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DOES A SILYLENE—METAL COMPLEX EXIST?

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Summary

The stability and the reactivity of the silicon—metal double bond in $(CO)_5Cr{=}SiH(OH)$ 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 dimethylsiladiyliron 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-Tropsh 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, $(CO)_5Cr{=}CH(OH)$ and $(CO)_4Fe{=}CH(OH)$ [5]. We now report the stability, reactivity, and electronic structure of the silicon—metal double bondy by the ab initio SCF MO method.

We calculated the values for a hypothetical complex, $(CO)_5Cr{=}SiH(OH)$, and compared the results with those of the Fischer-type carbene complex, $(CO)_5Cr{=}CH(OH)$ [5]. As the silylene, we have chosen SiH(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].

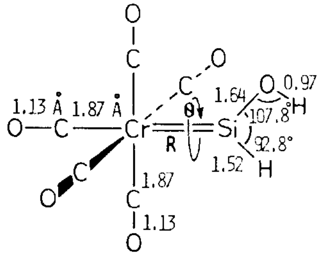

Fig. 1. Geometry of $(CO)_5Cr{=}SiH(OH)$. The bond lengths are in Å and the angles are in degrees.

Figure 1 shows the assumed geometry of $(CO)_5Cr{=}SiH(OH)$. 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 $(CO)_5Cr$ fragment is the same as that used in previous calculations of $(CO)_5Cr{=}CH(OH)$. 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 $(CO)_5Cr{=}CH(OH)$ [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 $(CO)_5Cr$ and SiH(OH) fragments.

In Table 1, we compared the properties of the Cr=Si bond with those of the Cr=C bond in $(CO)_5Cr{=}CH(OH)$ [5]. The energy of dissociation leading to the singlet fragments, $(CO)_5Cr$ 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, $(CO)_5Cr{=}SiH(OH)$, should energetically be stable. (The dissociation energy of the Fe=C bond in $(CO)_4Fe{=}CH(OH)$ 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 $(CO)_5Cr{=}SiH(OH)$ AND THOSE OF THE Cr=C BOND IN $(CO)_5Cr{=}CH(OH)$ PREVIOUSLY CALCULATED [a]

Properties	$(CO)_5Cr{=}SiH(OH)$	$(CO)_5Cr{=}CH(OH)$	
		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 $(CO)_5Cr{=}C(OMe)Ph$ [11]. [c] Experimental frequency of Cr—(CO) bond in $Cr(CO)_6$ [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.

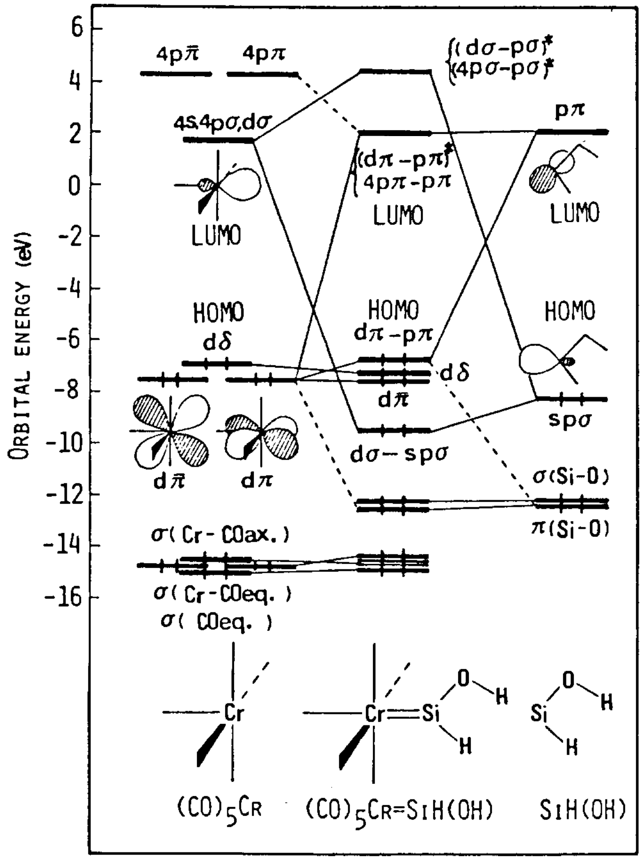

Fig. 2. Correlation diagram of the orbitals of (CO)$_5$Cr=SiH(OH) with those of the singlet fragments. ($\bar{\pi}$ denotes a MO perpendicular to the π MO.)

Figure 2 shows the correlation diagram between the MO's of (CO)$_5$Cr=SiH(OH) and the MO's of the singlet fragments, (CO)$_5$Cr and SiH(OH). The LUMO of the (CO)$_5$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 SiH(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 Cr=Si bond is formed by σ transfer of an electron from the HOMO of the SiH(OH) fragment to the LUMO of the (CO)$_5$Cr fragment. The π bond of the Cr=Si bond is formed by the π back transfer of an electron from one of the next HOMO's of (CO)$_5$Cr to the LUMO of SiH(OH). The d_δ lone pair MO of (CO)$_5$Cr is almost unaffected by the coordination of SiH(OH). Thus, the origin of the Cr=Si bond is the σ transfer and the π back transfer between SiH(OH) and (CO)$_5$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 Cr=Si bond. The smallness of the rotational barrier of the Cr=Si bond is due to the degenerate nature of the d_π and $d_{\bar{\pi}}$ MO's of the $(CO)_5Cr$ fragment. This is the same as in the complex, $(CO)_5Cr{=}CH(OH)$ [5]. The gross atomic charges are +0.87 and −0.06 on Cr and Si, respectively. They were +0.80 and −0.19 for Cr and C of the carbene—chromium complex [5].

The silylene—chromium complex seems to be more reactive to a nucleophile than is the carbene—chromium complex. The reaction site should be on the Si atom. It is well known that the Fischer-type carbene complex is readily attacked by a nucleophile at the carbene carbon atom [13]. The reactivity is controlled by the nature of the frontier orbital, i.e., the LUMO in the present case, and not by the atomic charge [5,14]. The LUMO of $(CO)_5Cr{=}SiH(OH)$, which is π-antibonding between Cr and Si, has the maximum coefficient of 0.85 at the Si atom and the orbital energy is 2.12 eV. On the other hand, for $(CO)_5Cr{=}CH(OH)$, the maximum coefficient of the LUMO is 0.66 on C and the orbital energy is 3.86 eV. Therefore, for a nucleophile, the silylene complex $(CO)_5Cr{=}SiH(OH)$ should be more reactive than the carbene complex $(CO)_5Cr{=}CH(OH)$.

In summary, the present calculation indicates that the silylene—metal complex can exist, but it also implies that the complex may be difficult to isolate because of its high reactivity.

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