

Does the Schrock-type metal–silylene complex exist?

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We have studied theoretically the stability and the reactivity of the Schrock-type metal–silylene complexes $(\text{CH}_3)_2\text{NbSiR}_2$ ($\text{R}=\text{H}, \text{OH}$) as well as those of the Fischer-type $(\text{CO})_4\text{FeSiR}_2$ and $(\text{CO})_5\text{CrSiR}_2$ ($\text{R}=\text{H}, \text{OH}$). The stability of the Nb–Si bond in $(\text{CH}_3)_2\text{NbSiR}_2$ is larger than that of the Fe–Si and Cr–Si complexes which have been synthesized recently. This suggests that the Schrock-type metal silylene complex may be synthesized as a stable one. An orbital correlation diagram shows that there is an obvious metal–Si double bond in $(\text{CH}_3)_2\text{NbSiR}_2$. Both electrophiles and nucleophiles will attack Nb, though a possibility of nucleophilic attack on Si also exists. First singlet and triplet excited states of $(\text{CH}_3)_2\text{NbSiH}_2$ lie within 1 eV of the ground state. These excitations do not weaken the Nb–Si bonding, though the Si–H bonds are considerably weakened.

1. Introduction

Recently much attention has been focused on metal–silylene complexes due to their similarity to metal–carbene complexes which are of considerable importance as intermediates in various organometallic syntheses [1]. We reported previously theoretical investigations of the bonding nature of the Fischer-type metal–carbene complexes $(\text{CO})_4\text{Fe}=\text{CH}(\text{OH})$ and $(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$, and the Schrock-type metal–carbene complex $(\text{CH}_3)_2\text{Nb}=\text{CH}_2$ [2,3]. We also studied the Fischer-type metal–silylene complex $(\text{CO})_5\text{Cr}=\text{SiH}(\text{OH})$, and predicted a possible existence of the metal–silylene complexes, though they may be more reactive than the corresponding carbene complexes [4].

Straus and Tilley reported evidence of the Ru–Si double bond in $[(\text{Cp}(\text{PMe}_3)_2\text{Ru}=\text{SiPh}_2\text{NCCH}_3)]^+$ in 1987 [5]. Zybilla and Muller synthesized the Fe–Si and Cr–Si double bonds in $(\text{CO})_4\text{Fe}=\text{Si}(\text{O}(t\text{-Bu}))_2\text{L}$ ($\text{L}=\text{THF}$ or HMPA) and $(\text{CO})_5\text{Cr}=\text{Si}(\text{O}(t\text{-Bu}))_2\text{L}$ ($\text{L}=\text{HMPA}$) [6]. Further, Ueno et al. also reported Fe–silylene bonding [7], Woo et al. the Os–

Si double bond [8], and Jutzi and Mohrke an Au–silylene complex [9]. All these complexes are Fischer-type ones whose existence has been predicted theoretically [4].

In this Letter, we examine the stability and reactivity of the Schrock-type metal–silylene complexes and the nature of the metal–Si bonding [10]. For Fischer-type complexes the present calculations are more accurate than the previous ones [4].

2. Calculations details

We carry out calculations for $(\text{CH}_3)_2\text{NbSiR}_2$, $(\text{CO})_4\text{FeSiR}_2$, and $(\text{CO})_5\text{CrSiR}_2$ ($\text{R}=\text{H}, \text{OH}$). The Nb compounds are the Schrock-type complexes, and the Fe and Cr complexes are the Fischer-type ones. Fig. 1 shows the structures of these complexes, and the geometrical parameters used in this Letter. The structures of the metal fragments are taken from the experimental data [6]. The structures of SiH_2 and $\text{Si}(\text{OH})_2$ are optimized by SCF calculations.

The Gaussian basis sets are the Huzinaga (433321/433/421) set for Nb, the (53321/531/41) set for Cr and Fe, the (5321/521) set for Si and the (621/41) set for C and O [11]. We add d functions for Si [11],

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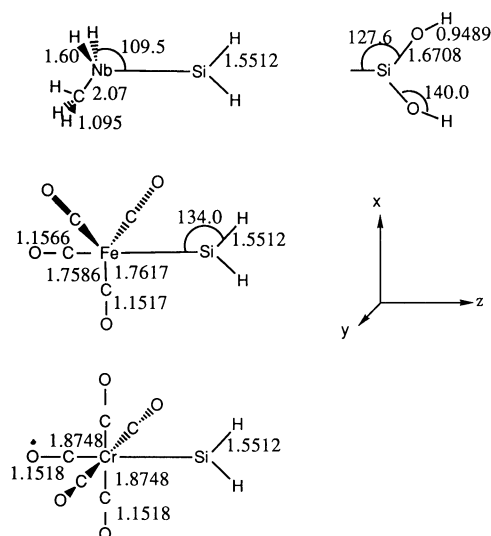


Fig. 1.

anion sp functions for O connected to Si [12], and diffuse p functions for Nb [11].

The ground states of $(\text{CH}_3)_2\text{NbSiR}_2$, $(\text{CO})_4\text{FeSiR}_2$, and $(\text{CO})_5\text{CrSiR}_2$ ($\text{R}=\text{H}, \text{OH}$) are calculated by the ab initio restricted Hartree-Fock method. For the Schrock-type silylene complex, $(\text{CH}_3)_2\text{NbSiH}_2$, which we are most interested in, electron correlation effects are considered by the SAC (symmetry-adapted cluster) method [13]. Some properties of the lower excited states are studied by the SAC-CI method [14]. The calculations are performed for 43 active orbitals with use of the SAC85 program [15]. Con-

figurations are selected by the threshold $\lambda_g = 10^{-5}$ and $\lambda_e = 10^{-5}$.

3. Results and discussions

Table 1 shows some properties of the metal-Si bond in these complexes. Calculated equilibrium lengths of the metal-Si bonds are in the range of 2.35–2.55 Å. The relation between the bond multiplicity and the bond length has not yet been established for the metal-Si bonds [16]. The bond energy and the force constant of Nb-Si are larger than those for Fe-Si and Cr-Si, suggesting that the Schrock-type metal-silylene complexes are more stable than the Fischer-type ones which have been synthesized already [5–9]. For metal-carbene complexes, we have already reported that the Schrock-type complexes have larger bond energies and force constants than the Fischer-type ones [3,4]. The complex $(\text{CH}_3)_2\text{NbSiH}_2$ has a larger bond energy and force constant than the complex $(\text{CH}_3)_2\text{NbSi}(\text{OH})_2$; this effect of the OH substitution is the same as that reported for the C-Si bond [17].

The barriers of the rotations around the Fe-Si and Cr-Si bonds are as small as that of the single bond, and the rotations are essentially free, though they have some double bond nature as in the carbene complexes [2]. However, the rotational barriers of the Nb-Si bonds are 9.45 and 12.78 kcal/mol for $(\text{CH}_3)_2\text{NbSiH}_2$ and $(\text{CH}_3)_2\text{NbSi}(\text{OH})_2$, respectively. This result can be explained from the fact that the $\text{Fe}(\text{CO})_4$ and $\text{Cr}(\text{CO})_5$ fragments have two de-

Table 1

Properties of the M-Si bonds in metal-silylene complexes; $(\text{CH}_3)_2\text{NbSiR}_2$, $(\text{CO})_4\text{FeSiR}_2$, and $(\text{CO})_5\text{CrSiR}_2$ ($\text{R}=\text{H}$ and OH)

Properties	$\text{H}_2(\text{CH}_3)\text{Nb}=\text{Si}$		$(\text{CO})_4\text{Fe}=\text{Si}$		$(\text{CO})_5\text{Cr}=\text{Si}$	
	SiH_2	$\text{Si}(\text{OH})_2$	SiH_2	$\text{Si}(\text{OH})_2$	SiH_2	$\text{Si}(\text{OH})_2$
bond length (Å)	2.46 (2.47) ^{a)}	2.55	2.41	2.43	2.35	2.36
bond energy (kcal/mol) ^{b)}	45.95 (40.0) ^{a,c)}	31.46	21.19	20.31	20.31	25.89
force constant (mdyn/Å)	1.92 (0.49) ^{a)}	1.16	0.62	0.99	1.20	1.05
rotational barrier (kcal/mol)	9.45 (5.30) ^{a)}	12.78	0.00	0.02	0.06	0.16

^{a)} Values in parentheses are the results including electron correlation effects which are calculated by the SAC (symmetry-adapted cluster) method.

^{b)} Bond energy is calculated for the dissociation into the singlet fragments.

^{c)} For $(\text{CH}_3)_2\text{NbSiH}_2$, the bond energy including electron correlation effects is 21.5 kcal/mol when it dissociates into triplet $\text{NbH}_2(\text{CH}_3)$ and singlet SiH_2 (ground state).

Table 2

Molecular orbital energies and coefficients of the next HOMO, HOMO, LUMO, and next LUMO of $\text{H}_2(\text{CH}_3)\text{Nb}=\text{SiH}_2$ ^{a)}

		Next HOMO $d\sigma-p\sigma$	HOMO $d\pi-p\pi$	LUMO $(d\pi-p\pi)^*$	Next LUMO $d\pi$ lone-pair
MO ordering		-2	-1	1	2
orbital energy (eV)		-11.21	-7.76	0.72	0.98
Nb	$4d_{x^2}$	0.10/0.02	0.00/0.00	0.00/0.00	0.00/0.00
	dy^2	0.15/0.04	0.00/0.00	0.00/0.00	-0.20/-0.20
	dz^2	-0.29/-0.14	0.00/0.00	0.00/0.00	0.15/0.04
	d_{xy}	0.00/0.00	0.18/0.12	-0.35/-0.26	0.00/0.00
	dxz	0.03/0.02	0.00/0.00	0.00/0.00	0.46/0.39
	dyz	0.00/0.00	-0.47/-0.33	0.36/0.27	0.00/0.00
	5s	-0.15/-0.01	0.00/0.00	0.00/0.00	-0.22/0.22
	5p _x	-0.03	0.00	0.00	0.27
	p _y	0.00	-0.17	-0.28	0.00
	p _z	0.01	0.00	0.00	-0.34
C	2s	0.01/0.00	0.00/0.00	0.00/0.00	0.02/-0.08
	2p _x	-0.01/-0.00	0.00/0.00	0.00/0.00	-0.10/-0.12
	p _y	0.00/0.00	-0.03/-0.04	0.05/0.05	0.00/0.00
	p _z	0.01/-0.01	0.00/0.00	0.00/0.00	-0.01/0.04
Si	3s	-0.18/-0.28	0.00/0.00	0.00/0.00	-0.04/0.13
	3p _x	0.00/-0.00	0.00/0.00	0.00/0.00	0.09/0.16
	p _y	0.00/0.00	-0.22/-0.26	-0.34/-0.38	0.00/0.00
	p _z	0.31/0.43	0.00/0.00	0.00/0.00	0.03/-0.05
H	1s	0.12/0.11	0.00/0.00	0.00/0.00	-0.04/-0.15

^{a)} For the split valence basis functions, the coefficients for inner and outer orbitals are shown as (inner)/(outer).

exists, since the outer 3p orbital of Si has the largest coefficient in the LUMO. This predicted reactivity is different from that for the Schrock-type metal-carbene complex [4].

Table 3 shows the coefficients of some MOs of $(\text{CO})_6\text{CrSiH}_2$ for comparison with $(\text{CH}_3)_2\text{NbSiH}_2$. The HOMO and the next two MOs are the π , δ and π (in plane) orbitals, respectively, which essentially localize at Cr. These π and π MOs mix easily under rotation around the Cr-Si bond and this makes the barrier very small. The σ -bonding MO is the next MO and is produced from $d\sigma$ at Cr and $p\sigma$ at Si. As a whole, the double bonding nature of $(\text{CO})_5\text{CrSiH}_2$ is smaller than that of $(\text{CH}_3)_2\text{NbSiH}_2$. The LUMO is the $d\pi-p\pi$ antibonding orbital, though the coefficients of $p\pi$ at Si are much larger than those of $d\pi$ at Cr. The next LUMO is essentially a 5s orbital at Cr, but its orbital energy is much higher. Therefore, electrophiles will attack the Cr atom and the nucleophile will attack the Si atom. This predicted reactivity for nucleophiles is the same as that of

Fischer-type metal-carbene complexes, though it is different from that of $(\text{CH}_3)_2\text{NbSiH}_2$.

Table 4 shows some singlet and triplet low-lying excited states of $(\text{CH}_3)_2\text{NbSiH}_2$. It is noticeable that the first singlet and triplet excited states with the symmetry A'' lie within 1 eV of the ground state: these states may be populated thermally. These excited states are produced by the excitation from the HOMO to the next LUMO, which is mainly the 4d-4d transition within the Nb: rotation by 90° (see table 2). As the Si fragment has two unoccupied 4p π orbitals in the molecular plane and out of plane, they can interact with both $d\pi$ orbitals at Nb and can make bonding orbitals. So, in these excited states, the Nb-Si bonding may not be weakened, though the Si-H bonds are weakened significantly.

The rotation around the Nb-Si bond by 90° in the ground state is approximately considered to be the two-electron excitation from the out-of-plane $d\pi$ to the in-plane $d\pi$. The first singlet and triplet excited states in table 4 are produced by the one-electron $d\pi$ -

Table 3
Molecular orbital energies and coefficients of the σ -bonding MO, $d\pi$ lone-pair MO, HOMO, LUMO, and next LUMO of $(\text{CO})_5\text{Cr}=\text{SiH}_2$ ^{a)}

		$d\sigma-p\sigma$	$d\pi$ lone-pair	HOMO $d\pi-p\pi$	LUMO $(d\pi-p\pi)^*$	next LUMO $(s\sigma-p\sigma)^*$
MO ordering ^{b)}		-4	-3	-1	1	2
orbital energy (eV)		-11.37	-10.23	-9.32	-0.12	2.11
Cr	3d _x ²	0.07/0.05	0.00/0.00	0.00/0.00	0.00/0.00	0.04/-0.08
	3d _y ²	0.08/0.06	0.00/0.00	0.00/0.00	0.00/0.00	0.04/-0.08
	3d _z ²	<u>-0.15/-0.11</u>	0.00/0.00	0.00/0.00	0.00/0.00	0.08/-0.07
	3d _{xy}	0.00/0.00	0.00/0.00	0.00/0.00	0.00/0.00	0.00/0.00
	3d _{xz}	0.00/0.00	<u>0.60/0.35</u>	0.00/0.00	0.00/0.00	0.00/0.00
	3d _{yz}	0.00/0.00	0.00/0.00	<u>-0.50/-0.33</u>	<u>-0.20/-0.12</u>	0.00/0.00
	4s	<u>0.16/0.11</u>	0.00/0.00	<u>0.00/0.00</u>	0.00/0.00	<u>-1.31/-1.69</u>
	4p _x	0.00	0.00	0.00	0.00	0.00
	4p _y	0.00	0.00	0.00	0.00	0.00
	4p _z	-0.01	0.00	0.00	0.00	0.00
C _{ax} ^{c)}	2s	0.03/0.08	0.00/0.00	0.00/0.00	0.09/0.12	0.02/0.13
	2p _x	0.00/0.00	0.00/0.01	0.00/0.00	0.00/0.00	0.00/0.00
	2p _y	0.00/0.00	0.00/0.00	0.00/0.00	0.00/0.00	0.02/-0.10
	2p _z	-0.02/-0.00	0.00/0.00	-0.11/-0.12	0.04/-0.02	0.20/0.20
C _{eq} ^{d)}	2s	0.00/-0.12	0.00/0.00	0.00/0.00	0.00/0.00	0.02/0.29
	2p _x	0.00/0.00	-0.08/-0.08	0.00/0.00	0.00/0.00	0.00/0.00
	2p _y	0.00/0.00	0.00/0.00	0.10/0.09	0.15/0.20	0.00/0.00
	2p _z	0.02/0.11	0.00/0.00	0.00/0.00	0.00/0.00	0.12/-0.01
Si	3s	<u>-0.22/-0.36</u>	0.00/0.00	0.00/0.00	0.00/0.00	<u>-0.28/0.18</u>
	3p _x	0.00/0.00	-0.03/0.02	0.00/-0.00	0.00/0.00	0.00/0.00
	3p _y	0.00/0.00	0.00/0.00	-0.09/-0.17	<u>0.46/0.53</u>	0.00/0.00
	3p _z	0.33/0.41	0.00/0.00	0.00/0.00	0.00/0.00	0.10/0.07
H	1s	0.12/0.12	0.00/0.00	0.00/0.00	0.00/0.00	0.04/0.14

^{a)} For the split valence basis functions, the coefficients for inner and outer orbitals are shown as (inner)/(outer).

^{b)} The next HOMO (MO ordering is -2) is the $d\delta$ lone-pair orbital.

^{c)} Axial carbon on the y axis.

^{d)} Equatorial carbon on the z axis.

Table 4
Excitation energy for the singlet and triplet states of $(\text{CH}_3)_2\text{H}_2\text{NbSiH}_2$ calculated by the SAC/DAC-CI method

Term	Energy eV (kcal/mol)	Orbital assignment
¹ A''	0.85 (19.6)	HOMO→next LUMO
¹ A'	2.79 (64.3)	HOMO→LUMO
³ A''	0.33 (7.6)	HOMO→next LUMO
³ A'	1.07 (24.7)	HOMO→LUMO

$d\pi$ transfer, so the excitation energy is expected to be of the order of the rotational barrier around the Nb-Si bond. This is seen from the results of tables 1 and 4. Further, in this excited state, the rotation around

the Nb-Si bond requires essentially no electron transition, so that this rotation should be essentially free and the excess energy would be relaxed, partly at least, through the coupling between the electronic and the rotational states.

4. Conclusion

(1) The Schrock-type metal-silylene complex $(\text{CH}_3)_2\text{H}_2\text{NbSiR}_2$ is more stable than the Fischer-type metal-silylene complexes $(\text{CO})_4\text{FeSiR}_2$ and $(\text{CO})_5\text{CrSiR}_2$ (R=H and OH). Considering that all the metal-silylene complexes already synthesized are Fischer-type ones, we strongly suggest a possibility

for the synthesis of the Schrock-type metal-silylene complex.

(2) Predicted reactivities of $(\text{CH}_3)_2\text{NbSiH}_2$ for nucleophiles and electrophiles are both at the Nb site, though a possibility of nucleophilic attack on Si also exists. This is different from that for the Schrock-type metal-carbene complexes.

(3) First singlet and triplet excited states of $(\text{CH}_3)_2\text{NbSiH}_2$ lie within 1 eV of the ground state. They are produced essentially by the $d\pi-d\pi$ excitation within Nb. As SiH_2 can make a bonding orbital with both $d\pi$ orbitals of Nb, the Nb-Si bonding nature would not be much weakened, though the Si-H bonds are weakened significantly. The rotational barrier in the excited state is expected to be essentially free.

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