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Does the Schrock-type metal-silylene complex exist?

H. Nakatsuji, M. Hada and K. Kondo

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan and Institute for Fundamental Chemistry, Takanonishihiraki-cho 34-4, Sakyo-ku, Kyoto 606, Japan

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We have studied theoretically the stability and the reactivity of the Schrock-type metal-silylene complexes $(CH_3)H_2NbSiR_2$ (R=H,OH) as well as those of the Fischer-type $(CO)_4FeSiR_2$ and $(CO)_5CrSiR_2$ (R=H,OH). The stability of the Nb-Si bond in $(CH_3)H_2NbSiR_2$ 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 $(CH_3)H_2NbSiR_2$. Both electrophiles and nucleophiles will attack Nb, though a possibility of nucleophilic attack on Si also exists. First singlet and triplet excited states of $(CH_3)H_2NbSiH_2$ 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 (CO)₄Fe=CH(OH) and (CO)₅Cr=CH(OH), and the Schrock-type metal-carbene complex (CH₃)H₂Nb=CH₂ [2,3]. We also studied the Fischer-type metal-silylene complex (CO)₅Cr=SiH(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 [(Cp(PMe₃)₂Ru=SiPh₂NCCH₃]⁺ in 1987 [5]. Zybill and Muller synthesized the Fe-Si and Cr-Si double bonds in (CO)₄Fe=Si(O(*t*-Bu))₂L (L=THF or HMPA) and (CO)₅Cr=Si(O(*t*-Bu))₂L (L=HMPA) [6]. Further, Ueno et al. also reported Fe-silylene bonding [7], Woo et al. the Os-

Correspondence to: H. Nakatsuji, Department of Synthetic Chem-istry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.

Si double bond [8], and Jutzi and Mohrke an Ausilylene 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 $(CH_3)H_2NbSiR_2$, $(CO)_4FeSiR_2$, and $(CO)_5CrSiR_2$ (R=H, 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 $Si(OH)_2$ 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],

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

Fig. 1.

The ground states of (CH₃)H₂NbSiR₂, (CO)₄Fe-SiR₂, and (CO)₅CrSiR₂ (R=H, OH) are calculated by the ab initio restricted Hartree-Fock method. For the Schrock-type silylene complex, (CH₃)H₂NbSiH₂, 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-silvlene 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 (CH₃)H₂NbSiH₂ has a larger bond energy and force constant than the complex (CH₃)H₂NbSi(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 (CH₃)H₂NbSiH₂ and (CH₃)H₂NbSi(OH)₂, respectively. This result can be explained from the fact that the Fe(CO)₄ and Cr(CO)₅ fragments have two de-

Table 1 Properties of the M-Si bonds in metal-silylene complexes; $(CH_3)H_2NbSiR_2$, $(CO)_4FeSiR_2$, and $(CO)_5CrSiR_2$ (R=H and OH)

Properties	$H_2(CH_3)Nb=$		(CO) ₄ Fe=		(CO) ₅ Cr=	
	SiH ₂	Si(OH) ₂	SiH ₂	Si(OH) ₂	SiH ₂	Si(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 (CH₃)H₂NbSiH₂, the bond energy including electron correlation effects is 21.5 kcal/mol when it dissociates into triplet NbH₂(CH₃) and singlet SiH₂ (ground state).

generate $d\pi$ orbitals [2], while the Nb(CH₃)H₂ fragment does not. A more detailed explanation was given previously for the metal-carbene complexes [2,3].

For the Schrock-type silvlene complex, (CH₃)H₂-NbSiH₂, we have included electron correlation effects using the SAC method. The results are shown in parentheses in table 1. The equilibrium bond length is slightly larger than that given by the Hartree-Fock calculations as expected from ordinary electron correlation effects. The bond energy and rotational barrier become small. In particular, the force constant of the Nb-Si bond becomes much smaller than that given by the Hartree-Fock method, indicating that the curvature of the potential near the minimum is altered by the effects of electron correlations. We note that the Nb-Si bond energy is reduced by only 6 kcal/mol from 46 (HF) to 40 kcal/ mol (correlated). We further note that this bond energy is calculated on the assumption that the complex dissociates into the two singlet fragments. When it dissociates into triplet NbH2(CH3) and singlet SiH₂, which are the ground states of the fragments, the bond energy is calculated to be 21.5 kcal/mol including electron correlation.

Next, we discuss the electronic structure and the reactivity of the Schrock-type complex (CH₃)H₂-NbSiH₂, which is the most stable, as measured from the bond energy, amongst the complexes shown in table 1. In our previous paper on the reactivity of metal-carbene complexes [2,3], we have shown that charge control is wrong for understanding the reactivity of these complexes: frontier control is the concept which explains the reactivity of the Fischer-type and Schrock-type metal-carbene complexes. In general, chemical reaction proceeds through frontier control. Charge control is meaningful only when it gives the same result as the frontier control.

Fig. 2 shows the orbital correlation diagram. Electronic structures of the two fragments, Nb(CH₃)H₂ and SiH₂ are calculated by the closed-shell RHF method. The highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) of Nb(CH₃)H₂ are π (5p, 4d) and σ (5s, 4d), respectively. The HOMO and LUMO of SiH₂ are σ (3p) and π (3p), respectively. Two HOMO-LUMO pairs form two stable σ and π bond-

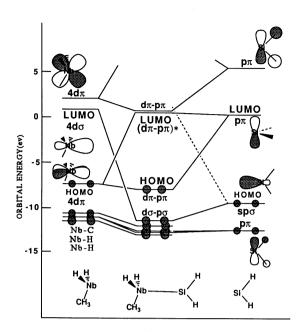


Fig. 2.

ing orbitals, so the Nb-Si bond has an obvious double bonding nature.

When the complex is formed from the fragments, electron density is donated from Si to Nb through the σ bonding, and from Nb to Si through the π bonding. Mulliken population analyses show that the total electron transfer from Nb to Si is 0.30. In (CO)₅CrSiH₂, the total electron transfer is 0.10. However, in (CO)₄FeSiH₂, the direction of the electron transfer is opposite to the Nb and Cr complexes. It is 0.13 from Si to Fe.

Table 2 shows the coefficients of the HOMOs and LUMOs of $(CH_3)H_2NbSiH_2$. The HOMO is the π bonding orbital whose main component is $4d\pi$ at Nb and $3p\pi$ at Si. The next HOMO is the σ bonding orbital whose main component is 3p at Si and 4d at Nb. The next HOMO is much more stable than the HOMO, so it may not have a large influence on the electrophile. Electrophilic reagents will attack the Nb atom from the side of the π bonding orbital. The LUMO is π antibonding with main components 4d at Nb and 3p at Si. The next LUMO is essentially a 4d lone-pair orbital localized on Nb. The LUMO and next LUMO have similar energy levels, so that nucleophiles will attack the Nb atoms as electrophiles do, though the possibility of attack at the Si site also

Table 2 Molecular orbital energies and coefficients of the next HOMO, HOMO, LUMO, and next LUMO of H₂(CH₃)Nb=SiH₂^{a)}

	Next HOMO dσ-pσ	HOMO dπ-pπ	LUMO $(d\pi-p\pi)^*$	Next LUMO dπ lone-pair
MO ordering	-2	-1	1	2
orbital energy (eV) -11.21	-7.76	0.72	0.98
Nb $4dx^2$	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
dxy	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
d <i>yz</i>	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 <i>x</i>	-0.03	0.00	0.00	0.27
p <i>y</i>	0.00	-0.17	-0.28	0.00
p <i>z</i>	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
2px	-0.01/-0.00	0.00/0.00	0.00/0.00	-0.10/-0.12
рy	0.00/0.00	-0.03/-0.04	0.05/0.05	0.00/0.00
p <i>z</i>	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
3px	0.00/-0.00	0.00/0.00	0.00/0.00	0.09/0.16
рy	0.00/0.00	-0.22/-0.26	-0.34/-0.38	0.00/0.00
pz	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 (CO)₆CrSiH₂ for comparison with (CH₃)H₂NbSi- H_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 do at Cr and po at Si. As a whole, the double bonding nature of (CO)₅CrSiH₂ is smaller than that of (CH₃)H₂NbSiH₂. The LUMO is the $d\pi$ -p π antibonding orbital, though the coefficients of p π at Si are much larger than those of d π 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 (CH₃)H₂NbSiH₂.

Table 4 shows some singlet and triplet low-lying excited states of $(CH_3)H_2NbSiH_2$. 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 $4p\pi$ 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 (CO)₅Cr=SiH₂^{a)}

		dσ-рσ	dπ lone-pair	HOMO dπ-pπ	LUMO $(d\pi-p\pi)^*$	next LUMO (sσ–pσ)*
MO or	rdering ^{b)}	-4	-3	-1	1	2
orbita	l energy (eV)	-11.37	-10.23	-9.32	-0.12	2.11
Cr	$3dx^2$	0.07/0.05	0.00/0.00	0.00/0.00	0.00/0.00	0.04/-0.08
	$3dy^2$	0.08/0.06	0.00/0.00	0.00/0.00	0.00/0.00	0.04/-0.08
	$3dz^2$	-0.15/-0.11	0.00/0.00	0.00/0.00	0.00/0.00	0.08/-0.07
	3dxy	0.00/0.00	0.00/0.00	0.00/0.00	0.00/0.00	0.00/0.00
	3dxz	0.00/0.00	0.60/0.35	0.00/0.00	0.00/0.00	0.00/0.00
	3dyz	0.00/0.00	0.00/0.00	-0.50/-0.33	-0.20/-0.12	0.00/0.00
	4s	0.16/0.11	0.00/0.00	0.00/0.00	0.00/0.00	-1.31/-1.69
	4p <i>x</i>	0.00	0.00	0.00	0.00	0.00
	4p <i>y</i>	0.00	0.00	0.00	0.00	0.00
	4p <i>z</i>	-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 <i>x</i>	0.00/0.00	0.00/0.01	0.00/0.00	0.00/0.00	0.00/0.00
	2py	0.00/0.00	0.00/0.00	0.00/0.00	0.00/0.00	0.02/-0.10
	2pz	-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
•4	2px	0.00/0.00	-0.08/-0.08	0.00/0.00	0.00/0.00	0.00/0.00
	2py	0.00/0.00	0.00/0.00	0.10/0.09	0.15/0.20	0.00/0.00
	2pz	0.02/0.11	0.00/0.00	0.00/0.00	0.00/0.00	0.12/-0.01
Si	3s	-0.22/-0.36	0.00/0.00	0.00/0.00	0.00/0.00	-0.28/0.18
	3px	0.00/0.00	-0.03/0.02	0.00/-0.00	0.00/0.00	0.00/0.00
	3p <i>y</i>	0.00/0.00	0.00/0.00	-0.09/-0.17	0.46/0.53	0.00/0.00
	3pz	0.33/0.41	0.00/0.00	0.00/0.00	0.00/0.00	0.10/0.07
Н	1 s	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).

 $\label{thm:continuous} Table~4 \\ Excitation~energy~for~the~singlet~and~triplet~states~of~\\ (CH_3)H_2NbSiH_2~calculated~by~the~SAC/DAC-CI~method~\\$

Term	Energy eV (kcal/mol)	Orbital assignment		
¹ A" ¹ A' ·	0.85 (19.6) 2.79 (64.3)	HOMO→next LUMO HOMO→LUMO		
³ A"	0.33 (7.6) 1.07 (24.7)	HOMO→next LUMO 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 $(CH_3)H_2NbSiR_2$ is more stable than the Fischer-type metal-silylene complexes $(CO)_4FeSiR_2$ and $(CO)_5-CrSiR_2$ (R=H and OH). Considering that all the metal-silylene complexes already synthesized are Fischer-type ones, we strongly suggest a possibility

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

c) Axial carbon on the y axis.

d) Equatorial carbon on the z axis.

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

- (2) Predicted reactivities of (CH₃)H₂NbSiH₂ 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 $(CH_3)H_2NbSiH_2$ 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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