for HC≡MoH<sub>3</sub> in solid argon.<sup>7</sup> Table 2 also shows that the symmetric Mo–H stretching mode is predicted 6 cm<sup>-1</sup> lower with 40% of the intensity, and the 1802.1 cm<sup>-1</sup> band is appropriate for this weaker infrared absorption. The H/D isotopic frequency ratios for these two observed bands, 1.3971 and 1.4010, are appropriate for molybdenum hydride vibrations,<sup>2,3</sup> and the slightly higher value is characteristic of the symmetric stretching coordinate. The calculated harmonic frequency ratios, 1.4019 and 1.4137, respectively, follow accordingly.

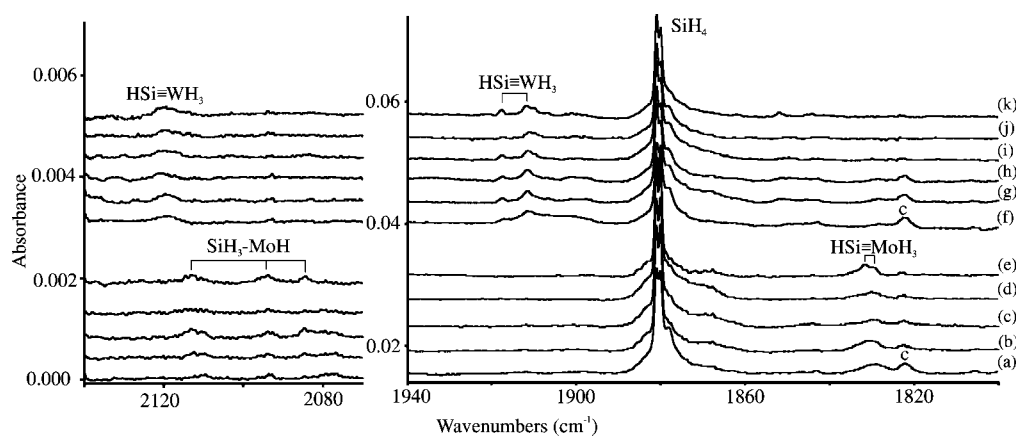
The three Si–H stretching bands at 2094.5, 2051.9, and 2044.2 cm<sup>-1</sup> and the Mo–H stretching band at 1747.7 cm<sup>-1</sup>



**Table 2.** Observed and Calculated Fundamental Frequencies of HSi≡MoH<sub>3</sub> and HSi≡WH<sub>3</sub> Complexes in the Ground <sup>1</sup>A<sub>1</sub> Electronic States with the C<sub>3v</sub> Structures<sup>a</sup>

approximate description	HSi≡MoH <sub>3</sub>			DSi≡MoD <sub>3</sub>			HSi≡WH <sub>3</sub>			DSi≡WD <sub>3</sub>		
	obs	calc	int	obs	calc	int	obs	calc	int	obs	calc	int
Si–H str, a <sub>1</sub>		2156	54		1555	28	2120	2180	37	1534	1573	19
M–H str, e	1806.2 <sup>b</sup>	1893	244 × 2	1292.8 <sup>c</sup>	1350	123 × 2	1894.9 <sup>d</sup>	1946	205 × 2	masked <sup>f</sup>	1383	104 × 2
M–H str, a <sub>1</sub>	1802.1 <sup>b</sup>	1887	195	1286.4 <sup>c</sup>	1335	97	1887.8 <sup>d</sup>	1957	208	masked <sup>f</sup>	1385	104
MH <sub>2</sub> bend, e		851	36 × 2		605	17 × 2		829	30 × 2		588	15 × 2
MH <sub>3</sub> def, e		607	0 × 2		449	36 × 2		546	37 × 2		397	18 × 2
Si≡M str, a <sub>1</sub>		590	26		549	4		615 <sup>e</sup>	41		534 <sup>d</sup>	5
MH <sub>3</sub> def, a <sub>1</sub>		483	25		366	23		499 <sup>e</sup>	9		403 <sup>d</sup>	20
HSiM def, e		312	18 × 2		225	10 × 2		342	7 × 2		250	4 × 2

<sup>a</sup>Frequencies and intensities are in cm<sup>-1</sup> and km/mol. Observed in an argon matrix. Frequencies and intensities computed with B3LYP/6-311++G(3df,3pd) in the harmonic approximation using the SDD core potential and basis set for Mo and W. Calculations using the BPW91 functional gave similar frequencies. The mode symmetry notations are based on the C<sub>3v</sub> structure. <sup>b</sup>Neon matrix band positions 1831.7 and 1829.4 cm<sup>-1</sup>. <sup>c</sup>Neon matrix band positions masked by methane impurity. <sup>d</sup>Neon matrix band positions 2020, 1917.6, and 1911.5 cm<sup>-1</sup>. <sup>e</sup>These non-degenerate modes are mixed internal coordinates. <sup>f</sup>Argon matrix counterparts masked by silane-d<sub>4</sub> combination band, but neon matrix positions are 1374.0 and 1373.3 cm<sup>-1</sup>.



**Figure 3.** Infrared spectra for Mo and W atom reaction products with silane in excess neon. (a) Spectrum after co-deposition of laser-ablated Mo and 0.5% SiH<sub>4</sub> in neon at 4 K for 60 min, (b) after annealing to 8 K, (c) after irradiation at >470 nm for 15 min, (d) after irradiation at >290 nm for 15 min, (e) after annealing to 10 K, (f) after co-deposition of laser-ablated W and 0.5% SiH<sub>4</sub> in neon at 4 K for 60 min, (g) after annealing to 8 K, (h) after irradiation at >470 nm for 15 min, (i) after irradiation at >290 nm for 15 min, (j) after 240–380 nm irradiation, and (k) after annealing to 10 K. “c” denotes a band common to silane experiments.

are appropriate for assignment to SiH<sub>3</sub>–MoH, as comparison with the calculated frequencies in Table 1 indicate. The H/D isotopic frequency ratios 1.3739, 1.3627, 1.3773, and 1.3934 are expected for the assigned modes. The silyl deformation mode in this case is masked by a strong common Si<sub>2</sub>H<sub>4</sub> product band in the 860 cm<sup>-1</sup> region.<sup>21</sup>

The neon matrix investigation produced leading absorptions at 1831.7 and 1829.4 cm<sup>-1</sup>, which also increased on annealing, decreased on visible, and increased on ultraviolet irradiation, as displayed in Figure 3. These bands are about 26 cm<sup>-1</sup> higher than the argon matrix bands and appropriate for the neon matrix absorptions of HSi≡MoH<sub>3</sub>. Weak absorptions at 2113.2, 2084.7, 2076.7, and 1768.2 cm<sup>-1</sup> increased on >530 nm photolysis and then decreased with exposure to >290 nm light. The latter bands are in the region for the silyl metal hydride, and comparison of the computed frequencies in Table 1 substantiates this assignment. Notice that the Si–H stretching modes for the Mo species are about 2 cm<sup>-1</sup> higher than those for the Cr species, and our calculations are in general agreement with this trend. The reaction with SiD<sub>4</sub> in neon revealed no leading absorption as these shifted under the CH<sub>4</sub> impurity band. However, weak absorptions at 1533.6, 1510.3, 1501.7, and 1270 cm<sup>-1</sup> increased on >530 nm irradiation and decreased on >290 nm photolysis.

**Table 3.** Calculated Fundamental Frequencies for the SiH<sub>2</sub>=MoH<sub>2</sub> and SiH<sub>2</sub>=WH<sub>2</sub> Silylidene Complexes in Ground <sup>3</sup>A' Electronic States with the C<sub>s</sub> Structures<sup>a</sup>

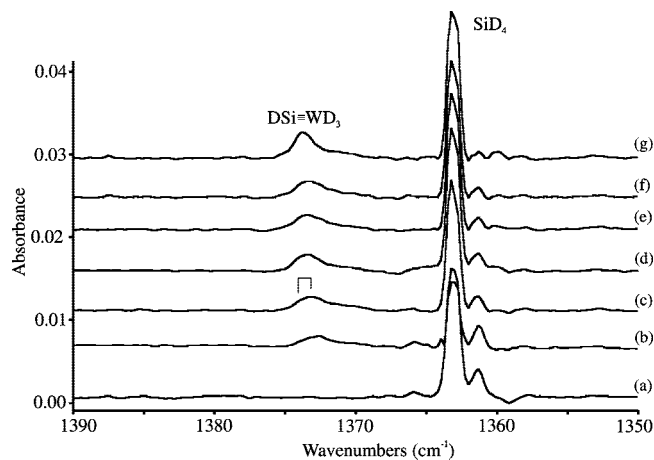
approximate description	SiH <sub>2</sub> =MoH <sub>2</sub>		SiD <sub>2</sub> =MoD <sub>2</sub>		SiH <sub>2</sub> =WH <sub>2</sub>		SiD <sub>2</sub> =WD <sub>2</sub>	
	calc	int	calc	int	calc	int	calc	int
Si–H str, a''	2180	82	1572	45	2181	79	1575	43
Si–H str, a'	2148	91	1539	46	2161	81	1548	43
M–H str, a'	1889	168	1341	85	1957	145	1387	73
M–H str, a''	1877	226	1337	115	1947	191	1383	97
SiH <sub>2</sub> bend, a'	935	103	680	48	933	104	680	51
MH <sub>2</sub> bend, a'	609	79	442	41	687	44	490	22
MH <sub>2</sub> def, a'	507	103	399	42	558	70	423	30
SiH <sub>2</sub> wag, a''	480	25	362	11	438	31	330	9
MH <sub>2</sub> def, a''	369	24	302	16	429	0	325	4
SiH <sub>2</sub> def, a'	356	1	262	13	372	3	309	11
Si=M str, a'	341	1	258	4	354	4	266	2
SiH <sub>2</sub> twist, a''	49	6	34	3	77	6	55	3

<sup>a</sup>Frequencies and intensities are in cm<sup>-1</sup> and km/mol. Frequencies and intensities computed with B3LYP/6-311++G(3df,3pd) in the harmonic approximation using the SDD core potential and basis set for Mo and W. Symmetry notations are based on the C<sub>s</sub> structure.

These bands define H/D ratios 1.3779, 1.3803, 1.3828, and 1.3924, which are near the above argon matrix values for our assignments to the Si–H and Mo–H stretching modes of the silyl metal hydride complex SiH<sub>3</sub>–MoH.

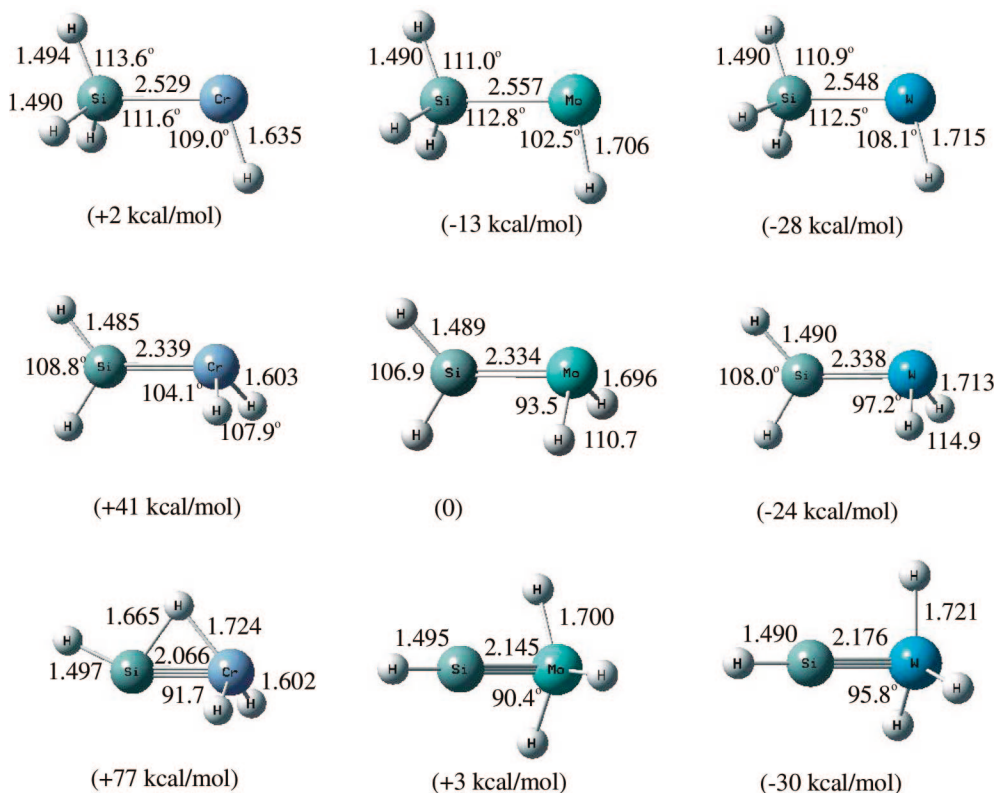
Following the example of the methane reaction,<sup>7</sup> structures of the three products expected from the Mo and SiH<sub>4</sub> reaction

(23) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2005**, *109*, 9021. (Mo + H<sub>2</sub>)



**Figure 4.** Infrared spectra for W atom reaction products with  $\text{SiD}_4$  in excess neon. (a) Spectrum after co-deposition of laser-ablated Mo and 0.5%  $\text{SiD}_4$  in neon at 4 K for 60 min, to serve as a placebo in this region, (b) after co-deposition of laser-ablated W and 0.5%  $\text{SiD}_4$  in neon at 4 K for 60 min, (c) after annealing to 8 K, (d) after annealing to 8 K, (e) after irradiation at  $>470$  nm for 15 min, (f) after irradiation at  $>380$  nm for 15 min, and (g) after annealing to 10 K.

are illustrated in Figure 5, with energies given relative to the Mo and  $\text{SiH}_4$  reagents. As found for methane, the first insertion product has the lowest energy and here is 13 kcal/mol more stable than the reagents all calculated at the B3LYP level of approximation. The silylidene  $\text{SiH}_2=\text{MoH}_2$  is isoergic with the reagents, and the silylydne  $\text{HSi}\equiv\text{MoH}_3$  is only 3 kcal/mol higher. The analogous methane reaction to form the methylidyne is endothermic by 7 kcal/mol, and this product was observed in solid argon.<sup>7</sup>



**Figure 5.** Structures of the silyl metal hydride, silylidene, and silylydne molecules of group 6 calculated using the B3LYP method, the 6-311++G(3df, 3pd) basis for H, Si, and C, and the SDD core potential for Cr, Mo, and W. Bond lengths in Å and angles in deg. (Energies given in kcal/mol relative to metal atom + silane.)

The reaction proceeds here with laser-ablated Mo atoms and on ultraviolet excitation to give the inserted metal hydride, followed by successive  $\alpha$ -H-transfers first to the  $\text{SiH}_2=\text{MoH}_2$  silylidene dihydride and second to the silylydne trihydride molecule  $\text{HSi}\equiv\text{MoH}_3$ , as shown in reaction 2. The reaction also proceeds on annealing, which means that the cold atom reaction is spontaneous and suggests that higher level calculations will find the silylydne intermediate to have lower energy than the reagents.



The strongest absorption for the inserted  $\text{SiH}_3-\text{MoH}$  molecule is the Mo-H stretching mode predicted  $59\text{ cm}^{-1}$  below the strongest mode of  $\text{HSi}\equiv\text{MoH}_3$ , which is observed here at  $1806.2\text{ cm}^{-1}$ . The  $1747.7\text{ cm}^{-1}$  band, which increases on  $>470$  nm irradiation, has precisely the predicted relative position and is appropriate for the  $\text{SiH}_3-\text{MoH}$  assignment. The most intense infrared absorptions for  $\text{SiH}_2=\text{MoH}_2$  are the Mo-H stretching modes, and the higher and weaker (Table 3) of these is calculated at about the same position as for  $\text{HSi}\equiv\text{MoH}_3$ ; any such absorption for the silylidene would be masked by the stronger silylydne bands. However, the stronger silylidene Mo-H stretching mode is calculated  $22\text{ cm}^{-1}$  lower, where it can be observed, and its absence means that the silylidene is not trapped here. In addition, the weaker Si-H stretching bands are not observed on the side of the strong precursor. As summarized in reaction 2, the silylidene is an intermediate in the overall reaction to form the major silylydne product, although we do not have direct evidence for the silylidene in these experiments.

We have found a bridged silylidene molybdenum dihydride (Figure S1) which is 7 kcal/mol lower in energy than the open

**Table 4.** Molybdenum and Tungsten Silyldiyne and Methylidyne Natural Charges, Electron Configurations, Bond Characters and Bond Orders<sup>a</sup>

property	HSi≡MoH <sub>3</sub>	HC≡MoH <sub>3</sub>	HSi≡WH <sub>3</sub>	HC≡WH <sub>3</sub>
$q(\text{H})^b$	-0.18	0.16	-0.16	0.17
$q(\text{Si,C})^b$	0.66	-0.19	0.51	-0.33
$q(\text{M})^b$	-0.05	0.46	0.22	0.75
$q(\text{H})^b$	-0.14 (×3)	-0.15 (×3)	-0.19 (×3)	-0.20 (×3)
H <sup>c</sup>	1s <sup>1.17</sup>	1s <sup>0.83</sup>	1s <sup>1.15</sup>	1s <sup>0.83</sup>
Si,C <sup>c</sup>	[core]3s <sup>1.33</sup> 3p <sup>1.99</sup>	[core]3s <sup>1.28</sup> 3p <sup>2.90</sup>	[core]3s <sup>1.31</sup> 3p <sup>2.17</sup>	[core]3s <sup>1.28</sup> 3p <sup>3.04</sup>
M <sup>c</sup>	[core]4d <sup>5.51</sup> 5s <sup>0.55</sup>	[core]4d <sup>4.61</sup> 5s <sup>0.60</sup>	[core]5d <sup>5.09</sup> 6s <sup>0.69</sup>	[core]5d <sup>4.61</sup> 6s <sup>0.69</sup>
H (×3) <sup>c</sup>	1s <sup>1.13</sup>	1s <sup>1.14</sup>	1s <sup>1.18</sup>	1s <sup>1.19</sup>
Si,C-H character <sup>d</sup>	38.1% s, 61.4% p	44.7% s, 55.2% p	39.8% s, 59.8% p	45.3% s, 54.7% p
Si,C-M character <sup>e</sup>	62.0% s, 38.0% p	55.0% s, 44.9% p	60.2% s, 39.7% p	54.5% s, 45.5% p
Si,C-M character <sup>f</sup>	99.3% p, 99.6% d	99.8% p, 99.9% d	99.8% p, 99.8% d	99.8% p, 99.8% d
Si≡M, C≡M MO <sup>g</sup>	1.93, 0.08, 3.87, 0.05	1.96, 0.07, 3.94, 0.04	1.96, 0.04, 3.88, 0.04	1.98, 0.05, 3.94, 0.04
eff. bond order <sup>h</sup>	2.83	2.90	2.88	2.92

<sup>a</sup> Computed with B3LYP/6-311++G(3df, 3pd) for H, Si, and C and the SDD core potential for W. <sup>b</sup> Natural charge. <sup>c</sup> Natural electron configuration (see ref 20). <sup>d</sup> Si and C orbital contributions to the Si-H and C-H bonds. <sup>e</sup> Si and C orbital contributions to the Si-M and C-M  $\sigma$  bonds. <sup>f</sup> Si and C orbital contributions to the Si-M and C-M  $\pi$  bonds. <sup>g</sup> Occupancies calculated for  $\sigma$ ,  $\sigma^*$ ,  $\pi$  (×2), and  $\pi^*$  (×2) molecular orbitals. <sup>h</sup> Effective bond order is the sum of bonding minus antibonding occupancies divided by 2.

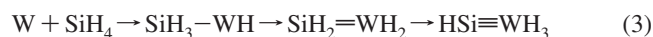
silylidene and 10 kcal/mol lower than the silyldiyne. This is not surprising, in view of the hydrogen-bridged structure observed and calculated for Si<sub>2</sub>H<sub>2</sub>.<sup>25,26</sup> However, the calculated frequencies (Table S2) do not fit the observed spectrum, which features a single strong absorption (within a 2 cm<sup>-1</sup> bandwidth) predicted to fall 6 cm<sup>-1</sup> below HC≡MoH<sub>3</sub>, whereas our 1806 and 1802 cm<sup>-1</sup> bands are 24–28 cm<sup>-1</sup> lower. Although the bridged molybdenum silylidene is a lower energy species, a 14 kcal/mol barrier separates it from the HSi≡MoH<sub>3</sub> molecule observed here. The transition state is illustrated in Figure S1: this structure has one imaginary frequency, i660 cm<sup>-1</sup>, the H-Si deformation mode. Under different experimental conditions, the lower energy bridged molybdenum silylidene might be observed, but it is not accessed through reaction 2 in the cold matrix isolation experiment.

W. Argon matrix experiments with tungsten gave two new bands at 1894.9 and 1887.8 cm<sup>-1</sup>, with intensities reversed from the two molybdenum product bands illustrated in Figure 2. A similar reversal in intensities was found for HC≡MoH<sub>3</sub> and HC≡WH<sub>3</sub> absorptions.<sup>7,8</sup> These bands are 9–12 cm<sup>-1</sup> below the 1907.5 and 1896.3 cm<sup>-1</sup> absorptions observed for HC≡WH<sub>3</sub>, and the calculated W-H stretching frequencies for HSi≡WH<sub>3</sub> compared in Table 2 are 11–13 cm<sup>-1</sup> lower than the calculated methylidyne values.<sup>8</sup> Although the deuterium counterpart is unfortunately masked by a precursor combination band, these absorptions can be assigned to HSi≡WH<sub>3</sub>.

The neon matrix experiment with SiH<sub>4</sub> shown in Figure 3 gives two similar bands at 1917.6 and 1911.7 cm<sup>-1</sup>, blue-shifted about 23 cm<sup>-1</sup> from the argon matrix values, and an associated broad, weak 2120 cm<sup>-1</sup> absorption. The neon-argon shifts are slightly more than found for WH<sub>4</sub> and WH<sub>6</sub>.<sup>24</sup> In solid neon, the SiD<sub>4</sub> combination band is sharp, and new product absorptions were observed at 1374.0 and 1373.3 cm<sup>-1</sup> (Figure 4), with an additional broad band at 1534 cm<sup>-1</sup>, all of which show the same annealing and photolysis behavior as the SiH<sub>4</sub> counterparts. The H/D frequency ratios, 1.3956 and 1.3920, are as expected for symmetric and antisymmetric W-H (W-D) stretching modes<sup>24</sup> and 1.382 for Si-H (Si-D) stretching mode,<sup>17</sup> which confirms our assignments.

Furthermore, our B3LYP calculations predict larger symmetric-antisymmetric mode separations for the WH<sub>3</sub> than the WD<sub>3</sub> subunits, as is observed here for HSi≡WH<sub>3</sub> and earlier for HC≡WH<sub>3</sub>.<sup>8</sup> In addition, our calculations predict the Si-H stretching mode for HSi≡WH<sub>3</sub> at 2180 cm<sup>-1</sup>, some 60 cm<sup>-1</sup> below the strong mode for silane, and our 2120 cm<sup>-1</sup> band is 72 cm<sup>-1</sup> below this silane absorption in solid neon. Finally, the neon matrix W-H stretching absorptions for HSi≡WH<sub>3</sub> at 1917.6 and 1911.7 cm<sup>-1</sup> are just below the antisymmetric stretching mode for WH<sub>4</sub> in solid neon at 1920.5 cm<sup>-1</sup>.<sup>24</sup>

In the tungsten case, the HSi≡WH<sub>3</sub> product has the lowest energy of the open structures, and reaction 3 proceeds directly to the silyldiyne product. Reaction 3 is computed to be 30 kcal/mol exothermic at the B3LYP level of theory, and the analogous methane reaction to form the methylidyne is exothermic by 40 kcal/mol.<sup>8</sup>



We have located a bridged tungsten dihydride silylidene (Figure S1), which is 9 kcal/mol lower in energy than the open silyldiyne at the B3LYP level of theory. The BPW91 functional found the bridged structure also 9 kcal/mol lower, and the CCSD wavefunction-based method determined 8 kcal/mol lower energy for the bridged silylidene. Again, the calculated frequencies for the bridged isomer do not fit the observed spectrum, this time even more definitively. First, the strongest WH<sub>2</sub> stretching modes of the bridged species (Table S2) are calculated to coincide with those for HC≡WH<sub>3</sub>, and our observed bands are about 10 cm<sup>-1</sup> lower than the bands observed for HC≡WH<sub>3</sub>.<sup>8</sup> Second, the third, longer W-H bond stretching frequency in the bridged silylidene is predicted 40 cm<sup>-1</sup> lower than the two higher W-H stretching modes and with observable intensity, and this region of the spectrum (Figure 2) is free of absorption. Third, the weak 2120 cm<sup>-1</sup> band for a Si-H stretching mode requires the open silyldiyne structure. A 10 kcal/mol transition state barrier (Figure S1) separates the methylidyne observed here from the lower energy tungsten dihydride silylidene. This transition-state structure has an imaginary i554 cm<sup>-1</sup> H-Si deformation frequency. Under higher temperature conditions, the bridged silylidene tungsten dihydride species might be observable.

(24) Wang, X.; Andrews, L. J. *Phys. Chem. A* **2002**, *106*, 6720. (W + H<sub>2</sub>)  
(25) Cordonnier, M.; Bogey, M.; Demuyneck, C.; Destombes, J. L. *J. Chem. Phys.* **1992**, *97*, 7984. and references therein.

(26) Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1992**, *97*, 7990. and references therein.



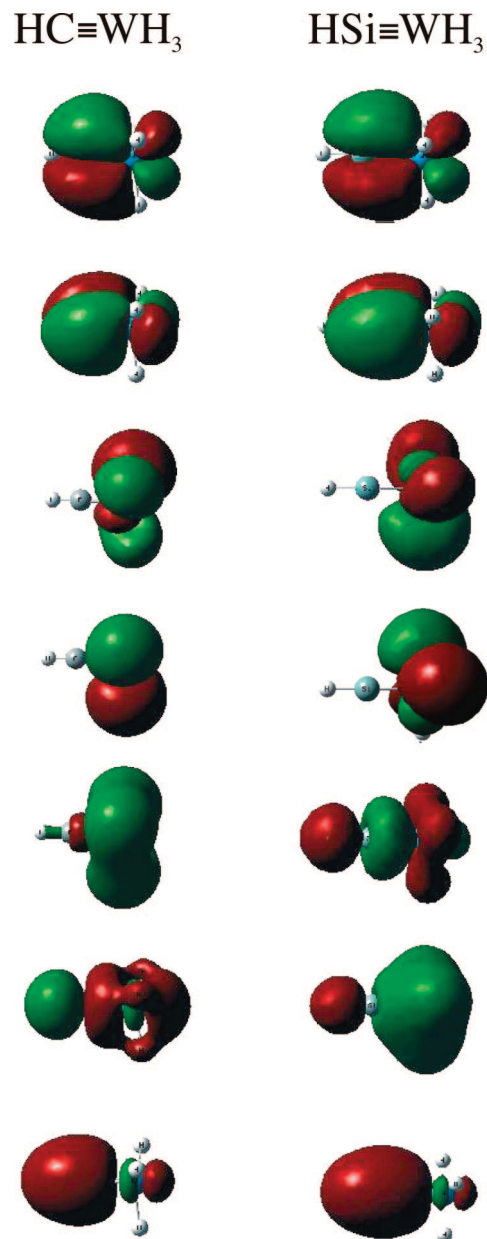
**Structure and Bonding.** The B3LYP-calculated structures for the three products of each group 6 metal atom reaction are collected in Figure 5. The three silyl metal hydrides have  $C_3$  structures comparable to those found for the methyl metal hydrides,<sup>7,8</sup> but of course, the Si–M single bonds are longer than their carbon analogues. The calculated Si–M single bond lengths range from 2.529 Å for Cr to 2.557 Å for Mo to 2.548 Å for the W compound. These open structures for silyl metal hydrides are in contrast to the hydrogen-bridged structure observed and calculated for  $Si_2H_2$ .<sup>25,26</sup>

One of the most interesting comparisons with carbon is for the open silylidene species. First, our computed Si=Mo double-bond length of 2.334 Å is near the 2.288 Å value measured for a chloromesityl silylene complex<sup>2</sup> and that for the Si=Ru bond (2.238 Å) in another silylene complex.<sup>27</sup> Second, notice that the  $SiH_2=MoH_2$  and the  $SiH_2=WH_2$  structures have a plane of symmetry, the two Si–H bonds and the two M–H bonds are equivalent, and therefore no agostic distortion results. Agostic distortion was found for  $CH_2=MoH_2$  at the B3LYP and even more at the CASPT2 level of theory<sup>7,28</sup> and for  $CH_2=WH_2$  using CCSD.<sup>8</sup> Clearly, the H bonded to Si is too far away from the metal center for any interaction that can lead to distortion of these silylidene molecules. And third, notice that the dimensions for the three group 6 metal silylidenes are nearly the same.

The  $HSi=MoH_3$  and  $HSi=WH_3$  structures are calculated to have  $C_{3v}$  symmetry, the same as their carbon analogues,<sup>7–9</sup> and our computed Si=Mo bond length of 2.145 Å may be compared to the 2.219 Å value measured recently for the  $\{[Cp^*(dmpe)(H)MoSiMes]\{B(C_6F_5)_4\}\}$  complex, which was characterized as having considerable silylydine character and the shortest such bond reported to date.<sup>2</sup> However, if our B3LYP calculation provides an accurate representation, the ligated complex may not have a full triple bond between Si and Mo.

It is also significant that the silyne  $HSi=WH_3$  is polarized quite differently from the carbyne  $HC=WH_3$ . Natural charges<sup>16,20</sup> for the atoms in order, left to right, for these two molecules, respectively, are  $-0.16, 0.51, 0.22, -0.19$  ( $\times 3$ ) and  $0.17, -0.033, 0.75, -0.20$  ( $\times 3$ ). This polarization affects the Si–H bond and reduces the s character (39.8%), with the balance (60.2%) in the  $\sigma$  Si–W bond, whereas the C–H bond has more s character (45.3%), with the remainder (54.5%) in the  $\sigma$  C–W bond. In both molecules, the  $\pi$  bonds are valence np–tungsten 5d, as summarized in Table 4. It is noteworthy that the C–H frequency of the methylidyne is about  $50\text{ cm}^{-1}$  higher than that of methane and that the Si–H frequency of the silylydine is  $72\text{ cm}^{-1}$  lower than that of silane. The analogous relationship is found for the silylydine  $HSi=MoH_3$  and the methylidyne  $HC=MoH_3$ , and the natural charges show that the Mo center is negatively charged and the Si=Mo triple bond is more polarized than the Si=W triple bond. The  $\pi$  orbital has slightly less Mo d character, as indicated by the natural bond order calculations (Table 4). Based on reaction energies,  $HSi=WH_3$  is more stable than  $HSi=MoH_3$ .

Finally, the seven highest occupied molecular orbitals for  $HC=WH_3$  and  $HSi=WH_3$  are compared in Figure 6. The two degenerate  $\pi$  orbitals that make up part of the triple bond are highest in both cases, and these orbitals have similar shapes. At the same iso density level, the Si–W  $\pi$  orbital is more diffuse than the C–W  $\pi$  orbital, and the Si center can be seen in the



**Figure 6.** Seven highest molecular orbitals calculated using B3LYP/6-311++G(3df, 3pd) for H, Si, and C and the SDD core potential for W, all plotted at the same 0.02 iso density. Molecular orbitals from top to bottom are degenerate  $\pi$ , degenerate  $\pi$ , degenerate W–H<sub>3</sub>, degenerate W–H<sub>3</sub>, W–H<sub>3</sub>, C(Si)–W  $\sigma$ , and H–C(Si)  $\sigma$ , respectively.

plot but the C center is covered. This is also a consequence of the different polarization (Table 4) in that silicon contains less valence electron density than carbon. Notice that the two degenerate  $WH_3$  and the non-degenerate  $WH_3$  molecular orbitals are almost the same for each molecule. There are only slight differences in the  $\sigma$  C–W and Si–W and the  $\sigma$  C–H and Si–H molecular orbitals, as expected for these isoelectronic valence shell molecules.

The effective bond order (EBO) for the triple bonds can be estimated from the orbital occupancies, which are listed in Table 4. First, note that the occupancies calculated by the B3LYP density functional are an approximation, but we believe a very good one. The total  $\sigma$  and  $\sigma^*$  occupancy is 2.01, and the total  $\pi$  and  $\pi^*$  occupancy is 3.97 for 5.98 electrons instead of the anticipated six. The EBO thus calculated for the Si=Mo triple

(27) Grumbine, S. K.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D. *Organometallics* **1998**, *17*, 5607.

(28) Roos, B. O.; Lindh, R. H.; Cho, H.-G.; Andrews, L. *J. Phys. Chem. A* **2007**, *111*, 6420. (theoretical study of  $CH_2=MH_2$  complexes)



bond is 2.83, which is slightly lower than our value for the C≡Mo triple bond in HC≡MoH<sub>3</sub>, namely 2.90. Our B3LYP approximation for HSi≡WH<sub>3</sub> is not quite as good, as we account for only 5.92 electrons in the triple bond: the EBO is 2.88, slightly less than the 2.92 value calculated for HC≡WH<sub>3</sub>. Finally, the EBO values calculated using the pure BPW91 density functional are 2.84 and 2.89 for the Si≡Mo and Si≡W triple bonds, which are essentially the same as those found with the hybrid B3LYP density functional, and they substantiate the slightly stronger triple bond for the heaviest group 6 metal and silicon.

## Conclusions

Silane reacts with laser-ablated group 6 metal atoms to form SiH<sub>3</sub>–MH hydride intermediates, which are identified from M–H and Si–H stretching modes. Next, α-H-transfer gives the silylidene SiH<sub>2</sub>=MH<sub>2</sub> and the HSi≡MH<sub>3</sub> (M = Mo, W) silyldiyne molecules, but only the latter are observed. Calculations for the group 6 silylidene molecules reveal C<sub>s</sub> structures with no evidence of agostic distortion, in contrast to the corresponding methyldiene molecules.<sup>7–9</sup> This first identification of the simplest molybdenum and tungsten trihydride silyldiyne molecules as major products from the strong M–H stretching modes is made possible through deuterium substitution and comparison with frequencies and intensities from density

functional calculations and from the analogous methyldynes. Density functional calculations find silyldiyne C<sub>3v</sub> structures with longer Si–H bonds than silane, but the C<sub>3v</sub> methyldiyne analogues have shorter C–H bonds than methane, and the Si≡Mo and Si≡W bonds are polarized differently from their carbon analogues. As might be expected, we find the effective triple bond orders of the silyldynes slightly lower than their methyldiyne counterparts. Finally, lower energy bridged metal dihydride silylidene isomers have been located, but these structures are separated by 10–14 kcal/mol higher energy transition states from the silyldynes identified in these low-temperature matrix isolation experiments.

**Acknowledgment.** We gratefully acknowledge financial support from NSF Grant CHE 03-52487 and NCSA computing Grant No. CHE07-0004N to L.A. and calculation of the HC≡WH<sub>3</sub> molecular orbitals by H.-G. Cho.

**Supporting Information Available:** Complete ref 16; Table S1, showing calculated chromium silylidene frequencies, Figure S1, showing calculated structures, and Table S2, showing calculated frequencies for bridged metal dihydride silylidene structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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