

## ORGANOMETALLOIDAL DERIVATIVES OF THE TRANSITION METALS

### IV \*. A MÖSSBAUER AND INFRARED SPECTRAL STUDY OF THE IRON–SILICON OR CARBON BOND IN THE SYSTEM $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}$

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#### Summary

A Mössbauer effect spectral investigation of the compounds  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}$ , where R represents a range of alkyl and silyl groups, reveals enhanced *s*-electron density at the iron nucleus for the silyl compounds. Coupled with an infrared spectral analysis, the data suggest that superior  $\sigma$ -donation by the silyl group, as compared with the alkyl group, is the major reason for this enhancement, rather than significant iron–silicon retrodonative  $\pi$ -bonding. Such  $\pi$ -bonding effects may, however, be observed for the phenylsilyl complexes,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiPh}_n\text{Me}_{3-n}$ .

#### Introduction

The physical and chemical properties of the iron–silicon bond are distinctly different than those of the iron–carbon bond. In general the metal–silicon bond is considered to be more “stable”. For example, whereas alkylmetal complexes of the type  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$  readily react under mild conditions with phosphine ligands (L) to yield the alkyl migration products [2]  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{L})(\text{COCH}_3)$ , related silyl complexes fail to exhibit such migratory behavior. In addition, the simple ligand displacement reaction, yielding  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{L})\text{SiR}_3$ , occurs only upon ultraviolet irradiation [3]. It has been suggested that such stability results in part from the ability of the silicon atom to  $\pi$ -bond with the electron rich iron atom via  $d_\pi\text{--}d_\pi$ -bonding [3,4]. There have been several reports [5–7] concerning the ability of Mössbauer spectroscopy to provide insight into the  $\sigma$ - and  $\pi$ -bonding aspects of complexes

\* For Part III see ref. 1.

TABLE 1  
MÖSSBAUER AND INFRARED SPECTRAL RESULTS <sup>a</sup>

Compound	78 K		Room temperature			$\nu(\text{CO})_{\text{antisym}}$ ( $\text{cm}^{-1}$ )		
	$\delta$	$\Delta E_Q$	$\Gamma$	$\delta$	$\Delta E_Q$		$\Gamma$	
								$\nu(\text{CO})_{\text{sym}}$ ( $\text{cm}^{-1}$ )
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SIPh}_3$	0.039	1.80	0.24	-0.039	1.78	0.25	2001.3	1953
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SIPh}_2\text{Me}$	0.046	1.78	0.27	-0.034	1.77	0.24	1998.1	1947.9
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SIPhMe}_2$	0.042	1.77	0.25	-0.044	1.77	0.23	1996	1944
$(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Fe}(\text{CO})_2\text{SiMe}_3$	0.046	1.76	0.27					
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_3$	0.052	1.77	0.27				1996.1	1943.9
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiEt}_3$	0.055	1.80	0.26				1992.1	1940.7
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Si}_2\text{Me}_5$	0.068	1.75	0.26				1993.7	1944.2
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Si}_3\text{Me}_7$	0.068	1.75	0.26				1992.7	1943.0
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{Si}_2\text{Me}_4$	0.072	1.72	0.27	-0.008	1.70	0.26		
$(\eta^2\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$	0.076	1.76	0.26				2010.2	1957.5
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2(\text{p-CIPh})$	0.084	1.68	0.26				2009.3	1959.0
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2(\text{p-Ph})$	0.085	1.74	0.26	0.004	1.72	0.24	2009.6	1959.8
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2(\text{o-MePh})$	0.094	1.72	0.26				2007.3	1959.0
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{SiMe}_3$	0.099	1.75	0.26				2007.4	1956.2
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{Si}_2\text{Me}_5$	0.105	1.69	0.25				2011.0	1958.5

<sup>a</sup> All Mössbauer effect data in mm/s relative to natural  $\alpha$ -iron foil. Infrared spectral data were obtained in hexane solution.

of the type  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ , including a very recent paper that suggested a relationship between the iron Mössbauer spectral parameters and the carbonyl infrared stretching frequencies [8]. We wish to report herein the use of this technique to investigate the bonding properties of the iron—Group IV complexes, with special emphasis upon the iron—silicon and iron—carbon bonding systems.

## Experimental

All complexes were prepared by using established and published procedures involving salt elimination reactions between  $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$  and the appropriate alkyl or silyl halide. Infrared spectra were measured in hexane solution on a Perkin—Elmer 421 spectrophotometer. The Mössbauer effect spectra were obtained on a Ranger Engineering Corp. constant-acceleration spectrometer which utilized a room-temperature rhodium matrix source and was calibrated with natural  $\alpha$ -iron foil. The Mössbauer effect absorbers were prepared by mixing the sample with vaseline in order to provide random polycrystallite orientation. The concentration of iron was adjusted such that typical absorbers contained ca. 7 mg  $^{57}\text{Fe}/\text{cm}^2$ .

## Results and discussion

The Mössbauer effect spectral parameters for a series of complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}$  are presented in Table 1. Many of these complexes are liquids at room temperature and hence no Mössbauer effect could be observed at this temperature. However, all complexes gave a clean well resolved quadrupole doublet spectrum at 78 K as is illustrated for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{Si-Me}_3$  in Fig. 1; Table 1 also includes the carbonyl stretching frequencies for the complexes as measured in hexane solution. All of the Mössbauer effect parameters presented in this table were calculated from a computer optimized parabola and Lorentzian fit obtained by using the National Bureau of Standards PARLOR computer program [9]. The error limits associated with the parameters for several of the compounds have been calculated from the variance of the peak position and half-width determined by the final computer iteration of the numerical fitting procedure [9,10]. Standard error propagation formulae, which took into account the standard errors in the calibration factors, were then used to calculate the final error limits. These results, and earlier experience [8] indicates that the error limits are ca.  $\pm 0.002$  mm/s for the isomer shift, and ca.  $\pm 0.01$  mm/s for the quadrupole interaction and the line-width. In many instances the error limits are smaller and these values represent the upper error limits for the data obtained at 78 K. From these results, we have concluded that we are observing real and reproducible relative differences in the chemical isomer shifts for the compounds listed in Table 1. The small variation in these isomer shift values points up the necessity of measuring the Mössbauer spectra under nearly as identical conditions as possible.

Although there have been numerous papers [11] dealing with the Mössbauer effect spectra of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$  compounds, relatively few of these papers have dealt with alkyl or silyl derivatives. Mays and Sears report [12] that

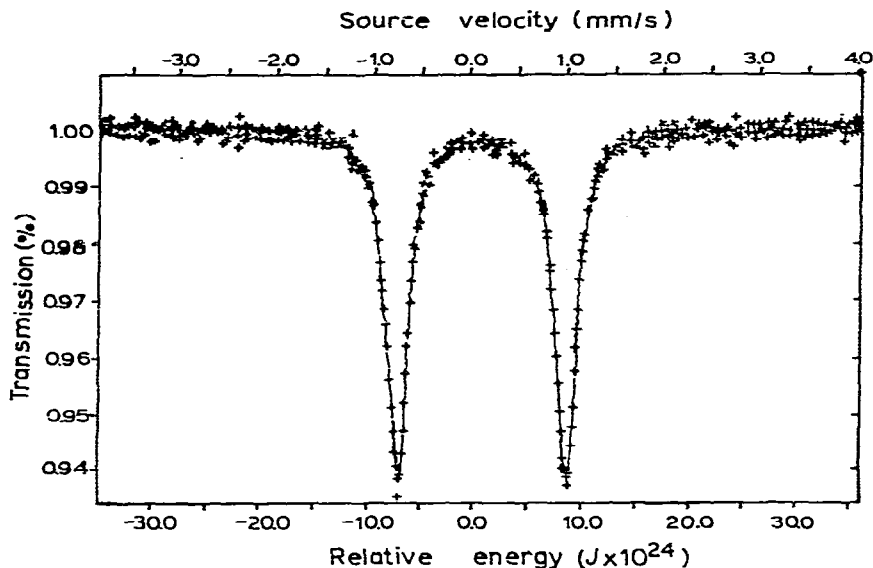


Fig. 1. The Mössbauer effect spectrum of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{SiMe}_3$  obtained at 78 K.

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$  has an isomer shift of  $-0.15$  mm/s and a quadrupole interaction of  $1.75$  mm/s at 80 K. Others report that  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{COCH}_3$  has an isomer shift [6] of  $0.019$  mm/s and a quadrupole interaction of  $1.66$  mm/s at room temperature and that  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{Ph}$  has an isomer shift [13] of  $0.05$  mm/s and a quadrupole shift of  $1.71$  mm/s at room temperature. Cheng et al. [14] indicate that  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{CH}_2$  has an isomer shift of  $0.05$  mm/s and a quadrupole interaction of  $1.80$  mm/s at 78 K. Apart from the Mays and Sears result, these results are quite consistent with the values reported in Table 1. Unfortunately, variations in experimental procedures prevent any direct comparison of these values. At this time we do not know the reason for the rather low value of the isomer shift reported by Mays and Sears [12] as compared with our results. Parish and Riley have recently [15] discussed the Mössbauer spectra of many organometallic complexes containing iron—silicon bonds. Unfortunately no direct comparisons can be made between their work and our results.

It is well known that a decrease in the Mössbauer effect isomer shift corresponds to an increase in the  $s$ -electron density at the iron nucleus [5]. Further it is generally accepted that such increases can be the result of either a  $\sigma$ -inductive release of electron density to the iron atom or a retrodonative metal to ligand  $\pi$ -bonding removal of  $d$ -electron density from the iron atom with a resulting increase in  $s$ -electron density at the iron nucleus. Thus, in a series of complexes,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ , where X represents a series of halides and pseudohalides, the halides (poor  $\sigma$ -donors and poor  $\pi$ -acceptors) gave the highest isomer shift values whereas cyanide (a good  $\sigma$ -donor and a good  $\pi$ -acceptor) gave the lowest value [8].

Infrared spectral investigations of metal carbonyl complexes abound, and a general conclusion is that the values of the carbonyl stretching frequencies may

be used as a monitor of the extent to which the carbonyl ligands participate in retrodonative  $\pi$ -bonding with the metal by utilizing their  $\pi^*$  carbonyl molecular orbitals. Thus, in a series of structurally related compounds, as in the case reported herein, the  $\nu(\text{CO})$  bond will be higher for the complexes that involve the least metal to carbonyl retrodonative  $\pi$ -bonding. This often implies that the other ligands bonded to the metal are themselves removing  $\pi$ -electron density by retrodonative bonding thereby lowering the ability or necessity of the carbonyl groups to bond in this fashion.

Bearing the above comments in mind, an examination of the Mössbauer and infrared data presented in Table 1 permits the following observations:

(i) All of the silyl complexes studied possess lower isomer shifts than all of the alkyl complexes.

(ii) There is a distinct variation in the isomer shift values as a function of substitution on the silicon or carbon atoms.

(iii) All the silyl complexes studied possess lower carbonyl stretching frequencies than all the alkyl complexes, but, variations within each group are of the same order as the experimental error in these frequencies. The only exceptions are the  $\text{SiPh}_n$  complexes.

(iv) The magnitude of the quadrupole interaction,  $\Delta E_Q$ , does not correlate with the nature of the alkyl or silyl substituent. This is in keeping with previous studies [5,8,16].

Several conclusions may be drawn from the above observations. First, the previous suggestion [8] of a correlation between the Mössbauer effect isomer shift and the carbonyl infrared stretching frequencies for complexes of the type  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$  is not a general relationship which holds for the alkyl and silyl derivatives [17] \*. Variations in  $\nu(\text{CO})$  are often minimal for the various alkyl and silyl complexes, whereas the isomer shift varies considerably. It seems that the Mössbauer effect is much more sensitive to the varying electronic effect of the changing ligand.

From the isomer shift data in Table 1 and our first observation, it is noted that the silyl complexes result in more  $s$ -electron density at the iron nucleus than the alkyl complexes. Either superior  $\sigma$ -donation or extensive retrodonative  $\pi$ -bonding can explain this result. If the latter is the case, then some effect upon the  $\nu(\text{CO})$  bands should be observed. Extensive retrodonative  $\pi$ -bonding of the iron to the silyl group would lead to less  $\pi$ -bonding of the iron to the carbonyl groups and, hence, higher stretching frequencies for the carbonyl groups in the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiR}_3$  complexes should be observed. This is contrary to the data and the second general observation that lower stretching frequencies are observed for the silyl complexes. Both of these general observations are thus in accord with, and best explained by, the simple conclusion that the silyl ligands act as superior  $\sigma$ -donors in complexes of the type  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{-SiR}_3$ .

While iron to silicon  $\pi$ -bonding may be minimal, it is not totally absent. Consider the series  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_{3-n}\text{Ph}_n$ . With an increase in  $n$  one would expect both a decrease in  $\sigma$ -electron release, and if present, an increase in retro-

\* Similar conclusions were reached for the system  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ ,  $\text{X} = \text{CO}, \text{CN}, \text{CNR}, \text{C}(\text{NHR})_2$  etc.

ductive  $\pi$ -bonding. If only  $\sigma$ -electron release were significant, the isomer shift should become progressively higher as  $n$  increases. However, if  $\pi$ -bonding is the dominant variable, then the isomer shift decreases as  $n$  increases. The experimental isomer shift data supports the latter expectation, as does the infrared data. The  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiPh}_3$  complex has significantly higher carbonyl stretching frequencies than the remaining silyl complexes.

The other variations of the isomer shift within the silyl series and the alkyl series are not readily explicable. For example, changes from the  $\text{CH}_3$  to  $\text{CH}_2\text{SiMe}_2$  to the  $\text{CH}_2\text{Si}_2\text{Me}_5$  derivatives would be expected to increase the  $s$ -electron density at the iron nucleus. However, the isomer shift values change significantly from 0.076 to 0.099 to 0.105 mm/s in the opposite sense.

In conclusion, the Mössbauer and infrared analysis appears useful in distinguishing which electronic factors are important in the bonding of iron-carbon and iron-silicon systems. While a general superiority of  $\sigma$ -donor capability, with silicon greater than carbon, is adequate to explain the major trends,  $\pi$ -bonding is also observed to be important for the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_{3-n}\text{-Ph}_n$  complexes.

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