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ORGANOMETALLIC DERIVATIVES OF THE TRANSITION METALS

VIII*. BONDING AND MOLECULAR MOTIONS IN SILYL TRANSITION METAL COMPLEXES STUDIED BY ^{29}Si NMR

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Summary

Complexes of the general type $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{L})_2\text{R}]$, $\text{L} = \text{CO}, \text{PR}'_3$; $\text{R} = \text{silyl}$, polysilyl, and silylmethyl, have been studied using ^{29}Si NMR. Chemical shift and nuclear Overhauser effect data have been obtained and related to the chemical bonding and molecular motion of the complexes. For the various dicarbonyl complexes sigma inductive effects by the iron substituent are noted, while upon phosphine substitution pi effects are observed with directly bonded silicon atoms present. From NOE η values segmental motion of the various chains may be noted, with the Fe iron atom effectively anchoring one end of the system.

Introduction

The interactions of silicon atoms with transition metals is of significance due to the use of metal complexes as catalysts for various reactions of organosilicon compounds, e.g. hydrosilylation [2] and polysilane formation [3,4]. A more fundamental interest exists due to the close relationship between Si and C as members of Group IV. In general the Si-M (and the Si-C-M) (M = transition metal) linkage is less kinetically reactive than the related C-M bond [5]. Thus no "insertion" reactions occur with the Si-M bond, and trimethylsilylmethyl complexes of a variety of transition metal systems are now well established as being both oxidatively and thermally more stable than their alkylmetal equiv-

* For part VII see ref. 1.

alents. This latter observation is thought to be primarily due to the greater steric bulk of, and lack of elimination pathways for, the silylmethyl ligands.

For silylmetal complexes, any enhanced thermodynamic stability, cf. the C—M bond, is at least ≈ 5 –10 kcal/mol in the system we are studying, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{L})_2\text{R}]$. Thus, while the complexes $\text{L} = \text{CO}$, $\text{R} = \text{—CH}_2\text{SiMe}_2\text{SiMe}_3$ and $\text{—CH}_2\text{SiMe}_2\text{H}$ readily rearrange to $\text{R} = \text{—SiMe}_2\text{CH}_2\text{SiMe}_3$ and —SiMe_3 , respectively [6,7], a reverse rearrangement $\text{R} = \text{—SiMe}_2\text{CH}_2\text{Cl}$ to $\text{—CH}_2\text{SiMe}_2\text{Cl}$ is also readily effected [8].

It has been suggested that $d_\pi\text{—}d_\pi$ bonding between the transition metal and silicon may be responsible for this extra stability. However, a recent combined infrared and Mössbauer study on $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}]$ system concluded that in this system at least, no significant retrodonative bonding of this type was needed to understand the various data [9]. A photoelectron spectroscopic study on the same system $\text{R} = \text{C, Si, Ge, Sn, and Pb}$ has reached an identical conclusion [10].

With the increasing availability of Fourier Transform NMR many investigations involving direct observation of the ^{29}Si nucleus have appeared, and several reviews are already in the literature [11–13]. To date, only a handful of literature reports concerning the utilization of this technique to sigma silylmetal complexes have appeared. Early reports by Ebsworth dealt with the chemical shift of the silicon atoms in $\text{Me}_3\text{SiHgSiH}_3$, ($\text{Me}_3\text{Si} = 63.7$; $\text{H}_3\text{Si} = 22.1$ ppm) and the coupling constants between Si and P and Pt in the complex $[\text{trans-PtCl}(\text{SiH}_2\text{Cl})(\text{PEt}_3)_2]$ ($J = 16.0$ and 1600 Hz, respectively) [14,15].

More comprehensive reports commenced in 1979. Fischer and coworkers studied a series of Group VI carbonyl silyl-substituted carbene and carbyne complexes, e.g. $[(\text{CO})_5\text{W}=\text{C}(\text{OEt})(\text{SiPh}_3)]$, $[(\text{CO})_4\text{BrW}\equiv\text{CSiPh}_3]$ [16]. From variations in chemical shift data for the various metals they have suggested that significant pi interactions occur between the metal and the silicon atom, but were unable to distinguish whether this was a hyperconjugative interaction or involved participation of the d -orbitals. Malisch and Ries reported the chemical shift, and various $J(\text{FSi})$, $J(\text{HSi})$ data for a series of complexes derived from the cyclopentadienyliron dicarbonyl system, i.e. $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiR}'\text{R}''\text{R}''']$. $\text{R} = \text{H, Cl, Me, F}$, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ [17]. They were unable to reach any conclusions regarding the variations of chemical shift upon replacing the various R groups, but did report that upon placing two metal atoms directly upon the Si atom they observed the lowest field chemical shifts for ^{29}Si thus far recorded. In a paper appearing at essentially the same time as the previous two, Gladysz, Servis and coworkers drew attention to the fact that good ^{29}Si NMR spectra of silyltransition metal complexes could be readily obtained using the Selective Population Transfer method, and reported the spectra of the trimethylsilyl derivatives of $\text{Co}(\text{CO})_4$, $\text{Mn}(\text{CO})_5$, $\text{Re}(\text{CO})_5$, and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ [18]. It was concluded that the ^{29}Si chemical shifts behaved in a fashion very similar to ^{119}Sn shifts previously reported by Lappert and McFarlane [19] and that pi bonding was an important feature, especially for the third row transition metal.

Finally, two papers have appeared describing ^{29}Si NMR data for a series of organosilyl pi complexes of the transition metals [20,21]. These studies illustrated a general low field shift of 6–11 ppm for a silicon atom bonded directly to a ligand C atom bonded to a single metal, and a shift of approximately twice

this value when two metals were bonded to the ligand C atom. It was also observed that coupling existed between a metal with a nuclear spin and silicon atoms in both the alpha and beta position, with respect to the metal, and that complexation of the organosilyl ligand to the metal severely restricted relaxation via spin-rotation mechanisms [20].

It is the purpose of this paper to report the results of a ^{29}Si NMR study on permethylated silyl complexes of the system $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{L})_2]\text{-L} = \text{CO}, \text{PR}_3$. We have chosen to restrict the study to permethylated silicon systems to avoid the problems associated with interpretation of variations of chemical shift upon substitution with halogens, etc. previously reported, and because the data from organosilicon systems is best understood for the methylated series of silyl compounds. Along with a simple chemical shift analysis, we have also studied nuclear Overhauser effects in order to learn something about the method of relaxation of the Si nuclei in a metal environment. This data provides information regarding the molecular motions of the complexes, i.e. overall molecular tumbling and free internal spinning of symmetrical groups.

Experimental section

The complexes were synthesized using well established and published procedures [6,7,22,23]. All spectra were recorded on a Bruker WP60 FT NMR spectrometer. Solutions of 50–250 mg were made up in thoroughly degassed benzene- d_6 . In order to study nuclear Overhauser effects no paramagnetic relaxation agents were added to the solutions. However, in a few cases where no signals could be obtained in this mode, $\text{Cr}(\text{acac})_3$ was added and the NOE was not measured. A pulse angle of 20–30° was used with a repetition time of 15–60 seconds. N.O.E. measurements were carried out by the method of Levy [28]. Spectra without N.O.E. were obtained using gated decoupling with a pulse delay of $\approx 5T_1$. Spectra with N.O.E. were obtained under identical conditions but with continuous proton decoupling. TMS was added as an internal standard and the TMS N.O.E. η value of -0.09 was applied as a correction factor. In a few cases the internal frequency of the spectrometer was used for standardization [24].

Results and discussion

Chemical shift and coupling data

The chemical shift parameters and coupling constants for the series of complexes studied are reported in Tables 1 and 2 respectively, ($\text{L} = \text{CO}, \text{PPh}_3$; $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, $\text{R} = \text{SiMe}_3, \text{SiMe}_2\text{SiMe}_3, \text{SiMe}_2\text{SiMe}_2\text{SiMe}_3, \text{SiMe}_2\text{CH}_2\text{SiMe}_3, \text{CH}_2\text{SiMe}_3$ and $\text{CH}_2\text{SiMe}_2\text{SiMe}_3$).

The current chemical shift range for the many hundreds of published ^{29}Si NMR spectra varies from +146 ppm to -350 ppm relative to TMS at 0 ppm, with high frequency (low field) shifts being positive. No comprehensive theoretical interpretation is available for these chemical shift variations, although Radeaglia et al. [25,26] have used a modified Jameson Gutowsky formulation with some success to reproduce the familiar "sagging pattern" of shifts with substituent electronegativity [14]. Harris and Kimber have demonstrated that

TABLE 1
 ^{29}Si CHEMICAL SHIFT PARAMETERS FOR $(\eta^5\text{-C}_5\text{H}_5)\text{FeLR}$ COMPLEXES AND MER COMPOUNDS

Complex	δ (ppm)			$\Delta\delta$ (ppm)			
	L	L	R	α	β	γ	
I	CO	CO	SiMe ₃ MeSiMe ₃	41.3 0.0	— —	— —	— —
II	CO	CO	SiMe ₂ SiMe ₃ MeSiMe ₂ SiMe ₃	16.95 -19.58	-11.3 -19.58	— —	8.28 —
III	CO	CO	SiMe ₂ SiMe ₂ SiMe ₃ MeSiMe ₂ SiMe ₂ SiMe ₃	21.22 -15.9	-36.54 -48.45	-15.07 -15.9	11.92 —
IV	CO	CO	CH ₂ SiMe ₃ MeCH ₂ SiMe ₃	— —	9.28 2.0	— —	7.28 —
V	CO	CO	CH ₂ SiMe ₂ SiMe ₃ MeSiMe ₂ SiMe ₃	— —	-6.7 -19.58	-19.92 -19.58	12.88 —
VI	CO	CO	SiMe ₂ CH ₂ SiMe ₃ MeSiMe ₂ CH ₂ SiMe ₃	42.86 0.32	— —	0.36 0.32	42.54 —
VII	CO	PPh ₃	SiMe ₃	34.75	—	—	34.75
VIII	CO	PPh ₃	SiMe ₂ CH ₂ SiMe ₃	36.99	—	0.30	36.67
IX	CO	PPh ₃	CH ₂ SiMe ₃	—	9.17	—	7.17
X	Ph ₂ PCH ₂ CH ₂ PPh ₂		SiMe ₃	25.16	—	—	25.16

TABLE 2
COUPLING CONSTANTS FOR SOME $(\eta^5\text{-C}_5\text{H}_5)\text{FeL}_2\text{R}$ COMPLEXES

Complex			$J(\text{SiP})$ (Hz)		
L	L	R	α	β	γ
CO	PPh ₃	SiMe ₃	30	—	—
Ph ₂ PCH ₂ CH ₂	PPh ₂	SiMe ₃	46	—	—
CO	PPh ₃	SiMe ₂ CH ₂ SiMe ₃	30	—	0
CO	PPh ₃	CH ₂ SiMe ₃	—	<1.5	—

for the system Me_3SiX , a rough correspondence between δSi and the electronegativity of X exists when X is a non-metal [4]. In this series the most electronegative groups tend to deshield the silicon nucleus. On the other hand, Schraml et al. studied a series of compounds $(\text{EtO})_n\text{Me}_{3-n}\text{Si}(\text{CH}_2)_m\text{Y}$ and showed that increasing the electronegativity of Y caused a high field shift, shielding the silicon nucleus. This was explained by invoking an overcompensation of $\text{O} \rightarrow \text{Si } p_\pi - d_\pi$ pi bonding to counterbalance the inductive effect of the Y substituent [27]. For the limited data available for X = transition metal, $d-d$ interactions and the "bulky atom" effect become significant, and the results seem to parallel trends observed for ^{119}Sn chemical shifts, with third row metals exhibiting the greatest high field shifts, the first row the greatest low field shifts.

Given these complicating features we have deliberately limited this initial study to single metal systems with limited substitutions on the metal and only methyl groups attached to the silicon atoms. The absolute values of the chemical shifts of the R ligands recorded in Table 1 offer little useful information. So that trends may be observed due to the presence of the transition metal, we have compared the ^{29}Si chemical shifts of the complexes with those of the corresponding RMe compound. In Table 1 a positive $\Delta\delta$ value signifies that the silicon atom in the iron complex appears to low field of the corresponding RMe silicon atom, i.e. $\Delta\delta = [\delta[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{L})_2\text{R}] - \delta\text{RMe}]$. Using this approach some significant features are apparent.

The silicon atom directly bonded to the transition metal (Si_α) exhibits the greatest $\Delta\delta$; each of the dicarbonyl complexes exhibits a $\Delta\delta$ in the narrow range from 36.5–42.5 ppm. Silicon atoms situated in the beta position with respect to the Fe (Si_β), have a low field shift in the range 8.3–12.9 ppm, i.e. considerably less, while the gamma silicon atoms (Si_γ) are essentially unaffected by the presence of the transition metal. It is significant that these chemical shift effects are apparently independent of the nature of the atoms that comprise the chain. For example the effect is similar in both FeSiSi and FeCSi , in FeSiCSi and FeSiSiSi , and this suggests that a simple inductive effect is operating and that transmission of the effect does not involve d orbital participation on the part of the silicon atom. It is also significant that the effect is rapidly attenuated, again symptomatic of a sigma bonding inductive feature rather than a pi interaction that might be expected to be transmitted over longer distances from the Fe atom in the case of the conjugated polysilyl ligands.

The effect of replacing the carbonyl ligands by phosphines was also studied.

A single replacement produces a high field shift for the silicon atom directly bonded to the Fe of 6.55 ppm (VII) and 5.87 ppm (VIII) compared to the dicarbonyl analog. Replacement of both of the carbonyls by the chelating "diphos" produces almost twice this shift, i.e. 16.1 ppm (X). The Si_β atom in (IX) and the Si_γ atom in (VIII) are unaffected by this substitution. Thus, directly bonded Si atoms become progressively shielded upon carbonyl substitution whereas silicon atoms insulated from the metal by methylene groups exhibit no shifts. Synthetically we have not been able to obtain polysilyl complexes with phosphine ligands due to elimination reactions previously described [4,23]; however, we are attempting new routes to such complexes. These results may be understood in terms of the capacity of silyl groups to pi bond in these phosphine substituted complexes. As noted in the introduction, Mössbauer, infrared, and PES spectroscopic studies have illustrated that in the dicarbonyl species there is no significant pi interaction between the Fe and directly bonded silicon atoms. This conclusion is now augmented by the ²⁹Si data on the dicarbonyl systems. However, there is chemical evidence that upon substitution of the CO ligands by PR₃ the extra electron density that is present on the Fe atom is partially delocalized onto a directly bound silicon atom via a pi interaction [23]. The ²⁹Si NMR data on the phosphine-substituted complexes reinforces this idea. The increase in shielding of the directly bound Si atoms due to phosphine substitution may be thought to result from a pi interaction, and this does not occur in the methylene-insulated silicon complexes. If the effect observed upon substitution were an inductive effect, then some variation should be observed upon the Si_β and Si_γ atoms insulated, as was the case for the dicarbonyl data discussed above. Clearly this interpretation on what is a limited set of complexes needs further study, and the synthesis of systems to directly investigate this aspect of the work is currently underway.

²J(SiP) coupling constants were observed for the directly bound silicon atoms in the two monophosphine complexes VII and VIII (doublet $J = 30$ Hz), and the diphos complex X (triplet, $J = 46$ Hz) (Table 2). Little can be said of these figures at the present, except that they are considerably larger than the ²J(SiP) coupling constant of 18 Hz for [*trans*-PtCl(SiH₂Cl)(PEt₃)₂] [15]. As more such data are developed much valuable information is to be gained from this aspect of the ²⁹Si NMR tool in transition metal silicon chemistry with respect to both geometry and bonding.

Nuclear Overhauser effects

For nuclei with a spin of 1/2, four main spin lattice relaxation methods are normally thought to be significant; dipole-dipole interactions (DD), the spin-rotation interaction (SR), the chemical shift anisotropy (CSA), and scalar interaction (SC). From the various studies performed using ²⁹Si NMR it is now apparent that in the absence of paramagnetic materials and quadrupolar nuclei, the major contributions to ²⁹Si relaxation are DD and SR relaxations. Thus, $1/T_{1(\text{obs})} = 1/T_{1(\text{DD})} + 1/T_{1(\text{SR})}$, where $T_{1(\text{DD})}$ and $T_{1(\text{obsd})}$ are related by the expression $T_{1(\text{DD})} = -2.52T_{1(\text{obsd})}/\eta$ where η is the observed NOE. [13] Thus, it may be noted that as the value of $-\eta$ approaches 2.52 so the relaxation of ²⁹Si atoms is becoming progressively more DD relaxation. In general, smaller, more mobile molecules relax predominantly via the SR mechanism as shown by

the small values of $-\eta$. Larger molecules with limited mobility therefore tend to relax more via DD mechanisms and possess correspondingly larger $-\eta$ values. Silicon atoms in chains, e.g. polysiloxanes, have been shown to undergo segmental motion. The terminal trimethylsilyl groups relax predominantly via SR mechanisms and DD mechanisms become progressively more significant in the middle of the chain indicating a type of flexing motion about the centre [28].

We have measured relaxation times for I and IV, but due to the very long acquisition times for a single spectrum, not for the complete series of complexes. We have, however, measured the NOE's for all the complexes and the data are collected in Tables 3 and 4.

Several trends may be observed from the data. All of the parent RMe compounds have relatively small $-\eta$ values in keeping with their being relatively small mobile species. However, even within these compounds the effects of increasing size are apparent, with η essentially zero for the symmetrical TMS, 0.25 for $\text{Me}_3\text{SiSiMe}_3$, and 0.4 for both Si atoms of the trisilane $\text{Me}_3\text{SiSiMe}_2\text{SiMe}_3$. The immediate effect of substituting an $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ for a methyl is to markedly increase the η values for all Si atoms in the molecule. In each case for the series FeSi , FeSi_2 , and FeSi_3 the terminal Si atom has an $-\eta$ value of 1.0 (null signal for the fully decoupled experiment). This illustrates that the relaxation is predominantly (60%) via an SR mechanism. This is probably due to the rotation of the Me_3Si group about its threefold axis coupled with a general tumbling motion of the molecule as a whole. In the case of the FeSi_2 molecule, for Si_α the DD mechanism is now predominant (58%) showing a marked difference between the two silicon atoms. For the trisilane complex, FeSi_3 , this effect is even more pronounced since the $-\eta$ values fall from 2.11, to 1.9 to 1.0 for the Si_α , Si_β , and Si_γ atoms. These trends can be understood in terms of the molecular tumbling of the entire molecule with the superimposition of the increasing motional freedom of the silicon atoms as they become further removed from the heavy Fe end of the complex. The Fe system can be seen to effectively anchor one end of the chain. Similar results are obtained for the FeCH_2SiSi and FeSiCH_2Si complexes. In the latter example the Si_α and Si_γ atoms show significantly larger $-\eta$ values than for the trisilane; it is possible that this difference reflects a further restriction of mobility due to steric hin-

TABLE 3
NOE η VALUES FOR SOME $(\eta^5\text{-C}_5\text{H}_5)\text{FeL}_2\text{R}$ COMPLEXES

Complex			$-\eta^{a,b}$		
L	L	R	α	β	γ
CO	CO	SiMe_3	1.0(40)	—	—
CO	CO	$\text{SiMe}_2\text{SiMe}_3$	1.45(56)	1.0(40)	—
CO	CO	$\text{SiMe}_2\text{SiMe}_2\text{SiMe}_3$	2.11(84)	1.9(75)	1.0(40)
CO	CO	$\text{CH}_2\text{SiMe}_2\text{SiMe}_3$	—	1.9(75)	0.8(32)
CO	CO	$\text{SiMe}_2\text{CH}_2\text{SiMe}_3$	2.31(92)	—	1.62(64)
CO	PPh_3	$\text{SiMe}_2\text{CH}_2\text{SiMe}_3$	2.46(98)	—	2.29(91)
CO	CO	CH_2SiMe_3	—	1.0(40)	—

^a $\pm 10\%$ accuracy. ^b % DD relaxation mechanism in parenthesis.

TABLE 4
RELAXATION TIMES FOR $(\eta^5\text{-C}_5\text{H}_5)\text{FeL}_2\text{R}$, s^a

R	T_1	T_1^{DD}	T_1^{SR}
SiMe ₃	79	198	130
CH ₂ SiMe ₃	75	189	124

^a ±5%. Measured by standard inversion-recovery sequence with gated decoupling during acquisition only.

drance resulting from the relative shortness of the Si—C bond, cf. Si—Si. Overall the data clearly illustrates the concept of segmental motion with the heavy transition metal acting to dampen motion at one end of the (Si)_nFe chain relative to the other.

Upon substituting a carbonyl ligand by a triphenylphosphine the $-\eta$ values of all Si atoms markedly increase. Thus, for the complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{-SiMe}_2\text{CH}_2\text{SiMe}_3]$ the $-\eta$ values come close to the limit, i.e. 2.46 (Si_α) and 2.29 (Si_γ). These values correspond to 98% and 90% DD relaxation, respectively, illustrating that the Fe end of the molecule is now so bulky and ponderous as to effectively swamp out any segmental motion and leave only a small SR contribution from the very small tumbling motion of the complex molecule.

In summary the NOE data shows that the substitution of the polysilyl groups on iron, or vice versa, perturbs the isotropic rotation of the molecule. Dipole-dipole relaxation is most significant for the Si_α atoms and spin rotation relaxation becomes progressively more important as the Si atoms are removed from the iron atom. The iron atom provides an anchor for the molecule, and segmental motion may be noted.

The relaxation times for I and IV are recorded in Table 4. They are long and duplicate runs require almost 5 days of instrument time. Within experimental error the two Si atoms of I and IV exhibit almost identical behavior. The removal of the Si atom from direct binding to Fe, which will provide more mobility and more Si—H DD interactions being offset by the extra mass of the complex.

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