

# Strategies for Designing a High-Valent Transition-Metal Silylidene Complex

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The electronic structure of complexes arising from the formation of a double bond between a silylene ligand (Si(R)R') and a high-valent transition-metal fragment have been investigated using ab initio wave functions including the effects of electron correlation. Using the analogy of carbon, these complexes may be referred to as Schrock-type silylenes or silylidenes. A prime motivation for this work is that complexes of this type, unlike their carbon analogues, have so far eluded attempts at experimental characterization. Several conclusions are reached as a result of these calculations. (a) The inclusion of electron correlation is necessary to adequately describe the MSi  $\pi$ -bond, while the MSi  $\sigma$ -bond is adequately described at the Hartree-Fock level. (b) The GVB overlap (an indicator of kinetic stability) and MSi force constants (an indicator of thermodynamic stability) increase upon replacement of H with ligands (e.g.,  $H_nM=SiH_2 \rightarrow Cl_nM=SiH_2$ ) and substituents (e.g.,  $H_nM=SiH_2 \rightarrow H_nM=SiCl_n$ ) that are more electron withdrawing than H. (c) The MSi force constants are larger for the group VB silylidenes when compared to analogous group IVB silylidenes preceding them in the same row of the periodic table (i.e., Nb > Zr and Ta > Hf). (d) Analysis of the molecular and electronic structural data using the MC/LMO/CI approach leads to the conclusion that stronger MSi double bonds arise when the MSi  $\pi$ -bond is made more back-bonding in nature. The results suggest several strategies for synthesizing a silylidene which is stable enough to allow for experimental characterization.

## 1. Introduction

Complexes with a multiple bond between the heavier main-group elements (e.g., Si, P, and S) and a transition metal,  $L_nM=ER_y$  (where E is a main-group element of the third row or lower), have been the target of synthetic efforts recently, with some success.<sup>1,2</sup> However, the number of such compounds which have been characterized in no way rivals their lighter congeners—oxo ( $L_nM=O$ ), carbene ( $L_nM=C(R)R'$ ), or imido ( $L_nM=NR$ ) complexes.<sup>3</sup> In the majority of  $L_nM=ER_y$  complexes involving the heavier group IVA elements, the transition metal is in a low formal oxidation state with  $\pi$ -donor substituents on the ligated group IVA atom.<sup>2</sup> Thus, these compounds can be considered analogous to Fischer-type carbenes, i.e. Fischer-type silylenes, germylenes, etc. During an investigation<sup>4</sup> into the coordinatively unsaturated complexes  $MSiH_2^+$ , we were struck by the apparent lack of examples in which silicon is multiply bonded to an early, high-valent transition metal. Using the analogy of carbenes, complexes of this type could be referred to as Schrock-type silylenes or silylidenes.

High-valent silylidene complexes have been proposed as intermediates in the polymerization of silanes and dehydrogenative coupling of silanes catalyzed by group IVB organometallics.<sup>5a</sup> Silylidenes must also be regarded as plausible intermediates in the laser-assisted chemical vapor deposition of transition-metal silicides from silane and metal halides.<sup>5b</sup> However, no silylidene has been successfully isolated and characterized.<sup>5</sup> Thus, the present state of affairs for silylidenes resembles that of the alkylidenes (i.e., Schrock-type carbenes) some 20 years ago; i.e., they are postulated as important intermediates, but they await the choice of suitable experimental conditions to permit characterization. Complexes were chosen for study on the basis of analogy with well-known alkylidenes.<sup>6</sup> The compounds fall into two classes—group IVB ( $M = Ti, Zr, Hf$ ) and group VB ( $M = Nb, Ta$ ).<sup>7</sup> The ligands and

substituents were modified as outlined below. Several questions are of primary interest.

(1) Multiple bonding by carbene equivalents (Ch, where Ch is a chalcogen; PnR, where Pn is a pnictogen; TR<sub>2</sub>, where T is a group IVA element) can be found in: (a) Mayer, J. M.; Nugent, W. A. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1989. Metal-Chalcogen Multiple Bonds: (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 56. (c) Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Bock, H.; Veltmann, A. *J. Am. Chem. Soc.* 1986, 108, 3134. (d) Hughes, D. L.; Lane, J. D.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* 1991, 1627. Metal-Pnictogen Multiple Bonds: (e) Cowley, A. H. *J. Organomet. Chem.* 1990, 400, 71. (f) Stephan, D. W.; Ho, J. Presented at the 74th Canadian Chemical Conference, Hamilton, Ontario, June 1991; IN-A2. (g) Cowley, A. H.; Pellerin, B.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* 1990, 112, 6734. (h) Cowley, A. H.; Geertz, R. L.; Nunn, C. M. *J. Am. Chem. Soc.* 1987, 109, 6523. (i) Mathey, F. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 275. (j) Hitchcock, P. B.; Lappert, M. F.; Leung, W. P. *J. Chem. Soc., Chem. Commun.* 1987, 1282.

(2) Characterized complexes with multiple bonds between silicon and its heavier congeners: (a) Petz, W. *Chem. Rev.* 1986, 86, 1019. (b) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* 1987, 109, 5872. (c) Jützi, P.; Möhrke, A. *Angew. Chem., Int. Ed. Engl.* 1990, 29, 893. (d) Zybilla, C.; Wilkinson, D. L.; Leis, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 203. Zybilla, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 669. Zybilla, C.; Müller, G. *Organometallics* 1988, 7, 1368. (e)  $MSiH_2^+$  complexes in the gas phase: Kang, H.; Jacobson, D. B.; Shin, S. K.; Beauchamp, J. L.; Bowers, M. T. *J. Am. Chem. Soc.* 1986, 108, 5668. (f) Nakatsuji and co-workers have published the results of ab initio calculations on the hypothetical complex  $(CO)_5Cr(Si(H)OH)$  at a relatively low level of theory: Nakatsuji, H.; Ushio, J.; Yonezawa, T. *J. Organomet. Chem.* 1983, 258, C1. (g) Numerous references to the original literature can be found in: Leis, C.; Zybilla, C.; Lachmann, J.; Müller, G. *Polyhedron* 1991, 10, 1163. Zhang, C.; Grumbine, S. D.; Tilley, T. D. *Polyhedron* 1991, 10, 1173. Berry, D. H.; Chey, J.; Zipin, H. S.; Carroll, P. J. *Polyhedron* 1991, 10, 1189.

(3) Multiply bonded second-row carbene, nitrene, and oxo complexes: (a) *Transition Metal Carbene Complexes*; Dötz, K. H., Ed.; Verlag Chemie: Weinheim, 1983; p 73. Imido or nitrene (NR) complexes: (b) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* 1980, 31, 123. (c) Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* 1981, 20, 413. (d) Examples of Fischer-type nitrenes,  $(CO)_5W=NR$ , are reported in: Sleiman, H. F.; Arndtsen, B. A.; McElwee-White, L. *Organometallics* 1991, 10, 541. Oxo complexes: (e) Holm, R. H. *Chem. Rev.* 1987, 87, 1401. (4) Cundari, T. R.; Gordon, M. S. *J. Phys. Chem.* 1992, 96, 631.

(5) (a) Harrod, J. F.; Ziegler, T.; Tschinke, V. *Organometallics* 1990, 9, 997. Brown-Wensley, K. A. *Organometallics* 1987, 6, 1596. Aitken, C.; Gill, U. S.; Harrod, J. F. *Can. J. Chem.* 1987, 65, 1804. Chang, L. S.; Corey, J. Y. *Organometallics* 1989, 8, 1885. (b) Herman, I. P. *Chem. Rev.* 1989, 89, 1323.

(6) (a) Schrock, R. R. *Acc. Chem. Res.* 1990, 23, 158. (b) Schrock, R. R. *Acc. Chem. Res.* 1979, 12, 98.

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Table I. Calculated Metal-Silicon Properties at Various Levels of Theory<sup>a</sup>

	H <sub>2</sub> Ti=SiH <sub>2</sub>	H <sub>2</sub> Zr=SiH <sub>2</sub>	H <sub>2</sub> Hf=SiH <sub>2</sub>	H <sub>3</sub> Nb=SiH <sub>2</sub>	H <sub>3</sub> Ta=SiH <sub>2</sub>
	RHF <sup>b</sup>				
R <sub>M<sub>Si</sub></sub> , Å	2.54	2.54	2.50	2.45	2.45
ν <sub>M<sub>Si</sub></sub> , cm <sup>-1</sup>	295	393	397	390	416
energy, hartrees	-63.3816	-52.3412	-54.2518	-62.6854	-63.6423
	GVB-1/TCSCF <sup>b</sup>				
R <sub>M<sub>Si</sub></sub> , Å	2.55	2.63	2.58 (TS)	2.51	2.49
ν <sub>M<sub>Si</sub></sub> , cm <sup>-1</sup>	354	336	335	374	361
energy, hartrees	-63.4431	-52.3750	-54.2786	-62.7158	-63.6705
	FORS-44 <sup>b</sup>				
R <sub>M<sub>Si</sub></sub> , Å	2.51	2.61	2.58	2.49	2.48
ν <sub>M<sub>Si</sub></sub> , cm <sup>-1</sup>	351	325	327	370	359
energy, hartrees	-63.4606	-52.3918	-54.2957	-62.7420	-63.6934

<sup>a</sup>The properties were calculated with the various wave functions using the basis sets described in the Calculations section. <sup>b</sup>See the Calculations section for a discussion of each of the three levels of theory—RHF, GVB-1/TCSCF, and FORS-44.

(1) What is the appropriate level of theory at which to study silylidenes? A preliminary study of MSiH<sub>2</sub><sup>+</sup> complexes show that an explicit account of electron correlation is necessary even for the calculation of properties such as equilibrium geometry.<sup>4</sup>

(2) How does the electronic structure of the silylidene change in response to modification of the ligands, metal, and substituent? A similar study<sup>8</sup> has been performed for high-valent alkylidene complexes (L<sub>n</sub>M=C(R)R').

(3) How does the bonding in silylidenes compare with that of their more well-studied carbon analogues? Alkylidenes, unlike silylidenes, are abundant throughout the chemical literature.<sup>1a,6</sup>

(4) Does the electronic structure of the silylidenes suggest how they may be stabilized to allow for experimental characterization?

## 2. Calculations

The calculations described herein are carried out at the ab initio level using the GAMESS quantum chemistry program package.<sup>9</sup> Effective core potentials (ECP's) are used to replace the core electrons of the transition metals, Si, and Cl.<sup>10a</sup> The C and H atoms are described at the all-electron level by employing the 3-21G basis set. The Si, Cl, and C basis sets are augmented with d polarization functions (x<sub>d</sub> = 0.45 for Si; x<sub>d</sub> = 0.75 for Cl; x<sub>d</sub> = 0.80 for C).<sup>10b</sup> Stationary points are located on the potential energy surface (PES) using the methods of Baker.<sup>11</sup> The force constant matrix is calculated at each stationary point in order to characterize the point as a minimum (no imaginary vibrational frequencies) or transition state (one imaginary frequency).

Three levels of theory, differing in the level of correlation used to describe the MSi double bond, are evaluated. The lowest level of theory, restricted Hartree-Fock (RHF), neglects the effects of electron correlation entirely. In the RHF wave function all occupied MO's are doubly occupied while the remaining MO's have an occupation number of 0 (eq 1). The highest level of

$$\Psi_{\text{RHF}} = |\dots\sigma_{\text{MSi}}^2\pi_{\text{MSi}}^2(\pi_{\text{MSi}}^*)^0(\sigma_{\text{MSi}}^*)^0\dots| \quad (1)$$

(7) As for the alkylidenes,<sup>8</sup> vanadium complexes of the form (R<sub>3</sub>V=SiX<sub>2</sub>) could not be isolated as stationary points on the potential energy surface. Geometry optimization of these specific resulted in transfer of a ligand from the metal to the α-silicon, resulting in a three-coordinate silyl complex (i.e., R<sub>3</sub>V=SiX<sub>2</sub> → R<sub>2</sub>V-SiX<sub>2</sub>R).

(8) (a) Cundari, T. R.; Gordon, M. S. *J. Am. Chem. Soc.* 1991, 113, 5231. (b) Cundari, T. R.; Gordon, M. S. *J. Am. Chem. Soc.* 1992, 114, 539. (c) Cundari, T. R.; Gordon, M. S. *Organometallics* 1992, 11, 55.

(9) GAMESS (General Atomic and Molecular Electronic Structure System): Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* 1990, 10, 52.

(10) (a) Krauss, M.; Stevens, W. J.; Jasien, P. G.; Basch, H. *Can. J. Chem.*, in press. (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(11) Baker, J. *J. Comput. Chem.* 1986, 7, 385.

correlation is the four-orbital/four-electron FORS-MCSCF (full optimized reaction space-multiconfiguration SCF) level of theory, denoted FORS-44. The FORS-44 wave function is constructed by creating all 20 configurations (φ<sub>i</sub> in eq 2) that can be formed

$$\Psi_{\text{FORS-44}} = \sum C_i \phi_i \quad (2)$$

by rearranging the four active electrons among the four active orbitals (σ<sub>MSi</sub><sup>2</sup>π<sub>MSi</sub><sup>2</sup>(π<sub>MSi</sub><sup>\*</sup>)<sup>0</sup>(σ<sub>MSi</sub><sup>\*</sup>)<sup>0</sup>).<sup>12</sup> The orbitals within each configuration and their contributions (C<sub>i</sub> in eq 2) to the total wave function (Ψ<sub>FORS-44</sub>) are optimized. An intermediate level of theory is also employed in which only the two π electrons are correlated. In this two-orbital/two-electron (ππ\*) FORS-MCSCF or TCSCF (two configuration SCF) two configurations are optimized (eq 3).

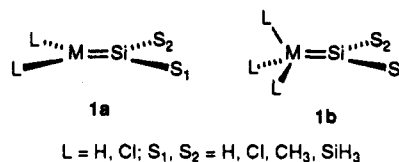
$$\Psi_{\text{TCSCF}} = C_1|\dots\pi_{\text{MSi}}^2(\pi_{\text{MSi}}^*)^0\dots| + C_2|\dots\pi_{\text{MSi}}^0(\pi_{\text{MSi}}^*)^2\dots| \quad (3)$$

All occupied MO's, other than π<sub>MSi</sub>, are assumed to have an occupation number of 2 (including σ<sub>MSi</sub>) in the TCSCF wave function. TCSCF is equivalent to a generalized valence bond (GVB-1)<sup>13</sup> calculation in which one pair is correlated.

## 3. Geometries

**a. Effect of Level of Electron Correlation.** The geometries of the simplest group IVB (H<sub>2</sub>MSiH<sub>2</sub>; M = Ti, Zr, Hf) and group VB (H<sub>3</sub>MSiH<sub>2</sub>; M = Nb, Ta) silylidenes are calculated at the three levels of theory detailed above, to assess the importance of electron correlation before calculating larger, substituted silylidenes. A previous study of MSiH<sub>2</sub><sup>+</sup> showed that explicit consideration of the effects of electron correlation is necessary in order to adequately describe the metal-silicon linkage.<sup>4</sup>

The MSi bond length, stretching frequency, and total energy of the RHF, TCSCF, and FORS-44 stationary points are listed in Table I. The group IVB silylidenes, shown by 1a, are planar and thus structurally resemble



ethylene. The group VB silylidenes, shown by 1b, are approximately tetrahedral about the metal and trigonal planar about the α-silicon; the silylene group is staggered

(12) Feller, D. F.; Schmidt, M. W.; Ruedenberg, K. *J. Am. Chem. Soc.* 1982, 104, 960. Ruedenberg, K.; Schmidt, M. W.; Dombek, M. M.; Elbert, S. T. *Chem. Phys.* 1982, 71, 41, 51, 65. Lam, B.; Schmidt, M. W.; Ruedenberg, K. *J. Phys. Chem.* 1985, 89, 2221.

(13) Bobrowicz, F. W.; Goddard, W. A. in *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 3, p 79.

Table II. Metal-Silicon Bond Lengths, Stretching Frequencies, and Force Constants for Silylidene Minima<sup>a</sup>

	H <sub>2</sub> M=SiH <sub>2</sub>	Cl <sub>2</sub> M=SiH <sub>2</sub>	H <sub>2</sub> M=Si(H)Cl	H <sub>2</sub> M=SiCl <sub>2</sub>	H <sub>2</sub> M=Si(H)Me	H <sub>2</sub> M=Si(H)SiH <sub>3</sub>
M = Ti						
<i>R</i> <sub>MSi</sub>	2.55	2.49	2.55	2.53	2.54	2.56
<i>ν</i> <sub>MSi</sub>	354	389	362	368	363	348
<i>k</i> <sub>MSi</sub>	1.30	1.57	1.36	1.41	1.37	1.26
<i>n</i> <sub>π</sub>	1.557	1.653	1.594	1.637	1.598	1.533
<i>n</i> <sub>π*</sub>	0.443	0.347	0.406	0.363	0.402	0.467
<i>S</i> <sub>GVB</sub>	0.304	0.372	0.329	0.357	0.332	0.288
M = Zr						
<i>R</i> <sub>MSi</sub>	2.63	2.59	2.63	2.63	2.63	2.64
<i>ν</i> <sub>MSi</sub>	336	355	331	334	334	345
<i>k</i> <sub>MSi</sub>	1.49	1.59	1.38	1.40	1.40	1.50
<i>n</i> <sub>π</sub>	1.748	1.783	1.765	1.788	1.771	1.737
<i>n</i> <sub>π*</sub>	0.252	0.217	0.235	0.212	0.229	0.263
<i>S</i> <sub>GVB</sub>	0.450	0.483	0.466	0.488	0.471	0.439
M = Hf						
<i>R</i> <sub>MSi</sub>	2.58	2.54	2.58	2.57	2.58	2.58
<i>ν</i> <sub>MSi</sub>	335	354	335	338	335	326
<i>k</i> <sub>MSi</sub>	1.56	1.78	1.60	1.63	1.60	1.52
<i>n</i> <sub>π</sub>	1.805	1.821	1.817	1.832	1.821	1.801
<i>n</i> <sub>π*</sub>	0.195	0.179	0.183	0.168	0.179	0.199
<i>S</i> <sub>GVB</sub>	0.505	0.523	0.518	0.536	0.522	0.501
M = Nb						
<i>R</i> <sub>MSi</sub>	2.51	2.47	2.51	2.52	2.50	2.50
<i>ν</i> <sub>MSi</sub>	374	389	377	367	380	370
<i>k</i> <sub>MSi</sub>	1.77	1.92	1.80	1.71	1.83	1.73
<i>n</i> <sub>π</sub>	1.769	1.792	1.804	1.824	1.804	1.757
<i>n</i> <sub>π*</sub>	0.231	0.208	0.196	0.176	0.196	0.243
<i>S</i> <sub>GVB</sub>	0.469	0.491	0.504	0.526	0.504	0.458
M = Ta						
<i>R</i> <sub>MSi</sub>	2.49	2.47	2.49	2.50	2.48	2.48
<i>ν</i> <sub>MSi</sub>	361	377	365	361	370	373
<i>k</i> <sub>MSi</sub>	1.86	2.03	1.90	1.86	1.95	1.99
<i>n</i> <sub>π</sub>	1.805	1.804	1.825	1.838	1.829	1.795
<i>n</i> <sub>π*</sub>	0.195	0.196	0.175	0.162	0.171	0.205
<i>S</i> <sub>GVB</sub>	0.505	0.504	0.527	0.542	0.531	0.495

<sup>a</sup> Equilibrium bond lengths (*R*<sub>MSi</sub>, Å), stretching frequencies (*ν*<sub>MSi</sub>, cm<sup>-1</sup>), force constants (*k*<sub>MSi</sub>, in mdyn Å<sup>-1</sup>), π-bonding (*n*<sub>π</sub>) and π-anti-bonding (*n*<sub>π\*</sub>) MO occupations, and GVB overlaps (*S*<sub>GVB</sub>) were calculated at the GVB-1/TCSCF level using the basis sets outlined in the Calculations section.

with respect to the group VB metal fragment. Other geometric parameters, e.g. MH and SiH bond lengths, are not sensitive to the level of theory and are not listed in Table I.

In general (Table I), the shortest MSi bond lengths (*R*<sub>MSi</sub>) and largest MSi stretching frequencies (*ν*<sub>MSi</sub>) are at the RHF level. The FORS-44 geometries have the longest *R*<sub>MSi</sub> and the lowest *ν*<sub>MSi</sub> values. The exception is for Ti, where the reverse is true. Note the planar H<sub>2</sub>Hf=SiH<sub>2</sub> (*C*<sub>2v</sub> symmetry) is a minimum at the RHF and FORS-44 levels but has a small imaginary frequency (40i) corresponding to pyramidalization at the Hf at the TCSCF level. All other silylidene minima are minima at all levels of theory. The TCSCF geometry results (*R*<sub>MSi</sub> and *ν*<sub>MSi</sub> in Table I) are much closer to the FORS-44 values than they are to the RHF values. The evidence indicates that electron correlation is more necessary for an accurate description of the MSi π-bond than the MSi σ-bond, since TCSCF only correlates the electrons in the MSi π-bond.

Comparing the lower levels of theory to the FORS-44 results indicates that GVB-1/TCSCF provides the best balance of computational efficiency and accuracy. The results are in agreement with MCSCF data<sup>4</sup> for MSiH<sub>2</sub><sup>+</sup> and the present results for H<sub>n</sub>M=SiH<sub>2</sub> with the FORS-44 wave function. An analysis of these MSiH<sub>2</sub><sup>+</sup> and H<sub>n</sub>M=SiH<sub>2</sub> MCSCF wave functions yields an occupation number of ~1.95 for σ<sub>MSi</sub>. The natural orbital occupation number (NOON) is the MCSCF equivalent of the molecular orbital occupation numbers in Hartree-Fock theory (2 and 0 in the RHF case). The closer the σ<sub>MSi</sub> NOON is to 2 the

better the bond is described at the Hartree-Fock level of theory. For these reasons the GVB-1/TCSCF wave function is used to calculate the remaining equilibrium geometries.

**b. Calculation of Equilibrium Geometries at the GVB-1/TCSCF Level of Theory.** The MSi equilibrium bond lengths, stretching frequencies, and force constants are listed in Table II for the silylidene complexes studied here. The MH and SiH bond lengths, as well as other geometric parameters, are routine. The coordinates for all the stationary points are given in the supplementary material. Also listed in Table II are the calculated occupation numbers for π<sub>MSi</sub> and π\*<sub>MSi</sub> (*n*<sub>π</sub> and *n*<sub>π\*</sub>, respectively) as well as the GVB overlap (*S*<sub>GVB</sub>).

For a GVB-1/TCSCF wave function (eq 3) the following quantities are of interest:

$$C_1^2 + C_2^2 = 1 \quad (4)$$

$$n_\pi = 2C_1^2 \quad n_{\pi^*} = 2C_2^2 \quad (5)$$

$$S_{\text{GVB}} = (C_1 - C_2)/(C_1 + C_2) = (\sqrt{n_\pi} - \sqrt{n_{\pi^*}})/(\sqrt{n_\pi} + \sqrt{n_{\pi^*}}) \quad (6)$$

The three properties *n*<sub>π</sub>, *n*<sub>π\*</sub>, and *S*<sub>GVB</sub> are a measure of the validity of a single configuration description and therefore of the amount of correlation that takes place between π<sub>MSi</sub> and π\*<sub>MSi</sub>. As *n*<sub>π</sub> approaches 2 (thus, *n*<sub>π\*</sub> approaches 0), the amount of correlation between the two MO's decreases, and the correct wave function becomes a single configuration. In the limit *n*<sub>π</sub> = 2, *S*<sub>GVB</sub> = 1. When

$n_r = 1$ ,  $S_{\text{GVB}} = 0$ . The GVB overlap can therefore be taken as a measure of the biradical character in a specific bond: when  $S_{\text{GVB}} = 1$ , there is no biradical character; as  $S_{\text{GVB}}$  approaches zero, the biradical character increases. The implication is that the greater the biradical character, the smaller the strength of interaction between the two  $\pi$ -electrons and the more susceptible the MSi bond should be to radical processes such as oxidation and polymerization.

The substituted silylidenes show several interesting changes (relative to  $\text{H}_n\text{M}=\text{SiH}_2$ ) due to modification of the ligands, substituents, and metal (Table II). For the present discussion the terms ligands and substituents describe the atom or functional group directly attached to the metal and  $\alpha$ -Si, respectively. The most noticeable change occurs with the replacement of two hydride ligands by two chloro ligands—the contraction of the MSi bond ranges from 0.06 Å ( $M = \text{Ti}$ ) to 0.02 Å ( $M = \text{Ta}$ ). The other silylidenes show decreased biradical character (i.e.,  $S_{\text{GVB}}$  increases) relative to  $\text{H}_n\text{M}=\text{SiH}_2$ , except for the silyl-substituted silylidenes. Other than Ti, the lowest amount of biradical character is found for the dichloro-silylidene complex ( $\text{H}_n\text{M}=\text{SiCl}_2$ ). For the Ti-silylidenes,  $\text{Cl}_2\text{Ti}=\text{SiH}_2$  has the highest  $S_{\text{GVB}}$  value (0.372).

When analogous silylidenes within a group of the periodic table are compared, the MSi force constant (Table II) increases as the atomic number increases (i.e.,  $\text{Hf} > \text{Zr} > \text{Ti}$  and  $\text{Nb} > \text{Ta}$ ). The group VB silylidenes have larger MSi force constants than their group IVB counterparts in the same row of the periodic table (i.e.,  $\text{Nb} > \text{Zr}$  and  $\text{Ta} > \text{Hf}$ ). The average  $k_{\text{MSi}}$  value for each metal is as follows (in  $\text{mdyn \AA}^{-1}$ ): Ti = 1.4; Zr = 1.5; Hf = 1.6; Nb = 1.8; Ta = 1.9. The calculated  $k_{\text{MSi}}$  values are much lower than that calculated for ethylene ( $k_{\text{CC}} = 8.2$ ) but comparable to those calculated for heavier congeners:  $\text{Si}_2\text{H}_4$ ,  $k_{\text{SiSi}} = 2.6$ ;  $\text{Ge}_2\text{H}_4$ ,  $k_{\text{GeGe}} = 2.3$ ;  $\text{Sn}_2\text{H}_4$ ,  $k_{\text{SnSn}} = 1.7$ . The ethylene analogues ( $D_{2h}$ ) were optimized using a FORS-44 wave function and the basis sets outlined above. Examples of the last three compounds, albeit substituted with very bulky ligands, have been structurally characterized.<sup>14</sup> The data imply stronger MSi bonds for Hf and Ta, when compared to their lighter congeners, with the latter metal possessing a slightly stronger MSi bond than the former.

The average GVB overlaps for each metal are 0.33 (Ti), 0.47 (Zr), 0.52 (Hf), 0.49 (Nb), and 0.52 (Ta). From the data in Table II there does not appear to be a 1:1 correlation between  $S_{\text{GVB}}$  and  $k_{\text{MSi}}$ . These  $S_{\text{GVB}}$  values are similar to those for the weakest main-group double bonds (cf.,  $\text{C}_2\text{H}_4$ , 0.65;  $\text{Si}_2\text{H}_4$ , 0.59;  $\text{Ge}_2\text{H}_4$ , 0.57;  $\text{Sn}_2\text{H}_4$ , 0.55). Thus, other than Ti-silylidenes, the amount of biradical character in the metal-silicon  $\pi$ -bond is similar to that for heavy, group IVA ethylene analogues. The  $S_{\text{GVB}}$  value is highest for the heavy silylidenes (Ta and Hf), with little change in the GVB overlap upon going from group IVB to VB.

On the basis of the preliminary data obtained from GVB-1/TCSCF optimization of some high-valent silylidene complexes, several preliminary observations can be made. A detailed analysis of their electronic structures is presented below.

(1) The replacement of H ligands and hydrogen substituents with electron-withdrawing groups causes a decrease in the biradical character (i.e.,  $S_{\text{GVB}}$  increases) of the metal-silicon  $\pi$ -bond. Silyl—the one substituent which is electron-releasing, relative to H—has the opposite effect.

(2) Replacement of the H ligands with Cl ligands causes a marked decrease in the MSi bond length, an increase in the MSi force constant, and a lowering of the biradical character. Although a silylidene with chloro ligands will be kinetically unstable, it is reasonable to expect that a bulkier, electron-withdrawing ligand (e.g., Cp or Cp\*) would have an effect similar to that of Cl on the MSi double bond. Our experience with alkylidenes plus work by others has shown that the replacement of the computationally demanding Cp with Cl is a reasonable approximation in ab initio work.<sup>15</sup>

(3) The replacement of two H substituents with Cl substituents causes a significant decrease in the biradical character of the MSi  $\pi$ -bond. In addition to the  $\sigma$ -withdrawing capability of chlorines (due to their electronegativity), they are also  $\pi$ -donors. A more detailed examination of the silylidene wave functions is needed to ascertain the extent to which these effects are operative.

(4) For silylidenes with identical ligands and substituents, the strongest MSi bond, as measured by  $k_{\text{MSi}}$ , and the lowest amounts of biradical character, as measured by  $S_{\text{GVB}}$ , occur for the heaviest member of each group—Hf and Ta. The former property can be taken as an indicator of thermodynamic stability, while the latter property is suggestive of kinetic stability.

#### 4. Electronic Structure of Silylidenes

On the basis of the changes in the calculated properties, metal-silicon bond lengths, and force constants, changes in the electronic structure, probably subtle, are expected. To probe this, a detailed analysis of the bonding has been carried out. Particular attention has been paid to the metal-silicon linkage, in order to ascertain if the changes in properties can be related to changes in the electronic structure of the silylidenes. In section b(i), the effects of ligand and substituent modification are studied. In section b(ii), a comparison of the various silylidenes is made with respect to changing the central transition metal. Where pertinent, the metal-ligand double bond in the silylidenes (present work) and their alkylidene analogues (previous work<sup>8</sup>) are compared and contrasted. As in previous studies of the metal-carbon<sup>8,16</sup> and metal-silicon<sup>4</sup> double bonds, the MC/LMO/CI procedure is used to describe the electronic structure of the silylidenes.

a. MC/LMO/CI Procedure. The MC/LMO/CI procedure has been described elsewhere<sup>16</sup> and is briefly summarized here. The procedure consists of three steps. In step 1, the canonical, metal-silicon  $\sigma$ ,  $\pi$ ,  $\pi^*$ , and  $\sigma^*$  molecular orbitals (MO's) are identified as the active space and a four-orbital, four-electron (20 configuration) FORS-MCSCF<sup>12</sup> single-point calculation is carried out at the GVB-1/TCSCF geometry. In step 2, the MCSCF natural orbitals are localized using the Boys technique<sup>17</sup> to yield "AO-like" MO's— $\sigma_{\text{Si}}$ ,  $\pi_{\text{Si}}$ ,  $\pi_{\text{M}}$ , and  $\sigma_{\text{M}}$ . The AO-like MO's are predominantly (>98%) located on either the

(14) (a)  $\text{Si}_2(\text{mesityl})_4$  and (*E*)- $\text{Si}_2(\text{mesityl})_2(t\text{-Bu})_2$ ; Fink, M. J.; Michalczuk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* 1984, 3, 793. (b)  $\text{Si}_2(2,6\text{-diethylphenyl})_4$ ; Masamune, S.; Murakami, S.; Snow, J. T.; Tobita, H.; Williams, D. J. *Organometallics* 1984, 3, 334. (c)  $\text{Ge}_2(2,6\text{-diethylphenyl})_4$ ; Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* 1984, 25, 4191. (d)  $\text{Ge}_2(\text{CH}(\text{SiMe}_3)_2)_4$  and  $\text{Sn}_2(\text{CH}(\text{SiMe}_3)_2)_4$ ; Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Chem. Commun.* 1986, 2387.

(15) Some papers, in addition to ref 8, in which the Cp  $\rightarrow$  Cl modification has been employed in ab initio work: (a) Goddard, W. A.; Steigewald, M. S. *J. Am. Chem. Soc.* 1985, 107, 5027. (b) Rappé, A. K. *Organometallics* 1987, 6, 354. (c) Hay, P. J.; Ryan, R. R.; Salazar, K. V.; Wroblewski, D. A.; Sattelberger, A. P. *J. Am. Chem. Soc.* 1986, 108, 313. (16) A more detailed description of the MC/LMO/CI procedure as used here is presented in ref 8a. The MC/LMO/CI method has also been applied to main-group compounds.<sup>12</sup>

(17) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* 1960, 32, 300.

Table III. Primary Resonance Contributors to Group IVB Silylidenes<sup>a</sup>

	H <sub>2</sub> M=SiH <sub>2</sub>	Cl <sub>2</sub> M=SiH <sub>2</sub>	H <sub>2</sub> M=Si(H)Cl	H <sub>2</sub> M=SiCl <sub>2</sub>	H <sub>2</sub> M=Si(H)Me	H <sub>2</sub> M=Si(H)SiH <sub>3</sub>	av <sup>c</sup>
M = Ti							
[2200)	0.3 (2.6)	0.3 (1.6)	0.3 (2.1)	0.2 (1.9)	0.3 (2.3)	0.3 (3.5)	0.3 (2.3)
[1201)	1.9 (9.7)	2.3 (7.1)	1.7 (7.2)	1.4 (5.6)	2.0 (9.3)	2.0 (13.5)	1.9 (8.7)
[0202)	0.8 (2.3)	1.0 (2.0)	0.8 (1.7)	0.7 (1.3)	0.9 (2.3)	0.9 (3.0)	0.9 (2.1)
[2110)	34.6 (36.2)	30.3 (33.8)	33.3 (39.1)	31.4 (42.0)	34.1 (34.1)	35.2 (35.0)	33.2 (36.7)
[1111)	44.6 (36.5)	42.7 (40.0)	43.7 (36.4)	42.9 (35.8)	43.1 (37.6)	45.3 (33.9)	43.7 (36.7)
[0112)	5.4 (2.6)	4.3 (3.2)	6.0 (2.6)	6.7 (2.6)	4.9 (2.8)	5.2 (2.3)	5.4 (2.7)
[2020)	8.2 (7.3)	13.2 (8.9)	9.2 (8.0)	10.2 (8.0)	10.0 (8.3)	7.5 (6.5)	9.7 (7.8)
[1021)	3.8 (2.6)	5.4 (3.4)	4.6 (2.7)	5.7 (2.6)	4.4 (3.1)	3.3 (2.1)	4.5 (2.8)
[0022)	0.2 (0.1)	0.3 (0.1)	0.3 (0.1)	0.5 (0.1)	0.3 (0.1)	0.2 (0.1)	0.3 (0.1)
Σ <sup>b</sup>	99.8 (99.9)	99.8 (100.1)	99.9 (99.9)	99.7 (99.9)	100.0 (99.9)	99.9 (99.9)	
M = Zr							
[2200)	1.6 (6.3)	1.3 (5.0)	1.5 (6.3)	1.4 (6.4)	1.6 (5.5)	1.4 (7.9)	1.5 (6.2)
[1201)	5.5 (14.1)	4.9 (12.3)	5.0 (12.9)	4.4 (11.8)	5.4 (13.5)	4.4 (16.8)	4.9 (13.6)
[0202)	2.0 (3.1)	1.8 (3.1)	1.9 (2.8)	1.8 (2.5)	1.9 (3.2)	1.8 (3.5)	1.9 (3.0)
[2110)	31.5 (30.9)	28.8 (29.8)	30.4 (32.9)	28.8 (35.0)	30.6 (27.9)	28.8 (30.5)	29.8 (31.2)
[1111)	40.0 (32.8)	39.5 (34.8)	39.6 (32.4)	39.3 (31.7)	39.1 (34.0)	39.3 (30.5)	39.5 (32.7)
[0112)	5.7 (3.1)	5.5 (3.6)	6.2 (3.0)	6.7 (2.8)	5.5 (3.3)	6.7 (2.6)	6.1 (3.1)
[2020)	8.6 (6.8)	11.3 (7.6)	9.3 (6.8)	10.2 (6.9)	9.9 (7.5)	10.2 (5.8)	9.9 (6.9)
[1021)	4.7 (2.9)	6.2 (3.6)	5.4 (2.8)	6.5 (2.7)	5.4 (3.5)	6.5 (2.2)	5.8 (3.0)
[0022)	0.4 (0.1)	0.4 (0.2)	0.5 (0.1)	0.6 (0.1)	0.4 (0.1)	0.6 (0.1)	0.5 (0.1)
Σ	100.0 (100.1)	99.7 (100.0)	99.8 (100.0)	99.7 (99.9)	99.8 (100.0)	99.7 (99.9)	
M = Hf							
[2200)	2.4 (8.1)	2.0 (6.8)	2.2 (8.2)	1.9 (8.4)	2.3 (7.3)	2.5 (10.0)	2.2 (8.1)
[1201)	7.7 (15.1)	7.0 (13.6)	7.1 (14.3)	6.4 (13.5)	7.5 (14.7)	8.4 (17.4)	7.4 (14.8)
[0202)	3.1 (3.1)	2.7 (3.0)	3.0 (2.9)	2.9 (2.7)	2.9 (3.2)	3.3 (3.3)	3.0 (3.0)
[2110)	27.8 (31.1)	26.8 (30.6)	26.6 (32.7)	25.2 (34.2)	27.2 (29.7)	27.8 (30.8)	26.9 (31.5)
[1111)	39.4 (30.4)	39.3 (32.2)	39.5 (30.1)	39.4 (29.4)	39.0 (31.7)	39.4 (28.2)	39.3 (30.3)
[0112)	6.7 (2.8)	6.6 (3.2)	7.5 (2.8)	8.1 (2.7)	6.8 (3.1)	6.8 (2.4)	7.1 (2.8)
[2020)	7.3 (6.4)	9.0 (7.1)	7.8 (6.4)	8.4 (6.4)	8.2 (7.0)	6.8 (5.6)	7.9 (6.5)
[1021)	4.9 (2.7)	5.9 (3.2)	5.6 (2.6)	6.5 (2.5)	5.5 (3.2)	4.5 (2.2)	5.5 (2.7)
[0022)	0.5 (0.1)	0.5 (0.1)	0.6 (0.1)	0.8 (0.1)	0.5 (0.1)	0.4 (0.1)	0.6 (0.1)
Σ	99.8 (99.8)	99.8 (99.8)	99.9 (100.1)	99.6 (99.9)	99.9 (100.0)	99.9 (100.0)	
M = Nb							
[2200)	0.9 (3.7)	0.5 (2.6)	0.9 (3.3)	0.8 (3.5)	0.9 (3.1)	0.9 (4.6)	0.8 (3.5)
[1201)	4.8 (11.7)	3.6 (9.7)	4.2 (10.2)	3.5 (9.4)	4.5 (11.0)	5.3 (14.2)	4.3 (11.0)
[0202)	1.9 (3.5)	1.8 (3.4)	1.6 (2.9)	1.3 (2.5)	1.7 (3.4)	2.1 (4.0)	1.7 (3.3)
[2110)	24.1 (26.3)	19.3 (24.0)	25.8 (27.4)	26.0 (30.6)	24.4 (24.6)	25.3 (25.8)	24.2 (26.5)
[1111)	41.5 (37.4)	43.4 (40.1)	39.0 (37.9)	36.9 (36.3)	40.1 (38.5)	42.5 (36.0)	40.6 (37.7)
[0112)	5.3 (4.4)	6.8 (5.5)	4.9 (4.3)	4.8 (3.8)	5.0 (4.8)	5.2 (4.1)	5.3 (4.5)
[2020)	13.2 (8.1)	13.7 (8.8)	15.1 (8.8)	16.8 (9.2)	14.6 (8.9)	11.6 (7.0)	14.2 (8.5)
[1021)	7.6 (4.5)	9.9 (5.6)	7.9 (4.9)	8.8 (4.4)	8.1 (5.4)	6.5 (3.8)	8.1 (4.8)
[0022)	0.5 (0.2)	0.7 (0.3)	0.5 (0.2)	0.6 (0.2)	0.5 (0.3)	0.4 (0.2)	0.5 (0.2)
Σ	99.8 (99.8)	99.6 (100.0)	99.9 (99.9)	99.5 (99.9)	99.8 (100.0)	99.8 (99.7)	
M = Ta							
[2200)	1.5 (5.5)	1.0 (4.3)	1.4 (5.2)	1.3 (5.3)	1.5 (4.8)	1.6 (6.8)	1.4 (5.3)
[1201)	6.3 (13.4)	5.2 (11.9)	5.6 (12.0)	4.8 (11.3)	6.1 (12.8)	7.0 (15.8)	5.8 (12.9)
[0202)	2.3 (3.3)	2.2 (3.3)	2.1 (2.9)	1.9 (2.6)	2.2 (3.3)	2.6 (3.7)	2.2 (3.2)
[2110)	26.5 (28.2)	22.5 (26.7)	26.1 (29.8)	25.7 (31.7)	25.5 (26.6)	26.4 (27.8)	25.5 (28.5)
[1111)	39.7 (34.1)	41.7 (36.1)	38.8 (33.9)	37.9 (33.3)	39.0 (35.1)	40.3 (32.4)	39.6 (34.2)
[0112)	5.5 (3.7)	6.7 (4.5)	5.7 (3.6)	5.9 (3.4)	5.4 (4.0)	5.5 (3.3)	5.8 (3.8)
[2020)	11.0 (7.6)	11.6 (8.1)	12.1 (8.1)	13.1 (8.3)	12.3 (8.3)	10.0 (6.8)	11.7 (7.9)
[1021)	6.5 (3.9)	8.3 (4.6)	7.4 (4.0)	8.3 (3.8)	7.5 (4.7)	6.0 (3.3)	7.3 (4.1)
[0022)	0.5 (0.2)	0.7 (0.3)	0.6 (0.2)	0.7 (0.2)	0.5 (0.2)	0.4 (0.1)	0.6 (0.2)
Σ	99.8 (99.9)	99.9 (99.8)	99.8 (99.7)	99.6 (99.9)	100.0 (99.8)	99.8 (100.0)	

<sup>a</sup>The contributions (in percentage terms) made by the various resonance structures were calculated using the basis sets described in the Calculations section. The resonance structures are denoted by  $|\sigma_{\text{Si}}^w \pi_{\text{Si}}^x \pi_{\text{M}}^y \sigma^z\rangle$  or  $|wxyz\rangle$ , where  $w$ ,  $x$ ,  $y$ , and  $z$  are the occupation numbers of the various AO-like MO's. The calculated values for their alkylidene analogues are taken from ref 7 and are given in parentheses. <sup>b</sup>The sum of the nine "chemical" configurations. <sup>c</sup>Average of the contributions for the six silylidenes (and alkylidenes) for each metal. In most cases, deviations from 100.0 are due to round-off.

metal (M) or silicon (Si) end of the MSi bond. Step 3, configuration interaction (CI) with an active space of the AO-like MO's, is used to generate the 20 possible configurations (corresponding to valence bond resonance structures) and to calculate the weight of each.

Of the 20 configurations, only a limited number are physically sensible. The resonance structures are denoted  $|\sigma_{\text{Si}}^w \pi_{\text{Si}}^x \pi_{\text{M}}^y \sigma^z\rangle$  or  $|wxyz\rangle$ , where  $w$ ,  $x$ ,  $y$ , and  $z$  are the occupation numbers of the various AO-like MO's.<sup>18</sup> It

seems logical to expect that those resonance structures which possess two electrons each in the  $\sigma$  and  $\pi$  manifolds (i.e.,  $w + z = x + y = 2$ ) will be the prime contributors. In this way the silylidene avoids large contributions from

(18) There are two [1111] configurations, since there are two ways of obtaining a singlet from four singly occupied spatial orbitals, i.e.  $\alpha\alpha\beta\beta$  and  $\alpha\beta\alpha\beta$ . The contributions from both [1111] spin configurations are summed together.

Number	Res. Structure	Config.	Sigma- and Pi-Bonds
I	$M \rightleftharpoons Si$	2200>	$\sigma$ -dative/ $\pi$ -dative
III	$M \rightleftharpoons Si$	1201>	$\sigma$ -covalent/ $\pi$ -dative
VI	$M \rightleftharpoons Si$	0202>	$\sigma$ -backbond/ $\pi$ -dative
VII	$M \rightleftharpoons Si$	2110>	$\sigma$ -dative/ $\pi$ -covalent
IX, XI	$M \rightleftharpoons Si$	1111> x 2	$\sigma$ -covalent/ $\pi$ -covalent
XIV	$M \rightleftharpoons Si$	0112>	$\sigma$ -backbond/ $\pi$ -covalent
XV	$M \rightleftharpoons Si$	2020>	$\sigma$ -dative/ $\pi$ -backbond
XVIII	$M \rightleftharpoons Si$	1021>	$\sigma$ -covalent/ $\pi$ -backbond
XX	$M \rightleftharpoons Si$	0022>	$\sigma$ -backbond/ $\pi$ -backbond

**Figure 1.** The nine "chemical" configurations which describe the metal-silicon double bond. The upper line (or arrow) describes the  $\pi$ -bond; the lower arrow (or line) represents the  $\sigma$ -bond. The usual convention of a straight line signifying a covalent linkage and an arrow representing a dative bond (pointing from ligand to metal) or back-bonding (pointing from metal to ligand) has been used. Other designations are explained in the text.

configurations with weaker one- and three-electron bonds. It is satisfying that the MC/LMO/CI scheme predicts (Table III) that only those configurations which conform to this chemical intuition make any appreciable contribution to the total wave functions. There are nine such "chemical" configurations, and as shown in Table III, these configurations account for nearly all (>99%) of the wave functions for the compounds considered here. The nine chemical configurations which describe the metal-silicon double bond, or any double bond, are depicted schematically in Figure 1.

To facilitate the analysis of the MC/LMO/CI results, the nine chemical configurations can be subdivided into groups, depending on how the four electrons in the metal-silicon bonding regions are distributed. The MSi  $\sigma$  bond can be described as  $\sigma$ -dative ( $|2xy0\rangle$ ),  $\sigma$ -covalent ( $|1xy1\rangle$ ), or  $\sigma$ -back-bonding ( $|0xy2\rangle$ ), where  $x, y = 0, 1, 2$  and  $x + y = 2$ . The MSi  $\pi$ -bond descriptions are  $\pi$ -dative ( $|w20z\rangle$ ),  $\pi$ -covalent ( $|w11z\rangle$ ), and  $\pi$ -back-bonding ( $|w02z\rangle$ ) where  $w, z = 0, 1, 2$  and  $w + z = 2$ . Each of the nine chemical configurations is, of course, a combination of two of these descriptions (as shown in Figure 1), one each for the  $\sigma$ - and  $\pi$ -bonds. The average contribution of each bonding type as a function of the metal is given in Table IV.

**b. MC/LMO/CI Results for Silylidenes. i. Effect of Ligand and Substituent Modification on Silylidenes.** The MSi bond is less sensitive to ligand and substituent modification than is the  $\pi$ -bond. Thus, for the silylidenes studied here the two electrons in the MSi  $\sigma$ -bond are distributed  $\sigma_M/\sigma_{Si} = 0.7/1.3$ , except for Ti, which is more heavily weighted toward the  $\alpha$ -Si ( $\sigma_M/\sigma_{Si} = 0.6/1.4$ ). That the metal-silicon  $\sigma$ -bond is less perturbed than the  $\pi$ -bond by ligand and substituent changes is not surprising, since the MSi  $\pi$ -bonding MO is less tightly bound.

Replacing the hydride ligands with chloro ligands (i.e.,  $H_nM=SiH_2 \rightarrow Cl_nM=SiH_2$ ) makes the  $\pi$ -bond more polarized toward the metal. Evidence for the greater polarization toward the metal is shown in Table III: as one gas from  $H_nM=SiH_2$  to  $Cl_nM=SiH_2$ , there is an increase in  $\pi$ -back-bonding resonance structures. For the group IVB silylidenes, the increase in the  $\sigma$ -dative/ $\pi$ -back-bond resonance structure ( $|2020\rangle$ ) is greater than that for the  $\sigma$ -covalent/ $\pi$ -back-bond ( $|1021\rangle$ ) resonance structure; the situation is reversed in the group VB alkylidenes (cf.  $H_3M=SiH_2 \rightarrow Cl_3M=SiH_2$ ). The increase in  $\pi$ -back-bond configurations comes at the expense of both the  $\pi$ -covalent ( $|w11z\rangle$ ) and  $\pi$ -dative ( $|w20z\rangle$ ) configurations for the

**Table IV. Average Configuration Contributions as a Function of the Metal<sup>a</sup>**

bond type	config	resonance structure types, <sup>b</sup> %				
		Ti	Zr	Hf	Nb	Ta
$\sigma$ -covalent	$ 1xy1\rangle$	50.1	50.2	52.2	53.0	52.7
$\sigma$ -dative	$ 2xy0\rangle$	43.2	41.2	37.0	39.2	38.6
$\sigma$ -back-bonding	$ 0xy2\rangle$	6.6	8.5	10.7	7.5	8.6
$\pi$ -covalent	$ w11z\rangle$	82.3	75.4	73.3	70.1	70.9
$\pi$ -dative	$ w20z\rangle$	3.1	8.5	10.7	7.5	8.6
$\pi$ -back-bonding	$ w02z\rangle$	14.5	16.2	14.0	22.8	19.6

<sup>a</sup>The values in this table are taken from the average contributions made by the different resonance structures (last column in Table III) of each of the six silylidenes studied for a particular metal. Note that the three  $\sigma$  types and  $\pi$  types separately sum to 100%. <sup>b</sup>The various bond types and the resonance structures which possess these bonding types are described in the text and listed in Figure 1.

second- and third-row metals, but mostly the former for the Ti-silylidenes. Since the  $\pi$ -bond in silylidenes is more polarized toward the metal in the parent  $H_nM=SiH_2$  complex, the modification  $H_nM=SiH_2 \rightarrow Cl_nM=SiH_2$  makes the  $\pi$ -bond in the latter more back-bonding in nature. A similar trend is seen for alkylidenes (Table III), but to a smaller extent. The silylidene results are also in agreement with previous calculations<sup>4</sup> on  $MSiH_2^+$ , which showed that making the metal more electronegative (by moving to the right in the transition series in the case of  $MSiH_2^+$ ) polarizes the  $\pi$ -bond toward the metal.

Interestingly, a double replacement of the H substituents with Cl substituents (i.e.,  $H_nM=SiH_2 \rightarrow H_nM=SiCl_2$ ) has the same outcome as replacing the hydride ligands with Cl ligands; i.e., the  $\pi$ -bond becomes more polarized toward the metal in the substituted silylidene. There is an increase in the weight of  $\pi$ -back-bond ( $|w02z\rangle$ ) and  $\pi$ -covalent ( $|w11z\rangle$ ) resonance structures coupled with a decrease in  $\pi$ -dative ( $|w20z\rangle$ ) resonance structures, as shown in Table III. Chlorine has a doubly occupied  $3p\pi$  orbital whose electrons will "repel" electrons in  $\pi_{Si}$  and lower the contribution of resonance structures in which  $\pi_{Si}$  is doubly occupied (i.e.,  $\pi$ -dative) relative to those in which  $\pi_{Si}$  is singly occupied and unoccupied (i.e.,  $\pi$ -covalent and  $\pi$ -back-bond configurations, respectively).<sup>8,19</sup> In other words, the Cl substituent is acting as a  $\pi$ -donor.

The changes brought about by the other ligands and substituents are even smaller than those brought about by replacement of H with Cl. The small changes indicate that the nature of the metal-silicon bond is fairly constant for a given metal<sup>20</sup> and that the metal is more crucial in determining the nature of the MSi bond in these complexes. The small changes also suggest that the intrinsic nature of the MSi double bond linkage is only slightly perturbed by moderate changes in its environment. Thus, one would expect that, apart from kinetic stability engendered by bulky substituents and ligands, the metal-silicon double bond in these Schrock-type silylidenes will be similar to models with experimentally more feasible ligands and substituents, e.g. *tert*-butyl, neopentyl, and cyclopentadienyl.

(19) An experimental analysis of the bonding in dihalocarbene complexes and the behavior of the halogens as  $\pi$ -donors is contained in the reviews by Roper and co-workers: Brother, P. J.; Roper, W. R. *Chem. Rev.* 1988, 88, 1293. Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* 1986, 25, 121.

(20) Modification of the ligands and substituents which incur drastic changes in the metal-silicon double bond can be envisioned, e.g. for Ta-alkylidenes in which a highly electropositive Li substituent replaces a  $H-(CMe_3CH_2)_3Ta=C(Li-N,N'$ -dimethylpiperazine) $CMe_3$ .<sup>20</sup> The TaC linkage is ostensibly a triple bond, and gross differences with "normal" alkylidenes are clearly evident in the electronic structure.<sup>8</sup> Schrock, R. R.; Guggenberger, L. J. *J. Am. Chem. Soc.* 1975, 97, 2935.

ii. **Effect of Metal Modification on Silylidenes.** Inspection of the data in Tables II–IV leads to the conclusion that changing the metal has a more profound impact on the electronic structure of the silylidene complexes than does changing the ligands or substituents. This is what one would expect on the basis of the calculated properties of the silylidenes (Table II).

As one proceeds from Ti to Zr to Hf, the MSi  $\sigma$ - and  $\pi$ -bonds become slightly less polarized. What resonance structures are responsible for the changes? An average<sup>21</sup> increase (Hf > Ti by +4.1%) in  $\sigma$ -back-bond ( $|0xy2\rangle$ ) resonance structures coupled with a decrease (Hf < Ti by 6.2%) in  $\sigma$ -dative configurations ( $|2xy0\rangle$ ) leads to less charge separation in the MSi  $\sigma$ -bond in the order Hf < Zr < Ti. However, the silylene ligand still performs the essential role of any ligand; i.e., it acts as a  $\sigma$ -donor.

The changes in the  $\pi$ -bond of the group IVB silylidenes are larger than those in the  $\sigma$ -bond. Inspection of the data in Table III shows the Zr- and Hf-silylidenes to be more similar to each other, with Ti-silylidenes being the most different. This is expected, since the second- and third-row transition metals have more similar properties (e.g., electronegativity, ionic and covalent radii, etc.) compared to their first-row congener. The  $\pi$ -back-bond configurations ( $|w02z\rangle$ ) remain roughly the same for all metals. The increase in  $\pi$ -dative configurations (Hf > Ti by 9.5%) has the effect of making the  $\pi$ -bond in Hf-silylidenes more evenly distributed than in Ti-silylidenes. On the average the Ti-silylidene  $\pi$ -electrons are partitioned  $\pi_M/\pi_{Si} = 1.1/0.9$ ; in Hf-silylidenes the two  $\pi$  electrons are nearly evenly shared between the metal and silicon ends of the bond. The changes in the  $\pi$ -bond, coupled with the small changes in the MSi  $\sigma$ -bond, result in MSi bonds in Hf- and Zr-silylidenes that are less polarized than in Ti-silylidenes. The MSi  $\sigma$ -bond has become less dative in nature, while the  $\pi$ -bond is more dative upon going from Ti to Zr to Hf.

The changes within the group VB silylidenes are even smaller than those seen in the group IVB silylidenes. The group VB silylidenes have on average a greater percentage of  $\pi$ -back-bond resonance structures than their group IVB relatives; the contributions of  $\pi$ -dative and  $\pi$ -covalent resonance structures are smaller for the group VB complexes. Thus, the MSi  $\pi$ -bond is more polarized toward the metal for the group VB silylidenes. The MSi  $\sigma$ -bond is perturbed only slightly upon proceeding from group IVB to group VB. These changes have the effect of making the metal-silicon double bond less polarized (i.e., an increasingly back-bonding metal-silicon  $\pi$ -bond balances out the dative MSi bond) for the group VB silylidenes (Nb < Zr and Ta < Hf).

## 5. Summary and Prospectus

The electronic structures of complexes which arise from the formation of a double bond between a divalent silylene ligand (Si(R)R') and a high-valent transition-metal fragment have been investigated using *ab initio* wave functions including the effects of electron correlation. Using the analogy of carbon, these complexes may be referred to as Schrock-type silylenes or silylidenes. Several points and possible extensions which suggest themselves are detailed below.

(1) The specific inclusion of electron correlation is necessary to describe the metal-silicon  $\pi$ -bond, while the MSi  $\sigma$ -bond is adequately described at the Hartree-Fock level. The occupation of the metal-silicon  $\pi^*$  molecular orbital in the compounds studied here ranges from 2 to

45%. This results in a lengthening of the MSi bond by as much as 0.06 Å upon the inclusion of correlation contributions. Thus, a wave function (e.g. two-configuration SCF, TCSCF) in which the metal-silicon  $\pi$ -bond is correlated must be considered as a minimum level of theory at which to calculate molecular properties of silylene complexes.

(2) The division of the nine chemical resonance structures (Figure 1) into groups based on the  $\sigma$ - and  $\pi$ -bond types (dative, covalent, or back-bonding) is a useful tool for the analysis of MC/LMO/CI results.

(3) The GVB overlap (an indicator of kinetic stability) and metal-silicon force constants (an indicator of thermodynamic stability) increase upon the replacement of H with ligands (e.g.,  $H_nM=SiH_2 \rightarrow Cl_nM=SiH_2$ ) and substituents (e.g.,  $H_nM=SiH_2 \rightarrow H_nM=SiCl_2$ ) more electron-withdrawing than H. The calculated GVB overlaps for the silylidenes (other than Ti-silylidenes) are comparable with those for prototypical, heavy-main-group double bonds (e.g.,  $H_2Sn=SnH_2$ ). For example, the metal-silicon force constants are much lower than those for ethylene but similar to those for  $Si_2H_4$ ,  $Ge_2H_4$ , and  $Sn_2H_4$ .

(4) The metal-silicon force constants are larger for the group VB silylidenes when compared to those for analogous group IVB silylidenes preceding them in the same row of the periodic table (i.e., Nb > Zr and Ta > Hf); the GVB overlap is little changed.

(5) The replacement of H ligands and substituents with Cl has the effect of polarizing the MSi  $\pi$ -bond toward the metal; i.e., the  $\pi$ -bond becomes more polarized. The polarization manifests itself in the MC/LMO/CI procedure by an increase in  $\pi$ -back-bond resonance structures. As a ligand, Cl is acting as an electron-withdrawer, making the metal fragment more electronegative; as a substituent, the Cl is acting as a  $\pi$ -donor and "repelling" electrons on the  $\alpha$ -silicon.

(6) The  $\pi$ -bonds in the group VB silylidenes are more back-bonding in nature (i.e.,  $\pi$ -back-bond resonance structures increase) than those in analogous group IVB complexes, thus compensating for the dative nature of the MSi  $\sigma$ -bond. These changes in the electronic structure make the electron density in the metal-silicon bond more evenly distributed between the metal and silicon ends of the bond in the group VB silylidenes.

(7) Consideration of the previous points and the results<sup>4</sup> for  $M^+=SiH_2$  ( $M = Sc-Ni$ ) leads to the interesting conclusion that stronger metal-silicon double bonds arise from modifying the silylidene to mimic the later, low-valent silylene complexes which have already been characterized.

The results summarized above suggest several strategies for synthesizing a silylidene which is stable enough to be experimentally characterized. For the present discussion we have assumed that qualitatively the greater the GVB overlap and MSi force constant, the more likely it is that a silylidene will be stable. First, one would wish to select a transition metal from the third transition series (e.g., Hf and Ta). Second, the metal ligands should be as electron withdrawing as possible. Substituted cyclopentadienyl ligands constitute an obvious choice, since they are electron withdrawing and can be substituted to make them more so. For example, Gassman and Winter<sup>22a</sup> have shown that the single ring replacement of one ring H in ferrocene by a trifluoromethyl group has a greater effect on the oxidation potential than the replacement of all 10 ring hydrogens with methyl groups. More heavily fluorinated

(21) These average values are taken from Table IV.

(22) (a) Gassman, P.; Winter, C. H. *J. Am. Chem. Soc.* 1986, 108, 4228. (b) Burk, M. J.; Arduengo, A. J.; Calabrese, J. C.; Harlow, R. L. *J. Am. Chem. Soc.* 1989, 111, 8938.

ligands have also been studied by Burk and co-workers.<sup>22b</sup> The greater steric bulk of substituted Cp ligands would also be expected to increase kinetic stability. Third, substituents which are good  $\pi$ -donors (e.g., OR and NR<sub>2</sub>) could be attached to the  $\alpha$ -silicon. Of course, heteroatom donors open up the possibility of rearrangements of the silylidene to form complexes in which the multiple bond is to the heteroatom. As with the ligands, greater steric bulk of the substituents would be expected to increase the kinetic stability of silylidenes by lowering the probability of dimerization (or polymerization) and the access to external reagents. This choice of bulky, electron-withdrawing ligands and bulky,  $\pi$ -donor substituents should, on the

basis of the present theoretical results, provide a good opportunity for the synthesis of a high-valent transition-metal silylidene complex.

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**Supplementary Material Available:** A table of GVB-1/TCSCF stationary points for silylidenes (7 pages). Ordering information is given on any current masthead page.

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## Nucleophilic Ring Opening of a Bridging Thietane Ligand in an Open Tetraosmium Carbonyl Cluster Complex

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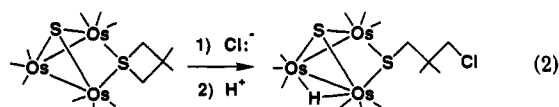
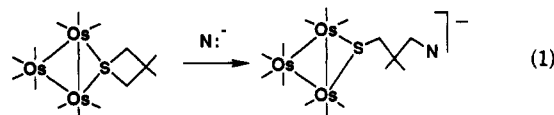
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The complex Os<sub>4</sub>(CO)<sub>12</sub>( $\mu$ -CO)[ $\mu$ -SCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>] (1) was found to react with bis(triphenylphosphine)nitrogen(1+) chloride, [PPN]<sup>+</sup>Cl<sup>-</sup>, at 25 °C to yield the salt [PPN][Os<sub>4</sub>( $\mu$ -CO)(CO)<sub>12</sub>( $\mu$ -SCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>Cl)] (2; 43%), in which the chloride ion was added to one of the methylene groups of the SCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub> ligand in a ring-opening reaction that involved the cleavage of one of the carbon-sulfur bonds. Compound 2 was converted to the neutral complex Os<sub>4</sub>(CO)<sub>13</sub>( $\mu$ -SCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>Cl)( $\mu$ -H) (3) by protonation with HCl. Complex 3 was characterized crystallographically and was found to contain a 4-chloro-3,3-dimethylpropanethiolato ligand bridging the wing-tip metal atoms of a butterfly tetrahedron of four metal atoms in the cluster. A hydride ligand bridges one of the edge metal-metal bonds of the cluster. Compound 3 was obtained in good yield (67%) in one step by the reaction of 1 with HCl. At 97 °C, 3 was decarbonylated to form the complex Os<sub>4</sub>(CO)<sub>12</sub>( $\mu$ -SCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>Cl)( $\mu$ -H) (4; 97%). Compound 4 was also characterized crystallographically and was found to contain a triply bridging 4-chloro-3,3-dimethylpropanethiolato ligand serving as a 5-electron donor. Data for 1: space group = P $\bar{1}$ ,  $a$  = 10.205 (4) Å,  $b$  = 14.399 (2) Å,  $c$  = 9.342 (2) Å,  $\alpha$  = 92.52 (2)°,  $\beta$  = 108.89 (3)°,  $\gamma$  = 85.82 (2)°,  $Z$  = 2, 2678 reflections,  $R$  = 0.029. Data for 3: space group = P $\bar{1}$ ,  $a$  = 20.646 (4) Å,  $b$  = 9.610 (1) Å,  $c$  = 8.753 (1) Å,  $\alpha$  = 116.308 (9)°,  $\beta$  = 102.27 (2)°,  $\gamma$  = 75.12 (1)°,  $Z$  = 2, 3186 reflections,  $R$  = 0.032. Data for 4: space group = P $\bar{1}$ ,  $a$  = 10.558 (1) Å,  $b$  = 13.673 (2) Å,  $c$  = 9.473 (1) Å,  $\alpha$  = 94.10 (1)°,  $\beta$  = 91.424 (9)°,  $\gamma$  = 76.08 (1)°,  $Z$  = 2, 2421 reflections,  $R$  = 0.036.

### Introduction

The most important step in the desulfurization of sulfur-containing heterocycles is the cleavage of the carbon-sulfur bonds.<sup>1-3</sup> We have recently shown that bridging coordination of the sulfur atom of thietane ligands in certain triosmium cluster complexes enhances the reactivity of the carbon-sulfur bond to ring-opening cleavage (eqs 1 and 2).<sup>4-6</sup>



It was found that the thietane ligand in the closed cluster complex Os<sub>3</sub>(CO)<sub>10</sub>[ $\mu$ -SCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>] was slightly more susceptible to ring opening than the thietane ligand in the open cluster complex Os<sub>3</sub>(CO)<sub>9</sub>[ $\mu$ -SCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>]( $\mu$ -S). We have recently synthesized the tetraosmium complex Os<sub>4</sub>(CO)<sub>12</sub>( $\mu$ -CO)[ $\mu$ -SCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>] (1)<sup>7</sup> and have now discovered that the bridging thietane ligand in this com-

(1) (a) Angelici, R. J. *Acc. Chem. Res.* 1988, 21, 387. (b) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* 1988, 21, 394. (c) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* 1989, 116, 11. (d) Prins, R.; De Beer, V. H. H.; Somorjai, G. A. *Catal. Rev. Sci. Eng.* 1989, 31, 1. (e) Sauer, N. N.; Markel, E. J.; Schrader, G. L.; Angelici, R. J. *J. Catal.* 1989, 117, 295. (f) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* 1980, 61, 128. (g) Curtis, M. D.; Penner-Hahn, J. E.; Schwank, J.; Beral, O.; McCabe, D. J.; Thompson, L.; Waldo, G. *Polyhedron* 1988, 7, 2411. (h) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* 1988, 7, 1171. (i) Kaesz, H. D.; King, R. B.; Manuel, T. A.; Nichols, L. D.; Stone, F. G. A. *J. Am. Chem. Soc.* 1960, 82, 4749. (j) Luo, L.; Ogilvy, A. E.; Rauchfuss, T. B.; Rhenigold, A. L.; Wilson, S. R. *Organometallics* 1991, 10, 1002 and references therein.

(2) (a) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* 1987, 109, 7899. (b) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* 1987, 109, 3872. (3) Calhorda, M. J.; Hoffmann, R.; Friend, C. M. *J. Am. Chem. Soc.* 1988, 110, 749.

(4) (a) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* 1991, 10, 2539. (b) Adams, R. D.; Pompeo, M. P. *Organometallics* 1992, 11, 460.

(5) Adams, R. D.; Pompeo, M. P. *J. Am. Chem. Soc.* 1991, 113, 1619.

(6) Adams, R. D.; Belinski, J. A. *Organometallics* 1992, 11, 2488.

(7) (a) Adams, R. D.; Pompeo, M. P. *Organometallics* 1990, 9, 2651.

(b) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* 1992, 11, 2016.