

Preliminary communication

DOES A SILYLENE–METAL COMPLEX EXIST?

HIROSHI NAKATSUJI, JIRO USHIO, and TEIJIRO YONEZAWA

Division of Molecular Engineering, Graduate School of Engineering, and Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606 (Japan)

(Received July 26th, 1983)

Summary

The stability and the reactivity of the silicon–metal double bond in $(\text{CO})_5\text{Cr}=\text{SiH}(\text{OH})$ were studied by the ab initio SCF MO method. The Cr=Si bond dissociation energy was calculated to be 29.6 kcal/mol, showing the possible existence of a silylene–metal complex. However, in the case of a nucleophile, the silylene–metal complex seems to be more reactive than the Fischer-type carbene–metal complexes.

Silicon–transition-metal complexes are of great interest due to their similarity to carbon–transition-metal complexes. Many compounds with silicon–metal single bonds have been reported [1], but only a few reports have as yet appeared of silicon–metal double bonds (silylene–metal complexes). Schmidt et al. reported the formation of base-stabilized silyleneiron complexes [2] and Sakurai et al. reported the isolation of dimethylsilyladiyliron complexes [3]. However, these almost hypothetical compounds enhanced our interest in the carbene–metal complexes, which are remarkably important as intermediates of many organometallic reactions [4] such as olefin metathesis [4a,4b], the Fischer-Tropsch reaction [4a,4c], the Ziegler–Natta reaction [4a,4d], etc.

Previously we studied the nature of the carbon–metal double bond theoretically in the carbene–metal complexes, $(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$ and $(\text{CO})_4\text{Fe}=\text{CH}(\text{OH})$ [5]. We now report the stability, reactivity, and electronic structure of the silicon–metal double bond by the ab initio SCF MO method.

We calculated the values for a hypothetical complex, $(\text{CO})_5\text{Cr}=\text{SiH}(\text{OH})$, and compared the results with those of the Fischer-type carbene complex, $(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$ [5]. As the silylene, we have chosen $\text{SiH}(\text{OH})$ rather than SiH_2 or SiR_2 for comparison, since in the Fischer-type carbene complexes the π -interaction between the carbene carbon and oxygen is important in the stabilisation of the complexes [6].

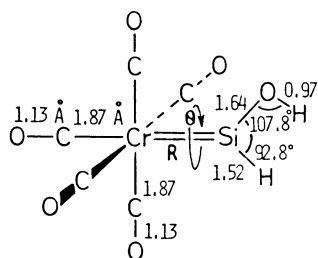


Fig. 1. Geometry of $(\text{CO})_5\text{Cr}=\text{SiH}(\text{OH})$. The bond lengths are in Å and the angles are in degrees.

Figure 1 shows the assumed geometry of $(\text{CO})_5\text{Cr}=\text{SiH}(\text{OH})$. We studied the stability and the nature of the Cr=Si bond by changing the bond length R and the rotational angle θ of the Cr=Si bond. The geometry of the $(\text{CO})_5\text{Cr}$ fragment is the same as that used in previous calculations of $(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$. The geometry of the SiH(OH) fragment was estimated from those of SiH_2 [7], H_3COSiH_3 , and CH_3OH [8]. The basis sets for Cr, C, O, and H are the same as those used for $(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$ [5]. For Si we used the MINI-1 basis [9]. The ab initio SCF MO program used is a slightly modified version of HONDOG [10]. We also calculated the singlet closed-shell states of $(\text{CO})_5\text{Cr}$ and SiH(OH) fragments.

In Table 1, we compared the properties of the Cr=Si bond with those of the Cr=C bond in $(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$ [5]. The energy of dissociation leading to the singlet fragments, $(\text{CO})_5\text{Cr}$ and SiH(OH), was calculated to be 29.6 kcal/mol. Though this value is smaller than that of the Cr=C bond, 44.4 kcal/mol, we expected that the complex, $(\text{CO})_5\text{Cr}=\text{SiH}(\text{OH})$, should energetically be stable. (The dissociation energy of the Fe=C bond in $(\text{CO})_4\text{Fe}=\text{CH}(\text{OH})$ was calculated to be 36.8 kcal/mol [5].) The equilibrium Cr=Si bond length was calculated to be 2.4 Å, which is reasonably shorter than the experimental metal-silicon single bond length, 2.6–2.7 Å [1d]. The vibrational frequency of the Cr=Si bond is smaller than that of the Cr=C bond. The rotational barrier of the Cr=Si bond is very small, as in the carbene-chromium complex [5], and the rotation around the bond is essentially free.

The nature of the Cr=Si bond is similar to that of the Cr=C bond [5].

TABLE 1

PROPERTIES OF THE Cr=Si BOND IN $(\text{CO})_5\text{Cr}=\text{SiH}(\text{OH})$ AND THOSE OF THE Cr=C BOND IN $(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$ PREVIOUSLY CALCULATED^a

Properties	$(\text{CO})_5\text{Cr}=\text{SiH}(\text{OH})$	$(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$	
		calc. ^a	exptl.
Bond energy (kcal/mol)	29.6	44.4	
Bond length (Å)	2.40	2.00	2.04 ^b
Force constant k (mdyn/Å)	0.94	1.62	
ω (cm^{-1})	200–290 ^d	330–530 ^d	391–449 ^c
Rotational barrier ^e (kcal/mol)	0.11	0.41	

^a Ref. 5. ^b Experimental value for $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{Ph}$ [11]. ^c Experimental frequency of Cr-(CO) bond in $\text{Cr}(\text{CO})_6$ [12]. ^d The vibrational frequency was calculated from the force constant in two approximations; the atoms and groups of atoms bonded to the Cr or Si atom are considered to follow completely or not to follow at all the vibration. The former approximation gives a minimum value and the latter a maximum one. ^e The most stable conformation is given in Fig. 1.

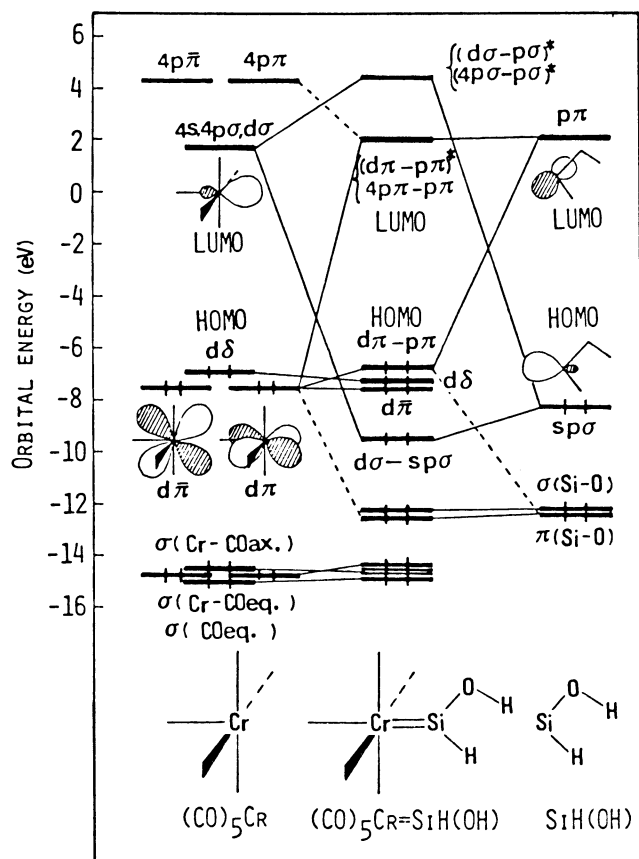


Fig. 2. Correlation diagram of the orbitals of $(\text{CO})_5\text{Cr}=\text{SiH}(\text{OH})$ with those of the singlet fragments. ($\bar{\pi}$ denotes a MO perpendicular to the π MO.)

Figure 2 shows the correlation diagram between the MO's of $(\text{CO})_5\text{Cr}=\text{SiH}(\text{OH})$ and the MO's of the singlet fragments, $(\text{CO})_5\text{Cr}$ and $\text{SiH}(\text{OH})$. The LUMO of the $(\text{CO})_5\text{Cr}$ fragment is an sp_σ hybrid MO extending outwards. The HOMO is the d_δ lone pair MO, and the next HOMO's are the degenerate d_π and $d_{\bar{\pi}}$ lone pair MO's. The LUMO of the $\text{SiH}(\text{OH})$ fragment is the π -MO localized on Si and the HOMO is the sp_σ lone pair MO localized on Si. The MO's of the complex are correlated with the MO's of the fragments as follows. The σ bond of the $\text{Cr}=\text{Si}$ bond is formed by σ transfer of an electron from the HOMO of the $\text{SiH}(\text{OH})$ fragment to the LUMO of the $(\text{CO})_5\text{Cr}$ fragment. The π bond of the $\text{Cr}=\text{Si}$ bond is formed by the π back transfer of an electron from one of the next HOMO's of $(\text{CO})_5\text{Cr}$ to the LUMO of $\text{SiH}(\text{OH})$. The d_δ lone pair MO of $(\text{CO})_5\text{Cr}$ is almost unaffected by the coordination of $\text{SiH}(\text{OH})$. Thus, the origin of the $\text{Cr}=\text{Si}$ bond is the σ transfer and the π back transfer between $\text{SiH}(\text{OH})$ and $(\text{CO})_5\text{Cr}$. The amounts of the σ transfer and the π back transfer of the charge are 0.080 and 0.199, respectively. Those in the carbene-chromium complex were 0.191 and 0.187 [5]. The amount of σ transfer is significantly smaller in the silylene-chromium complex than in the carbene-chromium complex. This is probably a reason for the weakness of the $\text{Cr}=\text{Si}$ bond. The smallness of the rotational barrier of the $\text{Cr}=\text{Si}$

