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Transition Metal Silyl Complexes LVI [1]. $(CO)_4Fe(H)SiR_3$ and $[(CO)_4FeSiR_3]^-$ – A Density Functional Study on the Influence of the Substituents at Silicon on the Electronic Properties of the Metal Center

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Summary. The effect of the substitution pattern at the silyl ligand in complexes of the type $(CO)_4Fe(H)SiR_3$ and the corresponding anions $[(CO)_4FeSiR_3]^-$ was investigated by a density functional study. Upon successive substitution of $R = H$ for $R = Cl$, a contraction of the Fe–Si bond takes place in both types of complexes. The effect of the substitution is much larger in the anionic complexes which is explained by a higher degree of back bonding from the metal center to the SiR_3 ligand. The optimized structures of the complexes are in good agreement with related experimental ones. The changes in electron density at the metal center are also reflected in calculated vibrational frequencies of the CO ligands and the proton affinities of the anionic complexes. An increasing electron withdrawal by the silyl ligand lowers the proton affinity.

Keywords. Density functional study; Silicon compounds; Metal silyl complexes; Anionic metal complexes.

Übergangsmetall-Silyl-Komplexe 56. Mitt. [1]. **$(CO)_4Fe(H)SiR_3$ und $[(CO)_4FeSiR_3]^-$ – eine Dichtefunktional-Studie zum Einfluß der Substituenten am Silicium auf die elektronischen Eigenschaften des Metallzentrums**

Zusammenfassung. Der Einfluß des Substitutionsmusters des Silylliganden wurde für Komplexe des Typs $(CO)_4Fe(H)SiR_3$ und der korrespondierenden Anionen $[(CO)_4FeSiR_3]^-$ durch eine Dichtefunktional-Studie untersucht. Schrittweise Substitution von $R = H$ gegen $R = Cl$ führt bei beiden Komplextypen zu einer Verkürzung der Fe-Si-Bindung. Der Substitutionseffekt ist bei den anionischen Komplexen viel größer, was durch die stärkere Rückbindung vom Metallzentrum zum SiR_3-Ligand erklärt wird. Die optimierten Strukturen der Komplexe stimmen gut mit experimentell ermittelten überein. Die Elektronendichteänderungen werden auch in den berechneten Schwingungsfrequenzen der CO-Liganden und den Protonenaffinitäten der anionischen Komplexe widergespiegelt. Zunehmender Elektronenabzug durch die Silylliganden verringert die Protonenaffinität.

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Introduction

The oxidative addition of hydrogenosilanes to transition metals is one of the most important preparative routes to transition metal silyl complexes. The stability of the resulting hydrido silyl complexes with regard to the reductive elimination of the silane is strongly dependent on the substitution pattern at the silyl ligand and the metal. Transition metal hydrido silyl complexes exhibit the acidic properties typical for many transition metal hydride complexes. The corresponding anionic silyl complexes were shown to be interesting starting compounds for organometallic syntheses [2].

Hieber et al. were among the first to study the dependence of the acidity of metal hydride complexes on the ligand properties. In their examination of cobalt complexes $HCoL(CO)_3$ they found that the acidity increases in the series $L = P(C_6H_5)_3 < P(OC_6H_5)_3 < CO$ [3]. This was attributed to the increasing electron withdrawing behaviour of the ligands. *Fenske-Hall* studies on the dependence of the acidity of differently substituted transition metal hydride complexes on the nature of the metal and the co-ligands have shown a connection between the acidity of the M–H bond and the valence energies of the corresponding anionic complexes [4]. It has been found that the acidity of the complexes strongly depends on the degree of substitution and the substitution pattern of the ligands.

In this paper we present a density functional study on the influence of the substitution pattern at silicon on the structures of complexes and on the electronic properties of the central metal. As model compounds we chose complexes of the type $(CO)_4Fe(H)SiR_3$ and the corresponding anionic complexes $[(CO)_4FeSiR_3]^-$ which have found wide-spread preparative application. The substitution pattern at silicon was successively changed from SiH_3 to $SiCl_3$. The interest in the calculations was focused not only on the electronic properties of the complexes but also on the macroscopically observable vibrational frequencies. Another good parameter for the electronic influence of the substituents in such complexes is the proton affinity of the reaction $L_nM^- + H^+ \rightarrow L_nMH$ which was also calculated.

Results and Discussion

Optimization of the geometries of the complexes $(CO)_4Fe(H)SiR_3 (R = H, Cl)$

The geometries were optimized without any symmetry constraints. With exception of the $SiCl_2H$ substituted structures, all structures converged to C_s symmetry where one of the silyl substituents is eclipsed with the rather small H atom at the iron. The triphenyl substituted derivative $(CO)_4Fe(H)SiPh_3$ is the only crystallographically investigated complex of this type [5]. The electronic properties of the SiH_3 ligand should be rather similar to $SiPh_3$, and therefore this complex is a good model compound. The optimized bond lengths and angles are shown in Table 1. The calculated bond lengths except the Fe-H distance are in very good agreement with the experimental ones. However, hydrogen atoms next to transition metals are difficult to locate by X-ray diffraction and usually have high standard deviations. The calculated angles of the SiH_3 complex deviate up to 4° from the experimental angles.

Table 1. Selected bond lengths (pm) and angles (°) of the geometry optimized $(CO)_4Fe(H)SiR_3$ complexes

	SiH_3	SiH_2Cl	$SiHCl_2$	$SiCl_3$	$SiPh_3$ exp. [5]
Fe–Si	242.4	240.0	238.3	237.2	241.5(3)
$Fe–C_{trans\ H}$	181.1	181.1	182.0	182.1	180(1)
$Fe\text{-}C_{cis\ H}$	179.0	179.1	179.5	180.0	178, 175(1)
$Fe\text{-}C_{trans\ Si}$	180.3	180.8	181.1	181.6	182(1)
Fe–H	153.1	152.9	153.0	152.9	164(10)
Si–H	147.3	147.1	146.6		
Si–Cl		206.7	206.5	206.6	
Fe–Si–H	110.7	111.2	114.2		
Fe–Si–Cl		113.0	112.4	112.6	
H–Fe–Si	85.1	86.2	82.8	85.7	82(3)
$H–Fe–C_{cis}$	80.0	79.9	80.9	79.7	76(3)
$H–Fe–C_{trans\ Si}$	87.0	86.6	86.1	87.3	
$Si–Fe–C_{cis,cis\ H}$	81.5	82.1	82.8	85.0	85.6(3)

The two *cis* CO ligands are bent towards the hydride ligand (H–Fe–C = 80°). This results in an overall distortion of the coordination octahedron of the iron atom. In all calculated structures the hydrogen atom is surrounded by the other ligands in an umbrella-like manner, each H-Fe-*L* angle being smaller than 90°.

Successive substitution of H against Cl results in a decrease of the Fe-Si distance. However, the Fe-Si distance is not linearly dependent on the number of chlorine atoms at silicon: Substitution of the first H atom leads to a shortening by 2.4 pm, whereas the second and third only result in an additional shortening by 1.7 and 1.1 pm. Thus, total shortening in going from a SiH_3 ligand to a $SiCl_3$ ligand is 5.2 pm. This is in good agreement with the study of *Ziegler et al.* who examined the change of the substitution pattern from CH_3 to CF_3 in complexes of the type $RMn(CO)_5$ [6]. They also found a non-linear decrease by a successive substitution of H for F atoms.

Only the Fe-C distance *trans* to SiR_3 is significantly affected by the substituents at silicon. With successive substitution of H against Cl, the bond length is increased in 0.5 pm steps from 180.3 pm in the SiH_3 complex to 181.6 pm in the $SiCl_3$ complex. For the other Fe-C bond lengths there is no clear trend. The Fe-H distance is not significantly influenced by all these changes.

To compare the properties of a silyl ligand with other ligands, calculations on the two compounds $(CO)_4FeH_2$ and $(CO)_4Fe(H)Cl$ were also carried out. In these complexes, the SiR_3 ligand is replaced by the more electropositive hydrogen or the more electronegative chlorine atom. Selected parameters of these compounds are shown in Table 2.

The complex $(CO)_4FeH_2$ has the ideal C_{2v} symmetry which is also observed in the electron diffraction experiments of *McNeill* and *Scholer* [7]. However, there are severe differences between the calculated and experimentally observed structure. Especially the H-Fe-H angle of 100° cannot be confirmed by the calculation. In structures of metal hydrides, the ligands are bent towards the hydride ligand(s).

Table 2. Selected bond lengths (pm) and angles (°) of the geometry optimized complexes $(CO)_4FeH_2$ and $(CO)_4Fe(H)Cl$

	$L = H$	$L = Cl$	$L = H$ exp. [7]
Fe-L	152.8	234.0	156(2)
Fe-$C_{trans\,H}$	181.5	179.5	180.2(3)
Fe-$C_{cis\,H}$	179.0	182.3	183.2(4)
Fe-$C_{trans\,L}$	181.5	185.4	
Fe-H	152.8	152.7	156(2)
H-Fe-L	83.9	91.6	100(10)
H-Fe-C_{cis}	79.5	81.3	
H-Fe-$C_{trans\,L}$	87.8	82.8	
L-Fe-$C_{cis,cis\,H}$	79.4	83.0	

Another hint that the H-Fe-H angle was not correctly determined in the diffraction experiment is that the homologous complex $(CO)_4OsH_2$ has an H-Os-H angle of 88.3(7)° [8]. Recently, a number of various transition metal carbonyl complexes has been examined by different theoretical methods; a structure of $(CO)_4FeH_2$ was found which is in good agreement with our calculation [9].

Most structural parameters of $(CO)_4FeH_2$ are in good agreement with the complex $(CO)_4Fe(H)SiH_3$. The Fe-C distances differ by 1.2 pm, and the equivalent angles by 1.1°. Even the H-Fe-H angle is only 2.2° smaller than the H-Fe-Si angle. This appears a rather small difference considering the increased size of the ligand and indicates that a hydride ligand is a good structural equivalent for a SiH_3 group.

A totally different picture is provided by the comparison of the Cl-substituted with the $SiCl_3$-substituted complex. The chloride ligand withdraws electron density from the iron and thus weakens the Fe–CO bonds, particularly the bond of the *trans* CO ligand. It is remarkable that the Fe-H distance is not changed relative to $(CO)_4FeH_2$ and that the CO ligand *trans* to H shows a decrease in bond length of 2.1 pm.

Optimization of the geometries of the anionic complexes $[(CO)_4FeSiR_3]^-$

The hydrido silyl complexes are acidic, and deprotonation leads to the corresponding anionic complexes. The calculated parameters of the anionic silyl complexes are summarized in Table 3. The optimized structures show C_s symmetry in the case of the unsymmetrically substituted complexes and C_{3v} symmetry in the case of the SiH_3 and $SiCl_3$ complexes. Only the $SiCl_3$-substituted derivative was crystallographically characterized, with $[NEt_4]^+$ as the counter ion [10]. A comparison between the solid state and the calculated structures shows that the calculation results in a longer Fe–Si bond (6.7 pm) and a longer Si–Cl bond (3.0 pm).

In the structures of the anionic complexes, all iron-ligand bonds are shorter than in the corresponding hydrido silyl complexes. The principal trends upon changing the substituents at silicon in the anionic complexes are the same as in the hydride compounds. However, the effect of each substitution step is larger than in

Table 3. Selected bond lengths (pm) and angles (°) of the geometry optimized $[(CO)_4FeSiR_3]^-$ complexes

	SiH_3	SiH_2Cl	$SiHCl_2$	$SiCl_3$	$SiCl_3$ exp. [10]
Fe–Si	236.4	232.0	230.1	229.1	222.4
Fe–C_{ax}	176.1	176.0	176.7	177.1	176.5
Fe–C_{eq}	176.5	176.7	177.3	177.5	175.0
Si–H	148.5	147.9	147.4		
Si–Cl		215.8	210.8	210.0	207.0
Fe–Si–H	118.5	115.4	117.1		
Fe–Si–Cl		116.6	115.7	115.8	116.0
Si–Fe–C_{cis}	83.1	85.0	85.0	85.0	86.0

the hydride structures. The first step from SiH_3 to SiH_2Cl shortens the Fe-Si bond by 4.4 pm, the second substitution by 1.9 pm, and the third by 1.0 pm. This leads to a total shortening of 7.3 pm in going from SiH_3 to $SiCl_3$. The main reason for the larger changes could be the different charge distribution in these complexes. The negative charge in such complexes is mainly centred on the iron atom. This higher electron density at the metal center results in an increase of back bonding to the π^* orbitals of the CO groups, decreasing the *M*-C(CO) distances. In the same way, backbonding in the σ^* orbitals of the SiR_3 ligand results in a shortening of the Fe-Si distance and lengthening of the Si-*R* bonds. An alternative explanation for the *M*-Si bond shortening is the increase in polarity of the bond leading to an electrostatic contraction as recently suggested in a study by *Zybill et al.* [11]. This effect is also supported by the following NBO studies.

We also examined the anionic complexes derived from $(CO)_4FeH_2$ and $(CO)_4Fe(H)Cl$. The calculated parameters are shown in Table 4. Both anionic complexes have the ideal trigonal bipyramidal C_{3v} symmetry. The Fe-*L* ($L = H, Cl$) bonds in these structures are lengthened relative to the neutral hydride complexes, the Fe-CO distances being shorter. This observation confirms the previous explanation, because the CO ligands are influenced by the higher electron density at the metal center by an increased backbonding, whereas pure σ donor ligands are influenced in the opposite direction.

Table 4. Selected bond lengths (pm) and angles (°) of the geometry optimized anions $[(CO)_4FeH]^-$ and $[(CO)_4FeCl]^-$

	$L = H$	$L = Cl$
Fe–*L*	154.3	240.6
Fe–C_{ax}	177.5	175.8
Fe–C_{eq}	176.2	179.3
L–Fe–C_{cis}	81.0	85.4

Natural Bond Orbital (NBO) Population Analysis

The charge distribution in the complexes was calculated by the NBO population analysis. We used the NBO and not the *Mulliken* population analysis because it is not as much basis set dependent [12].

The charges of the hydride complexes are shown in Table 5. The calculated values show no big change of the charge at the iron atom by changing the substitution pattern of the silyl ligand. Even the dihydride complex shows a similar behaviour compared to the hydrido silyl complexes, only the substitution of the silyl substituent by chloride leads to a rather big change in the charge of the metal center. Despite the changes in the polarity of the Fe–Si bond, there is no big change of the electron density at the iron center. Obviously, the $Fe(CO)_4H$ fragment behaves like a charge buffer. The H atoms at the metal have hydridic character in all complexes.

The anionic complexes behave similarly (Table 6). The negative charge in these complexes is located at the iron atom. Therefore, the Fe–Si bond is more polar due to the larger negative charge on the iron atom than in the hydride complexes; no change of the charges on the Si atoms occurs. This change in polarity is also observed in the hydride and chloride substituted complexes in going from the neutral to the anionic complexes. Due to the theory of bond contraction by changes in polarity this should lead to a shortening of the Fe–*L* bond in all cases; however, this effect cannot be observed in the hydride and chloride substituted compounds where a bond lengthening takes place. Therefore, we favour σ^* back bonding as an explanation of the Fe–Si bond contraction. This is also supported by the population of the antibonding orbitals in the complexes, which is rather high for orbitals centred at the Si atom.

Table 5. Charges from the NBO analysis of $(CO)_4Fe(H)L$

	H	SiH_3	SiH_2Cl	$SiHCl_2$	$SiCl_3$	Cl
Fe	−0.42	−0.44	−0.47	−0.46	−0.45	−0.10
Si/Cl		0.47	0.71	0.87	0.97	−0.58
C/O$_{cis\mathrm{H}}$	0.71/−0.56	0.69/−0.55	0.69/−0.54	0.70/−0.51	0.70/−0.50	0.72/−0.52
C/O$_{trans\,\mathrm{H}}$	0.76/−0.54	0.73/−0.54	0.74/−0.53	0.74/−0.51	0.74/−0.51	0.73/−0.52
C/O$_{trans\,\mathrm{L}}$		0.75/−0.53	0.75/−0.53	0.74/−0.52	0.74/−0.51	0.75/−0.51
H	−0.17	−0.15	−0.13	−0.14	−0.13	−0.17
Si$_{total}$		−0.09	−0.12	−0.20	−0.27	

Table 6. Charges from the NBO analysis of $[(CO)_4FeL]^-$

	H	SiH_3	SiH_2Cl	$SiHCl_2$	$SiCl_3$	Cl
Fe	−0.54	−0.58	−0.61	−0.63	−0.64	−0.25
H/Si/Cl	−0.21	0.42	0.70	0.88	0.99	−0.67
C/O$_{\mathrm{eq}}$	0.60/−0.69	0.59/−0.67	0.58/−0.66	0.60/−0.64	0.62/−0.63	0.62/−0.65
			0.61/−0.65	0.62/−0.64		
C/O$_{\mathrm{ax}}$	0.68/−0.67	0.69/−0.65	0.69/−0.64	0.70/−0.63	0.70/−0.62	0.64/−0.65
L_{total}		−0.22	−0.27	−0.34	−0.42	

Calculation of the v(CO) and v(MH) vibrational frequencies

The calculation of vibrational frequencies, especially of the CO groups, is a good parameter for the comparison of calculated and experimental structures and for the electronic situation at the metal center (Table 7). With the successive substitution of $R = \mathrm{H}$ for Cl in $(CO)_4Fe(H)Si\mathit{R}_3$, the wavenumber of the CO vibration increases. The experimental wavenumbers are shifted relative to the calculated ones by 20–50 cm^{-1} to higher values. This can be due to the solvent effect, because all calculations correspond to the unperturbed structure in the gas phase. The calculated frequencies are in good agreement with those found in calculations of other carbonyl complexes using the density functional theory [13, 14].

The M-H vibrational frequencies in the silyl substituted complexes show no systematic changes with the substitution pattern. The chloro complex has the highest *M*-H wavenumber due to the electron withdrawing effect of the chloride ligand.

The change of the wavenumbers shows the same relative trends in the anionic complexes (Table 8). There is also a difference of 30–50 cm^{-1} between the experimental and the calculated values. In the anionic compounds, the experimental vibrational spectra are additionally affected by anion-cation interactions. Compared to the neutral hydride complexes, the *v*(CO) vibrations are shifted to lower wavenumbers due to the increased electron density at the iron atom. In contrast to the neutral compounds, the anionic chloro complex shows similar wavenumbers as the anionic $SiCl_3$-substituted compound.

Table 7. Calculated IR wavenumbers (cm^{-1}) of the optimized $(CO)_4Fe(H)\mathit{L}$ complexes

	L								
	H	SiH_3	SiH_2Cl	$SiHCl_2$	$SiCl_3$	Cl	H exp. [11]	SiH_3 exp. [12]	$SiCl_3$ exp. [10]
v(CO)	2075	2056	2062	2070	2074	2090	2119	2107	2124
	2013	2001	2009	2017	2022	2044	2050	2050	2069
	2009	1996	2001	2015	2019	2038	2043	2044	2058
	2005	1982	1992	2002	2013	2021	2035	2036	2053
v(Fe-H)	1894	1877	1887	1880	1884	1865		1880	
	1871								
v(Si-H)		2315	2304	2300				2142	
		2291							

Table 8. Calculated IR wavenumbers (cm^{-1}) of the optimized $[(CO)_4Fe\mathit{L}]^-$ complexes

	H	SiH_3	SiH_2Cl	$SiHCl_2$	$SiCl_3$	Cl	$SiCl_3$ exp. [15]
v(CO)	1948	1946	1957	1966	1975	1971	2031
	1885	1871	1883	1893	1900	1884	1950
	1847	1848	1865	1875	1885	1884	1916
	1847	1847	1855	1869	1882	1883	1940
v(Si-H)		2214	2232	2243			
		2210	2231				

Table 9. Proton affinities (kcal/mol) of $(CO)_4Fe(H)L$ for different ligands L; zero point vibrational energies were taken into consideration

L					
H	SiH_3	SiH_2Cl	$SiHCl_2$	$SiCl_3$	Cl
299	295	290	285	281	280

Proton affinities

Another parameter for the influence of ligand on the electron density at the central metal atom in a hydride complex is the proton affinity of the corresponding anion. It can be estimated by subtracting the total energy of the corresponding anionic complex and that of a proton from the total energy of $(CO)_4Fe(H)L$. This energy difference should correspond to an ionic M–H bond fission and therefore to the acidity of the complex in the gas phase. In this paper we are only interested in relative changes of the acidity and not in absolute proton affinities which need a more complex formalism of calculation [16].

An increase of the donor character and a decrease of the acceptor character of the ligands generally results in less acidic metal complexes. This has been systematically studied in solution [17]. It has been found that the solvent plays a major role in such reactions and can lead to an opposite reactivity when comparing the experimental values in solution with those of gas phase reactions [18].

The calculated proton affinities show the expected order: the proton affinity of the $SiCl_3$-substituted complex is by 14 kcal/mol lower than that of the SiH_3-substituted complex. Each of the substitution steps leads to an decrease of 5 kcal/mol (Table 9). This means that the SiH_3-substituted anionic complex is a stronger base than the $SiCl_3$-substituted one. The only experimental value for a complex of the examined type is the gas phase acidity of $(CO)_4FeH_2$ of 319 ± 5 kcal/mol which is about 20 kcal/mol higher than calculated.

Conclusions

The gradient corrected density functional method gives good agreement of the optimized structures $(CO)_4Fe(H)L$ and $[(CO)_4FeL]^-$ with the experimental ones. It was shown that a change in the substitution pattern at the silyl ligand has a big influence on the Fe–Si bond, but only a minor influence on the rest of the compound.

Going from the hydride complexes to the corresponding deprotonated complexes, a Fe–Si bond contraction takes place which was mainly traced back to an increase in back bonding from the Fe atom in low lying σ^* orbitals of the silyl ligand.

The calculated IR frequencies for the CO and M-H vibrations are in good agreement with the experiment. The wavenumbers of the ν(CO) vibrations increase with the degree of Cl substitution in the silyl ligand, caused by the decreased electron density at the Fe atom.

The proton affinities show the expected sequence: the $SiCl_3$-substituted complex has the highest acidity and the SIH_3-substituted complex the lowest.

Method

The calculations were carried out at the gradient density functional level by using the local spin density approximation [19], combined with *Becke's* gradient correction [20] and *Lee*, *Yang* and *Parr's* correlation functional [21] (B3LYP) implemented in the *GAUSSIAN94* [22] package. The effective core potential of *Hay* and *Wadt* [23] implemented in the *GAUSSIAN94* package (LANL2DZ) was used for the iron atom. The chlorine and silicon atoms were described by the same potential with additional polarization functions (α(Cl) = 0.75, α(Si) = 0.45). The carbon and oxygen atoms were described with the [6/1/1/1/4/1] basis set of *Dunning* [24]. The natural bond orbital formalism [25] was applied for the population analysis which was performed by single point MP2 calculations on the B3LYP optimized structures.

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