2454 *Organometallics* **1990**, *9*, 2454-2462

character. Because of the distortion a large number of energy levels can be populated either by thermal means or by low energy radiation. Whereas $[CpCr(\mu_3\text{-}O)]_4$ is diamagnetic below 50 K, $[CpCr]_4(\mu_3\text{-}\eta^2\text{-}C_5H_4)(\mu_3\text{-}O)_3$ is paramagnetic, because two singly degenerate levels have very similar energies.

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Supplementary Material Available: Tables of temperature-dependent ^1H NMR shifts and orbital energy levels, symmetries, and metal d compositions, tables of atomic parameters of hydrogen atoms, thermal parameters, all bond distances and angles, and least-squares planes at 295 and 100 K, and a drawing of I (20 pages); tables of observed and calculated structure factors for I at 295 and 100 K (46 pages). Ordering information is given on any current masthead page.

Nature of the Fe–Si Bonds in Oligosilane Complexes of the Indenyliron Dicarbonyl System: $(\eta^5\text{-}C_9H_7)Fe(CO)(L)Si_n$ (Si_n = $SiMe_3$, Si_2Me_5, 2-Si_3Me_7; L = CO, PPh_3)[1]

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Complexes of the general type $(\eta^5\text{-}C_9H_7)Fe(CO)(L)Si_n$ ($\eta^5\text{-}C_9H_7$ = η^5-indenyl; Si_n = $SiMe_3$, Si_2Me_5, 2-Si_3Me_7; L = CO, PPh_3) have been synthesized and characterized via X-ray crystallography. Substitution of the CO ligand by PPh_3 results in a significant increase in both the Fe-Si and Si-Si bond distances. The results rule out a significant contribution of any π-bonding to the Fe-Si bond in both the dicarbonyl and carbonyl phosphine systems and imply that steric considerations dominate the various structural changes. The η^5-indenyl groups exhibit their characteristic "slipfold" distortion, which becomes larger as the steric bulk of the other ligands increases. The synthesis of $(\eta^5\text{-}C_9H_7)Fe(CO)(L)SiMe(SiMe_3)_2$ was accomplished via photochemical rearrangement of $(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_2SiMe_2SiMe_3$ in the presence or absence of PPh_3. ^{29}Si NMR data are in accord with the structures and previous NMR studies on silyliron complexes.

Introduction

The study of transition-metal-substituted silanes is a well-established area of organometallic chemistry due to the potential of transition metals to catalyze the reactions of organosilicon compounds, especially hydrosilylation and the formation of Si-Si bonds.[2,3] The nature of the silicon–transition-metal bond has been studied extensively, and the degree to which π-bonding between filled *n*d metal orbitals and vacant 3d silicon orbitals is important has been a matter of considerable interest. Most of the studies concerning such bonding have involved spectroscopic techniques, and the systematic structural data needed to evaluate the possibility of multiple bonding have not been available.

One series of transition-metal silyl compounds that has been well studied spectroscopically is the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$–silyl system, but, since such complexes usually are oils and waxes, only a few structural studies have been published.[4] Furthermore, those few structures have not allowed a discussion of the contribution of π-bonding to the Fe–Si bond.

Chart I

L = CO (a), PPh_3 (b); R_3Si = Me_3Si (Ia,b), Me_5Si (IIa,b), 2-$MeSi_3$ (IIIa,b)

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We have initiated a study of the related η^5-indenyl complexes $(\eta^5\text{-}C_9H_7)Fe(CO)_2$–silane, and thus far most of the complexes have been isolated as stable crystalline materials. We have performed an X-ray crystallographic analysis of mono-, di-, and trisilane derivatives of this system. Furthermore, photochemical treatment of these silyl complexes has yielded the corresponding phosphine-substituted complexes $(\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)Si_n$ (n = 1–3) without loss of silyl fragments. This latter result is in direct contrast to that obtained with use of permethylated di- and trisilyl complexes of the cyclopentadienyl system $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si_n$ (n = 2, 3; Fp–Si$_n$), where irradiation leads to the formation of monosilyl complexes $FpSiMe_3$.[5]

Using the $(\eta^5\text{-}C_9H_7)Fe(CO)(L)$ system (L = CO, PPh_3), we have obtained a suite of complexes (Chart I) that permits assessment of the π-bonding possibilities in the Fe–Si bond and present here the results of this study.

Experimental Section

All manipulations were performed under inert atmospheres of N_2 or Ar with use of dry, oxygen-free solvents. Organosilicon compounds were synthesized with use of literature procedures ($Me_3SiSiMe_2Cl$,[6] $Me_3SiSiMe_2SiMe_2Cl$[7]) from starting silicon materials purchased from Petrarch Systems Inc., Bristol, PA; $Fe(CO)_5$ was purchased from Strem Chemicals, Newburyport, MA. Reagent-grade silica gel (grade 950, 60–200 mesh) was purchased from MCB Reagents, Gibbstown, NJ. Analyses were performed by Galbraith Laboratories, Knoxville, TN. Infrared spectra were recorded on a Perkin-Elmer 580B grating spectrophotometer and NMR spectra on a Bruker NR 200-MHz spectrometer.

Typical experimental procedures are outlined below.

Synthesis of $(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_2SiMe_3$ (IIa). To a solution of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2]^-Na^+$ prepared from 2.57 g (5.65 mmol) of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2]_2$[8] at 0 °C was added 2.0 g (12 mmol) of $Me_3SiSiMe_2Cl$ over a period of 20 min. The solution was stirred for 30 min and warmed to room temperature and stirred for a further 12 h. The solvent was removed under vacuum, and the residue was extracted with 2 × 25 mL of hexane. This solution was filtered, the solvent removed, and the residue placed upon a silica gel column (2.0 × 20 cm) made up in hexane. Elution with hexane formed a yellow band that produced a yellow semisolid after elution and removal of the solvent. The semisolid was placed in a sublimation apparatus and heated to 45 °C at 0.1 mmHg for 24 h to remove residual indene. Further heating to 60 °C produced the title complex, which could be further purified by crystallization from hexane; yield 2.0 g (5.6 mmol, 50%). Analytical and spectral data for the complexes are presented in Table I.

Table I. Spectral and Analytical Data for the New Complexes $(\eta^5\text{-}C_9H_7)Fe(CO)(L)SiR_3$[a]

	$(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_3$ (Ia)
^1H	7.45, 7.18 (C_6H_4); 4.89 (m) 0.35 ($SiMe_3$)
^{13}C	215.0 (CO); 126.4, 124.1, 105.4, 91.9, 71.7 (C_9H_7); 7.2 ($SiMe_3$)
^{29}Si	47.5
ν(CO)[b]	1993, 1941
anal. calcd (found)	C, 56.0 (55.9); H, 5.37 (5.33)
mp[c]	75–76
	$(\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)SiMe_3$ (Ib)
^1H	7.1–7.7, 5.01, 4.53, 3.75 (C_9H_7, Ph); 0.1 ($SiMe_3$)
^{13}C	214 (CO); 127.3, 126.1, 105.5, 91.0, 71.0 (C_9H_7); 136.8, 136.1, 133.5, 129.0, 104.8 (Ph_3P); 7.5 (Me_3Si)
^{29}Si	41.7 (d, $^2J_{Si\text{-}P}$ = 27.7 Hz)
ν(CO)	1911
anal. calcd (found)	C, 66.8 (67.0), H, 5.97 (5.74)
	$(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_2SiMe_3$ (IIa)
^1H	7.09, 6.83, 4.89 (m, C_9H_7); 0.46, 0.22 (Si_2Me_5)
^{13}C	215.0 (CO); 127.0, 124.5, 105.8, 90.9, 72.0 (C_9H_7); 3.67, −0.16 (Si_2Me_5)
^{29}Si	25.1 (Fe–Si); −11.9 (Fe–Si–*Si*)
ν(CO)	1994, 1944
anal. calcd (found)	C, 53.6 (53.4); H, 6.19 (6.23)
mp	59–60
	$(\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)SiMe_2SiMe_3$ (IIb)
^1H	7.8–6.8, 5.0, 4.54, 3.8 (Ph, C_9H_7); 0.25, 0.15 (Si_2Me_5)
^{29}Si	18.2 (Fe–Si, d, $^2J_{Si\text{-}P}$ = 27.5 Hz); −10.3 (Fe–Si–*Si*)
ν(CO)	1911
anal. calcd (found)	C, 66.9 (67.4); H, 6.30 (6.37)
	$(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe(SiMe_3)_2$ (IIIa)
^1H	7.47, 7.21, 4.99 (m, C_9H_7); 0.20, 0.16 (Si_3Me_7)
^{13}C	215.0 (CO); 127.2, 124.5, 105.4, 89.3, 71.8 (C_9H_7); 1.44, −3.0 (Si_3Me_7)
^{29}Si	−8.7 ($SiMe_3$); −12.7 (Fe–Si)
ν(CO)	1996, 1946
anal. calcd (found)	C, 51.9 (51.7); H, 6.78 (6.72)
mp	85–86
	$(\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)SiMe(SiMe_3)_2$ (IIIb)
^1H	7.9–6.8, 5.00, 4.54 (m, Ph, C_9H_7); 0.10, 0.0 (Si_3Me_7)
^{29}Si	−7.2 ($SiMe_3$); −20.5 (Fe–Si, d, $^2J_{Si\text{-}P}$ = 27.9 Hz)
ν(CO)	1911
Anal. calcd (found)	C, 64.6 (64.7); H, 6.60 (6.39)

[a] NMR spectral data are all relative to TMS at 0.0 ppm. ^1H and ^{13}C spectra were recorded in $CDCl_3$ and ^{29}Si data in C_6D_6. [b] IR data (in cm^{-1}) for dicarbonyls were recorded in hexane and for phosphine complexes in CH_2Cl_2. [c] All melting points (in °C) were determined in open capillary tubes and are uncorrected.

Photochemical Treatment of $(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_2SiMe_3$ with PPh_3. To a solution of $(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_2SiMe_3$ (0.54 g, 1.5 mmol) in 15 mL of hexane, in a quartz flask, was added 0.42 g (1.6 mmol) of PPh_3. The solution was irradiated by a Hanovia 450-W medium-pressure lamp at a distance of 5 cm. Monitoring of the reaction with use of infrared spectroscopy indicated that after 6 h the ν(CO) bands of the starting material had been replaced by a single CO stretching frequency at 1911 cm^{-1}. The solvent was removed under vacuum, the residue was dissolved in the minimum volume of a 1:1 methylene chloride–hexane mixture, the solution was placed upon a silica gel column (15 × 2 cm), and the column was eluted with hexane. A bright red band yielded 0.44 g (0.74 mmol, 49%) of $(\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)SiMe_3$ (IIb). Full spectral and analytical details are presented in Table I.

X-ray Structural Determination. Intensity data for all compounds were collected on a Nicolet-Siemens R3m/V four-circle diffractometer at room temperature, using graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.71073 Å). The ω-scan technique was applied in the 2θ range 3.5 ≤ 2θ ≤ 45.0° with variable scan speeds. The intensities of 3 check reflections were measured every 50 reflections (100 for Ib), and these decreased only slightly. Compounds Ia and IIa proved to be sensitive to air and humidity;

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Table II

	Ia	Ib	IIa
empirical formula	$C_{14}H_{16}O_2SiFe$	$C_{31}H_{31}OSiPFe$	$C_{16}H_{22}O_2Si_2Fe$
fw	300.2	534.5	358.4
cryst syst	monoclinic	triclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	*Pbca*
a, Å	10.769 (8)	10.574 (2)	8.331 (5)
b, Å	11.060 (9)	15.393 (3)	14.218 (8)
c, Å	13.309 (9)	17.430 (3)	31.62 (2)
α, deg		103.17 (1)	
β, deg	111.19 (8)	93.02 (1)	
γ, deg		95.13 (1)	
V, Å	1478 (2)	2743.5 (8)	3745 (4)
Z	4	4	8
D_{calc}, Mg m^{-3}	1.349	1.294	1.271
μ(Mo K$\bar{\alpha}$), mm^{-1}	1.089	0.669	0.930
F(000)	624	1120	1504
approx cryst size, mm	0.10 × 0.20 × 0.30	0.20 × 0.40 × 0.50	0.06 × 0.12 × 0.13
cryst color	orange	red	orange
scan speed, deg min^{-1}	3.0–20.0	6.0–20.0	2.5–20
index ranges	$-2 \leq h \leq 11, 0 \leq k \leq 11, -14 \leq l \leq 13$	$-5 \leq h \leq 11, -16 \leq k \leq 16, -18 \leq l \leq 18$	$0 \leq h \leq 8, 0 \leq k \leq 15, 0 \leq l \leq 34$
no. of rflns collected	2296	7865	2973
no. of indep rflns	1895	7155	2416
R_{int}	0.013	0.032	0.068
no. of obsd data [$F > 3.0\sigma(F)$]	1392	7147	1715
structure soln	direct methods	direct methods	heavy-atom method
weighting g	0.0003	0.0013	0.0289
R_{obs}	0.051	0.049	0.054
R_w	0.049	0.057	0.093
R_{tot}	0.073	0.050	0.072
goodness of fit	1.41	1.08	0.53
largest and mean Δ/σ	0.206, −0.003	0.935, −0.005	0.043, −0.001
data-to-param ratio	8.5:1	11.3:1	9.0:1
largest diff peak, e Å^{-3}	0.29	0.29	0.60
largest diff hole, e Å^{-3}	−0.30	−0.30	−0.39
	IIb	**IIIa**	**IIIb**
empirical formula	$C_{33}H_{37}OSiPFe$	$C_{18}H_{28}O_2Si_3Fe$	$C_{35}H_{43}OSi_3PFe$
fw	592.6	416.5	650.9
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/a$	$P2_1/n$
a, Å	14.520 (7)	14.865 (5)	11.195 (3)
b, Å	10.155 (5)	8.699 (5)	18.432 (5)
c, Å	21.096 (9)	18.039 (9)	17.184 (4)
β, deg	98.59 (4)	98.96 (5)	98.07 (2)
V, Å	3076 (3)	2304 (2)	3510.7 (14)
Z	4	4	4
D_{calc}, Mg m^{-3}	1.280	1.201	1.231
μ(Mo K$\bar{\alpha}$), mm^{-1}	0.640	0.813	0.598
F(000)	1248	880	1376
approx cryst size, mm	0.40 × 0.40 × 0.50	0.03 × 0.30 × 0.30	0.40 × 0.22 × 0.60
cryst color	red	orange	red
scan speed, deg min^{-1}	3.0–20.0	2.0–20.0	3.0–15.0
index ranges	$-2 \leq h \leq 15, -5 \leq k \leq 10, -22 \leq l \leq 22$	$0 \leq h \leq 15, 0 \leq k \leq 9, -19 \leq l \leq 19$	$-6 \leq h \leq 12, -19 \leq k \leq 19, -18 \leq l \leq 18$
no. of rflns collected	4615	3342	8728
no. of indep rflns	4325	2871	4251
R_{int}	0.008	0.010	0.013
no. of obsd data [$F > 3.0\sigma(F)$]	4273	2243 [$F > 4.0\sigma(F)$]	3639
structure soln	direct methods	heavy-atom method	direct methods
weighting g	0.0262	0.0011	0.0001
R_{obs}	0.044	0.047	0.046
R_w	0.089	0.061	0.042
R_{tot}	0.058	0.062	0.057
goodness of fit	0.50	1.42	2.07
largest and mean Δ/σ	3.467, 0.064	0.245, −0.009	0.554, −0.008
data-to-param ratio	12.5:1	10.3:1	9.8:1
largest diff peak, e Å^{-3}	0.47	0.22	0.26
largest diff hol, e Å^{-3}	−0.46	−0.24	−0.33

therefore, these crystals were fully covered by glue. ψ-Scan data were collected for Ib and IIIa (minimum and maximum transmission factors were nearly equal: Ib, 0.559 and 0.581; IIIa, 0.423 and 0.494), showing that the data are not subject to serious absorption effects.

The structures were refined by anisotropic, full-matrix least squares. The quantity minimized was $\sum w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F) + gF^2$ with variable g. Hydrogen atomic positions were generated from the assumed geometry. They were included in structure factor calculations with their isotropic U values fixed at 0.08. Crystal data, data collection, and least-squares parameters are listed in Table II. All calculations were performed by the Nicolet SHELXTL PLUS program package on a MicroVAX II computer. Atomic coordinates are reported in Table III, and relevant bond angles and distances were presented in Table IV. The structures of the new complexes are presented in Figure 1.

Results and Discussion

The monosilyl-, disilyl-, and trisilyl(η^5-indenyl)dicarbonyliron complexes were prepared in moderate to good yields via the standard salt elimination reaction outlined in eq 1.

$$[(\eta^5\text{-}C_9H_7)Fe(CO)_2]^-Na^+ + R_3SiCl \xrightarrow{THF} \underset{\text{Ia–IIIa}}{(\eta^5\text{-}C_9H_7)Fe(CO)_2SiR_3} + NaCl \quad (1)$$

R_3Si =
Me_3Si (Ia), Me_5Si_2 (IIa), 1-Me_7Si_3, 2-Me_7Si_3 (IIIa)

All the complexes are yellow, crystalline materials whose spectroscopic data are recorded in Table I. The branched trisilyl complex (η^5-C_9H_7)$Fe(CO)_2SiMe(SiMe_3)_2$ (IIIa) was more conveniently synthesized via the photochemical transformation of the linear trisilyl complex (eq 2).

$$(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_2SiMe_2SiMe_3 \xrightarrow{h\nu} (\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe(SiMe_3)_2 \quad (2)$$

This latter reaction is an example of the general transformation of oligosilyl complexes that we have previously observed for the (η^5-C_5H_5)$Fe(CO)_2$–silyl (Fp–silyl) systems.[9] There is a difference between the cyclopentadienyl and the indenyl complexes. In the former case the linear trisilane finally transforms to the monosilane complex, Fp–$SiMe_3$, via the 2-substituted trisilane and disilane (eq 3).

$$Fp\text{–}SiMe_2SiMe_2SiMe_3 \xrightarrow{h\nu} Fp\text{–}SiMe(SiMe_3)_2 \xrightarrow{h\nu} Fp\text{–}SiMe_2SiMe_3 \xrightarrow{h\nu} Fp\text{–}SiMe_3 \quad (3)$$

The absence of the silyl group expulsions in the case of the indenyl complexes is currently under investigation and will be the subject of a forthcoming article. The phosphine derivatives were obtained in good yields via the photochemical substitution reactions outlined in eq 4.

$$(\eta^5\text{-}C_9H_7)Fe(CO)_2SiR_3 + PPh_3 \xrightarrow[THF]{h\nu} \underset{\text{Ib–IIIb}}{(\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)SiR_3} + CO \quad (4)$$

R_3Si = Me_3Si (Ib), Me_5Si_2 (IIb), 2-Me_7Si_3 (IIIb)

The ^{29}Si NMR data for the new complexes are recorded in Table I and verify the various conclusions we have reached from the corresponding data for the Fp–oligosilyl complexes.[5,9,10] Bonding of the iron group to a silicon atom causes a significant low-frequency shift of the silicon resonance compared to that for the methyl-substituted counterpart. Thus, for (η^5-C_9H_7)$Fe(CO)_2SiMe_3$ the resonance occurs at +47.5 ppm, a shift of 47.5 ppm compared to Me–$SiMe_3$. This shift, $\Delta\delta$, is tabulated in Table V for the six complexes that we have structurally characterized in this paper. The silicon atoms directly bonded to Fe (α-position) have shifts in the range 35–48 ppm, and those in the β-position, 6–12 ppm. When the CO ligand is replaced with PPh_3, the shifts of the silicon atoms in the α-position are attenuated by approximately 6–8 ppm due to the electron-donating capacity of the phosphine. The $\Delta\delta$ values for silicon atoms in the β-position are actually *increased* by 1–2 ppm upon phosphine substitution.

In theory, the electron donation of the phosphine ligands could alter the capacity of the silyl groups to accept electron density from the Fe atom via π-bonding since the more strongly electron-donating, but more weakly π-accepting, phosphine increases the electron density at the Fe atom. This buildup of electron density results in significantly reduced stretching frequencies for the remaining CO group, which are generally thought to result from an increase in retrodative π-bonding between filled Fe d orbitals and the empty π^* orbitals of the CO group. It has been claimed, and this claim is generally accepted, that "the most convincing evidence, pro or con, in the π-bonding controversy comes from crystallographic determination of bond lengths".[11] Close inspection of the Fe–C(CO) and C–O bond lengths of the complexes recorded in Table IV illustrates this aspect of the phosphine substitution process. There is a clear decrease in the Fe–C(CO) bond lengths upon changing from the dicarbonyl complexes to the monocarbonyl phosphine complexes. Thus, the average Fe–C(CO) bond length for the six Fe–CO groups in the dicarbonyl complexes Ia, IIa, and IIIa is 1.743 (6) Å compared to an average value of 1.719 (4) Å for the monocarbonyl phosphine complexes. These data reflect the increase in retrodative π-bonding in the phosphine complex, thereby increasing the contribution of the resonance structure Fe=C=O to the iron carbonyl group. At the same time, it is possible to observe a corresponding small elongation in the C–O bond lengths of the phosphine-substituted complexes. Overall, the decrease in ν(CO), decrease in Fe–C(CO) bond length, and increase in C–O bond length support the idea of increased retrodative π-bonding between the CO group and Fe in the phosphine-substituted complexes Ib, IIb, and IIIb.

The same variations with respect to the Fe–Si bond logically could be expected if there is any significant π-bonding between the Fe and Si atoms. We have not attempted to characterize ν(FeSi); thus, infrared spectroscopic analysis of this bond is not yet possible. Previous studies of the ν(CO) stretching frequencies of (η^5-C_5H_5)-$Fe(CO)_2$–silyl complexes, coupled with a Mössbauer spectroscopic study, concluded that no π-bonding occurred between the Fe and Si atoms in the dicarbonyl complexes.[12] The ^{29}Si NMR data of the same complexes supported this conclusion but suggested that substitution of CO by PPh_3 could provide a system where π-bonding becomes significant.[10]

In a structural study of two Ta–silyl complexes, [(η^5-C_5Me_5)$Ta(SiMe_3)Cl_3$] and [(η^5-C_5Me_5)$Ta(SiMe_3)(PPh_3)$-Cl_2], i.e., Ta(V) and Ta(IV) complexes, the two Ta–Si bond distances were reported as 2.669 (4) and 2.642 (1) Å, respectively.[13] This significant reduction of at least 0.01 Å in changing from the d^0 to d^1 metal configuration was cited as being possibly due to some degree of π-bonding between the Ta(IV) metal center and silicon. While there are several Fp–silyl complexes whose structures have been reported, they do not provide information concerning the involvement of π-bonding in the Fe–Si bond. However, the following conclusions may be noted.

(a) The presence of electron-withdrawing substituents on silicon sharply reduces the Fe–Si bond length. The complex Fp–$SiCl_3$ exhibits the shortest Fe–Si bond length (2.215 Å),[4e] while 1-Fp and 1,5-$(Fp)_2$ complexes of 1,3,3,5,5-pentachloro- and 1,3,3,5-tetrachloro-1,3,5-trisilacyclohexane exhibit Fe–Si bond lengths of 2.264 and 2.363

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Table III. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
(a) Compound Ia									
Fe	−83 (1)	229 (1)	2542 (1)	48 (1)	C(6)	710 (6)	1889 (6)	2118 (5)	58 (3)
Si	−57 (2)	−1873 (1)	2572 (1)	54 (1)	C(7)	1140 (6)	811 (6)	1730 (5)	66 (3)
O(1)	−1398 (4)	−24 (4)	4081 (3)	78 (2)	C(8)	1900 (6)	113 (7)	2625 (6)	76 (3)
O(2)	−2503 (5)	−5 (5)	676 (4)	94 (2)	C(9)	1841 (6)	668 (6)	3558 (5)	67 (3)
C(1)	1166 (6)	1793 (6)	3257 (5)	61 (3)	C(10)	−872 (5)	79 (5)	3468 (4)	50 (2)
C(2)	873 (7)	2757 (8)	3853 (6)	79 (4)	C(11)	−1548 (7)	88 (5)	1422 (5)	58 (3)
C(3)	206 (8)	3731 (8)	3318 (8)	93 (5)	C(12)	−1654 (6)	−2570 (6)	2536 (6)	80 (3)
C(4)	−234 (7)	3815 (6)	2198 (7)	86 (4)	C(13)	246 (7)	−2488 (6)	1369 (5)	81 (3)
C(5)	−27 (7)	2909 (6)	1595 (6)	71 (3)	C(14)	1270 (6)	−2457 (6)	3826 (5)	77 (3)
(b) Compound Ib									
Fe(1)	992 (1)	2858 (1)	1016 (1)	42 (1)	Fe(2)	−2710 (1)	3283 (1)	5568 (1)	41 (1)
P(1)	1441 (1)	2387 (1)	−224 (1)	38 (1)	P(2)	−1756 (1)	2039 (1)	5266 (1)	41 (1)
Si(1)	2955 (1)	2807 (1)	1680 (1)	51 (1)	Si(2)	−2595 (1)	3696 (1)	4359 (1)	56 (1)
O(1)	465 (3)	1070 (2)	1251 (2)	70 (1)	O(2)	−5178 (3)	2476 (2)	4840 (2)	81 (1)
C(1)	−372 (4)	3790 (2)	746 (2)	56 (1)	C(32)	−2065 (3)	3623 (2)	6844 (2)	51 (1)
C(2)	−1163 (5)	3753 (3)	51 (2)	75 (2)	C(33)	−1790 (4)	3054 (3)	7340 (2)	68 (2)
C(3)	−2360 (5)	3329 (3)	−22 (3)	93 (2)	C(34)	−2714 (5)	2789 (3)	7760 (2)	83 (2)
C(4)	−2826 (4)	2896 (3)	544 (3)	91 (2)	C(35)	−3950 (5)	3050 (3)	7698 (2)	81 (2)
C(5)	−2097 (4)	2896 (3)	1206 (3)	77 (2)	C(36)	−4283 (4)	3566 (3)	7198 (2)	65 (2)
C(6)	−853 (3)	3367 (2)	1330 (2)	55 (1)	C(37)	−3313 (3)	3882 (2)	6759 (2)	48 (1)
C(7)	87 (4)	3542 (3)	1976 (2)	65 (2)	C(38)	−3294 (3)	4470 (2)	6234 (2)	54 (1)
C(8)	1109 (4)	4105 (3)	1807 (2)	68 (2)	C(39)	−2025 (4)	4623 (2)	6043 (2)	62 (1)
C(9)	870 (4)	4219 (2)	1038 (2)	64 (2)	C(40)	−1274 (3)	4084 (2)	6371 (2)	57 (1)
C(10)	696 (3)	1786 (2)	1148 (2)	48 (1)	C(41)	−3275 (4)	2896 (3)	3403 (2)	80 (2)
C(11)	4208 (4)	3757 (3)	1670 (3)	77 (2)	C(42)	−943 (4)	4053 (3)	4126 (2)	85 (2)
C(12)	2731 (4)	2858 (3)	2760 (2)	76 (2)	C(43)	−3532 (5)	4669 (3)	4355 (3)	108 (2)
C(13)	3812 (4)	1777 (3)	1390 (2)	70 (2)	C(44)	−2529 (3)	1093 (2)	5611 (2)	47 (1)
C(14)	1908 (3)	3279 (2)	−731 (2)	41 (1)	C(45)	−2152 (4)	230 (2)	5391 (2)	63 (1)
C(15)	3037 (3)	3835 (2)	−460 (2)	58 (1)	C(46)	−2734 (4)	−462 (2)	5661 (3)	75 (2)
C(16)	3446 (4)	4499 (2)	−837 (2)	69 (2)	C(47)	−3709 (4)	−319 (3)	6154 (3)	77 (2)
C(17)	2735 (4)	4636 (3)	−1466 (2)	71 (2)	C(48)	−4099 (4)	520 (3)	6371 (2)	75 (2)
C(18)	1591 (4)	4120 (2)	−1714 (2)	69 (2)	C(49)	−3518 (3)	1230 (2)	6100 (2)	55 (1)
C(19)	1195 (3)	3448 (2)	−1349 (2)	56 (1)	C(50)	−88 (3)	2122 (2)	5663 (2)	45 (1)
C(20)	103 (3)	1702 (2)	−862 (2)	39 (1)	C(51)	798 (3)	2769 (2)	5500 (2)	58 (1)
C(21)	194 (3)	1356 (2)	−1669 (2)	51 (1)	C(52)	2062 (4)	2832 (3)	5771 (3)	75 (2)
C(22)	−804 (4)	809 (2)	−2124 (2)	61 (1)	C(53)	2470 (4)	2266 (3)	6209 (3)	80 (2)
C(23)	−1898 (3)	571 (2)	1793 (2)	57 (1)	C(54)	1620 (4)	1640 (3)	6394 (2)	75 (2)
C(24)	−1994 (3)	896 (2)	−1005 (2)	57 (1)	C(55)	340 (3)	1563 (3)	6119 (2)	61 (1)
C(25)	−1011 (3)	1463 (2)	−542 (2)	46 (1)	C(56)	−1661 (3)	1474 (2)	4224 (2)	45 (1)
C(26)	2636 (3)	1593 (2)	−511 (2)	41 (1)	C(57)	−2738 (4)	967 (2)	3815 (2)	62 (1)
C(27)	2379 (3)	728 (2)	−408 (2)	50 (1)	C(58)	−2737 (4)	566 (3)	3023 (2)	71 (2)
C(28)	3225 (4)	88 (2)	−637 (2)	60 (1)	C(59)	−1666 (5)	654 (3)	2631 (2)	74 (2)
C(29)	4324 (4)	312 (3)	−967 (2)	66 (2)	C(60)	−592 (4)	1138 (3)	3027 (2)	73 (2)
C(30)	4571 (4)	1152 (3)	−1079 (3)	75 (2)	C(61)	−572 (3)	1547 (2)	3826 (2)	59 (1)
C(31)	3732 (3)	1789 (2)	−860 (2)	62 (1)	C(62)	−4175 (3)	2785 (2)	5129 (2)	51 (1)
(c) Compound IIa									
Fe	787 (1)	1705 (1)	930 (1)	46 (1)	C(7)	3215 (8)	2037 (6)	838 (2)	68 (3)
Si(1)	340 (2)	2203 (1)	1627 (1)	52 (1)	C(8)	2255 (10)	2862 (6)	846 (3)	76 (3)
Si(2)	−1095 (2)	3628 (1)	1687 (1)	60 (1)	C(9)	1145 (8)	2833 (5)	522 (2)	61 (2)
O(1)	−2669 (7)	1625 (4)	832 (2)	89 (2)	C(10)	−1289 (9)	1657 (5)	870 (2)	60 (3)
O(2)	1231 (8)	−111 (4)	1314 (2)	104 (3)	C(11)	1039 (9)	599 (5)	1169 (2)	67 (3)
C(1)	1441 (8)	2000 (5)	276 (2)	55 (2)	C(12)	2269 (11)	2316 (7)	1922 (3)	97 (4)
C(2)	732 (9)	1618 (6)	−90 (2)	76 (3)	C(13)	−872 (11)	1333 (6)	1944 (3)	93 (4)
C(3)	1339 (10)	799 (6)	−253 (2)	77 (3)	C(14)	−705 (13)	4496 (6)	1265 (3)	116 (5)
C(4)	2562 (9)	320 (6)	−50 (3)	78 (3)	C(15)	−667 (14)	4178 (7)	2204 (3)	111 (4)
C(5)	3267 (9)	645 (5)	306 (2)	67 (3)	C(16)	−3254 (10)	3327 (8)	1689 (4)	122 (5)
C(6)	2736 (7)	1510 (4)	479 (2)	49 (2)					
(d) Compound IIb									
Fe	3017 (1)	910 (1)	905 (1)	39 (1)	C(11)	3769 (3)	−641 (4)	2337 (2)	60 (1)
P	2520 (1)	2946 (1)	704 (1)	38 (1)	C(12)	3432 (3)	2157 (4)	2571 (2)	57 (1)
Si(1)	2959 (1)	759 (1)	2012 (1)	44 (1)	C(13)	573 (4)	−587 (6)	1804 (3)	95 (2)
Si(2)	1498 (1)	314 (1)	2363 (1)	59 (1)	C(14)	1703 (5)	−695 (6)	3105 (3)	105 (3)
O	4877 (2)	1811 (3)	1397 (1)	63 (1)	C(15)	936 (4)	1854 (5)	2573 (3)	95 (2)
C(1)	2317 (3)	87 (4)	−36 (2)	50 (1)	C(16)	3145 (2)	3862 (3)	149 (2)	46 (1)
C(2)	2002 (3)	680 (4)	−635 (2)	56 (1)	C(17)	3756 (2)	3199 (4)	−191 (2)	49 (1)
C(3)	2587 (4)	695 (4)	−1082 (2)	72 (2)	C(18)	4225 (3)	3900 (5)	−625 (2)	63 (2)
C(4)	3492 (3)	181 (5)	−955 (2)	69 (2)	C(19)	4077 (3)	5237 (5)	−702 (2)	68 (2)
C(5)	3821 (3)	−369 (4)	−377 (2)	57 (1)	C(20)	3486 (3)	5874 (4)	−368 (2)	67 (2)
C(6)	3238 (3)	−439 (3)	95 (2)	52 (1)	C(21)	3027 (3)	5205 (4)	49 (2)	58 (1)
C(7)	3325 (3)	−1049 (3)	715 (2)	57 (1)	C(22)	2608 (3)	4176 (3)	1347 (2)	42 (1)
C(8)	2459 (3)	−967 (3)	935 (2)	58 (1)	C(23)	3480 (3)	4674 (3)	1592 (2)	50 (1)
C(9)	1844 (3)	−205 (4)	509 (2)	53 (1)	C(24)	3595 (3)	5576 (4)	2091 (2)	60 (1)
C(10)	4122 (3)	1452 (3)	1192 (2)	46 (1)	C(25)	2842 (3)	5963 (3)	2364 (2)	61 (2)

Table III (Continued)

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
				(d) Compound IIb					
C(26)	1977 (3)	5489 (4)	2135 (2)	60 (2)	C(30)	131 (3)	3636 (5)	−571 (2)	71 (2)
C(27)	1845 (3)	4602 (3)	1625 (2)	52 (1)	C(31)	−541 (3)	3117 (5)	−260 (3)	80 (2)
C(28)	1304 (2)	3079 (3)	322 (2)	48 (1)	C(32)	−321 (3)	2573 (5)	339 (3)	80 (2)
C(29)	1048 (3)	3620 (4)	−284 (2)	57 (1)	C(33)	617 (3)	2530 (4)	631 (2)	62 (1)
				(e) Compound IIIa					
Fe	2000 (1)	783 (1)	1627 (1)	54 (1)	C(7)	2377 (4)	3071 (6)	1502 (3)	76 (2)
Si(1)	2657 (1)	31 (2)	2852 (1)	55 (1)	C(8)	3139 (3)	2128 (7)	1515 (3)	82 (2)
Si(2)	4008 (1)	−1412 (2)	2883 (1)	72 (1)	C(9)	2975 (3)	1082 (7)	929 (3)	85 (2)
Si(3)	2902 (1)	2058 (2)	3725 (1)	76 (1)	C(10)	1820 (3)	−1172 (7)	1465 (3)	71 (2)
O(1)	1675 (3)	−2470 (5)	1336 (2)	103 (2)	C(11)	1021 (3)	1080 (6)	2029 (3)	67 (2)
O(2)	362 (2)	1303 (5)	2267 (2)	101 (2)	C(12)	1878 (3)	−1357 (7)	3273 (3)	85 (2)
C(1)	2109 (3)	1450 (6)	487 (2)	69 (2)	C(13)	4553 (4)	−1706 (9)	3871 (3)	132 (3)
C(2)	1586 (4)	813 (7)	−175 (3)	95 (2)	C(14)	4866 (3)	−576 (8)	2351 (4)	110 (3)
C(3)	753 (4)	1437 (9)	−434 (3)	102 (3)	C(15)	3719 (4)	−3346 (7)	2463 (4)	108 (3)
C(4)	409 (4)	2643 (9)	−76 (3)	102 (3)	C(16)	4041 (4)	3010 (8)	3759 (3)	114 (3)
C(5)	855 (4)	3287 (7)	550 (3)	85 (2)	C(17)	2861 (5)	1250 (8)	4675 (3)	128 (3)
C(6)	1735 (3)	2685 (6)	850 (2)	65 (2)	C(18)	1994 (4)	3559 (8)	3559 (3)	111 (3)
				(f) Compound IIIb					
Fe	946 (1)	2023 (1)	1010 (1)	45 (1)	C(16)	−630 (4)	3628 (3)e	−1272 (2)	79 (2)
P	2253 (1)	1996 (1)	151 (1)	48 (1)	C(17)	−2382 (3)	2542 (3)	−743 (3)	86 (2)
Si(1)	19 (1)	3172 (1)	728 (1)	48 (1)	C(18)	1684 (3)	1494 (2)	−747 (2)	48 (1)
Si(2)	−1400 (1)	3336 (1)	−424 (1)	58 (1)	C(19)	649 (3)	1757 (2)	−1201 (2)	61 (2)
Si(3)	−1024 (1)	3532 (1)	1779 (1)	66 (1)	C(20)	116 (4)	1394 (3)	−1857 (3)	70 (2)
O	2509 (3)	2872 (2)	2138 (2)	87 (1)	C(21)	585 (4)	754 (3)	−2072 (3)	71 (2)
C(1)	660 (3)	825 (2)	967 (2)	52 (1)	C(22)	1583 (4)	474 (2)	−1629 (3)	72 (2)
C(2)	1424 (4)	249 (2)	805 (3)	66 (2)	C(23)	2154 (3)	842 (2)	−970 (2)	58 (2)
C(3)	2155 (4)	−60 (3)	1410 (3)	85 (2)	C(24)	2890 (3)	2830 (2)	−216 (3)	56 (2)
C(4)	2191 (4)	187 (3)	2179 (3)	88 (2)	C(25)	2674 (4)	3061 (2)	−993 (3)	73 (2)
C(5)	1492 (4)	748 (3)	2366 (3)	74 (2)	C(26)	3213 (5)	3689 (3)	−1216 (4)	100 (3)
C(6)	681 (3)	1067 (2)	1753 (2)	55 (2)	C(27)	3951 (5)	4085 (3)	−678 (5)	113 (3)
C(7)	−220 (3)	1615 (2)	1755 (2)	61 (2)	C(28)	4176 (4)	3861 (3)	82 (4)	100 (3)
C(8)	−838 (3)	1675 (2)	978 (2)	58 (2)	C(29)	3655 (4)	3241 (2)	318 (3)	75 (2)
C(9)	−262 (3)	1224 (2)	487 (2)	55 (1)	C(30)	3697 (3)	1560 (2)	514 (2)	55 (2)
C(10)	1884 (3)	2532 (2)	1675 (2)	56 (2)	C(31)	4593 (3)	1490 (2)	31 (3)	71 (2)
C(11)	1029 (3)	3993 (2)	660 (3)	67 (2)	C(32)	5698 (4)	1198 (3)	305 (4)	94 (2)
C(12)	−1341 (4)	4533 (2)	1733 (3)	92 (2)	C(33)	5940 (5)	991 (3)	1071 (4)	108 (3)
C(13)	−2497 (4)	3057 (3)	1795 (3)	95 (2)	C(34)	5093 (4)	1064 (3)	1565 (3)	96 (2)
C(14)	−121 (5)	3413 (3)	2762 (3)	107 (3)	C(35)	3970 (3)	1341 (2)	1285 (3)	66 (2)
C(15)	−2460 (4)	4097 (3)	−274 (3)	87 (2)					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Å, respectively, illustrating the capacity of an extra Cl atom to decrease the Fe–Si bond.[4a]

(b) For the complexes that contain a Si–Si bond in the α-position, i.e. Fp–Si–Si, the bond is elongated compared to that in the corresponding Me–Si–Si compound.[4b,h]

Close examination of the various Fe–Si bond lengths in complexes Ia,b–IIIa,b provides no evidence for Fe–Si π-bonding in the phosphine-substituted complexes. In each of the pairs of complexes characterized by X-ray analysis the Fe–Si bond is significantly *longer* in the phosphine-substituted complex: 2.325 (3) Å (Ia) vs 2.339 (1) Å (Ib); 2.341 (2) Å (IIa) vs 2.354 (2) Å (IIb); 2.365 (2) Å (IIIa) vs 2.378 (1) Å (IIIb). This clear trend is exactly *opposite* to that expected if any appreciable π-bonding were present and is evidence for the lack of significance of such retrodative bonding in these Fe–Si bonds. The data are, however, very clear in suggesting that simple steric factors are primarily the cause of the varying Fe–Si bonds. For the dicarbonyl complexes, the Fe–Si bond length increases regularly in the order of increasing silyl group bulk, Ia → IIa → IIIa, with an increasing incremental change, 0.015 Å between Ia and IIa and 0.024 Å between IIa and IIIa. A similar Fe–Si bond length increase is observed for the phosphine-substituted complexes, Ib → IIb → IIIb, with the same incremental changes of 0.015 and 0.024 Å as the overall bulk of the complexes increases. The values for the Fe–Si bond length in Ia, IIa, and IIIa are in the "normal" range thus far noted for such complexes and compare to values of 2.349 Å for $c\text{-}Si_5Me_9SiMe_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (IV) and 2.363 Å for $c\text{-}Si_5Me_8[(\eta^5\text{-}C_5H_5)Fe(CO)_2]SiMe_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (V) (ring-bonded Fp group)[4b] and the longest bond of this type reported to date of 2.378 Å for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2Si_2Me_4$ (VI).[14] The essential equivalence of the Fe–Si bond lengths in IIIa and V reflects the similarity in the immediate environment of the Fe–Si linkage in both complexes, i.e. Fe–Si(Si)$_2$.

Other aspects of the structural parameters of the various silyl groups reflect the trend of increasing size on changing from I → II → III and from the dicarbonyl complexes to the carbonyl phosphine complexes. Thus, the bond angle Fe–Si–Si changes from 114.6 (1) and 113.3 (1)° (114.6 (1)°) for IIa and IIIa, respectively, to 119.0 (1) and 120.3 (3)° (109.9 (1)°) for the phosphine-substituted counterparts IIb and IIIb. The silyl groups β with respect to the Fe atom thus are observed to be pushed away from the metal center upon phosphine coordination. The angle Fe–Si(1)–Si(2) in complex IIIb is 120.3 (1)° as compared to a value of 109.9 (1)° for the related Fe–Si(1)–Si(3) angle. The former trimethylsilyl group, $Me_3Si(2)$, points directly toward the

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Table IV. Relevant Bond Distances (Å) and Angles (deg)

	Ia	Ib[a]	IIa	IIb	IIIa	IIIb
			Bond Distances			
Fe-Si	2.325 (3)	2.339 (1)	2.341 (2)	2.354 (2)	2.365 (2)	2.378 (1)
		2.341 (1)				
Fe-C*[b]	1.739 (7)	1.721 (4)	1.742 (8)	1.718 (4)	1.739 (6)	1.718 (4)
	1.742 (6)	1.723 (3)	1.758 (8)		1.743 (5)	
Fe-P		2.207 (1)		2.210 (1)		2.220 (1)
		2.215 (1)				
C-O	1.147 (7)	1.163 (5)	1.16 (1)	1.175 (4)	1.166 (8)	1.167 (5)
	1.155 (8)	1.161 (4)	1.120 (9)		1.146 (6)	
Si-Si			2.361 (3)	2.393 (2)	2.361 (2)	2.377 (1)
					2.354 (2)	2.378 (1)
Si[c]-C			1.886 (9)	1.906 (4)	1.910 (6)	1.904 (4)
			1.866 (9)	1.907 (4)		
Si[d]-C	1.869 (7)	1.894 (4)	1.85 (1)	1.886 (6)	1.856 (6)	1.877 (5)
	1.874 (8)	1.888 (4)	1.846 (9)	1.848 (6)	1.859 (7)	1.873 (5)
	1.877 (6)	1.878 (4)	1.848 (9)	1.858 (6)	1.868 (6)	1.867 (5)
		1.895 (4)			1.878 (6)	1.879 (5)
		1.877 (4)			1.862 (6)	1.870 (5)
		1.870 (5)			1.868 (7)	1.856 (4)
Fe-η^5 centroid	1.753	1.774	1.747	1.785	1.744	1.779
			Bond Angles			
C*-Fe-C*	94.3 (3)		97.5 (3)		95.6 (2)	
P-Fe-C*		93.3 (1)		91.6 (1)		93.2 (1)
		94.7 (1)				
C*-Fe-Si	84.2 (2)	83.1 (1)	87.6 (2)	80.9 (1)	85.2 (2)	81.8 (1)
	85.8 (2)	81.3 (1)	83.4 (3)		84.4 (1)	
P-Fe-Si		100.8 (1)		101.1 (1)		101.2 (1)
		98.3 (1)				
Fe-Si-Si			114.6 (1)	119.0 (1)	113.3 (1)	120.3 (1)
					114.6 (1)	109.9 (1)
Si-Si-Si					109.9 (1)	104.8 (1)
C-Si-Fe	114.0 (2)	115.2 (1)	111.1 (3)	107.1 (1)	111.0 (1)	118.3 (1)
	110.7 (2)	109.6 (1)	112.8 (3)	120.1 (1)		
	111.1 (2)	119.0 (1)				
Si-Si[c]-C			108.8 (3)	106.0 (2)	102.7 (2)	100.4 (1)
			104.4 (3)	101.7 (1)	104.4 (2)	100.6 (1)
			115.2 (3)	118.7 (2)	109.8 (2)	110.0 (1)
			109.7 (3)	109.1 (2)	115.4 (2)	111.0 (1)
			107.1 (3)	111.0 (2)	109.2 (2)	116.2 (1)
					113.3 (2)	110.6 (2)
					108.0 (2)	114.1 (2)
					112.6 (2)	113.3 (2)
C-Si[c]-C			104.5 (4)	100.8 (2)		
C-Si[d]-C	105.8 (3)	105.8 (2)	108.8 (4)	105.6 (3)	108.5 (3)	105.2 (2)
	106.2 (3)	103.7 (2)	109.2 (4)	105.2 (3)	107.7 (3)	105.6 (2)
	108.9 (3)	102.0 (2)	106.5 (5)	106.6 (3)	106.0 (3)	108.2 (2)
		102.9 (2)			107.2 (3)	107.4 (2)
		100.7 (2)			108.8 (3)	103.3 (2)
		106.1 (2)			106.6 (3)	107.5 (2)

[a] Two molecules per asymmetric unit. [b] C* = carbonyl C atom. [c] Si atom in α-position to Fe. [d] Terminal Si atom.

Table V. Chemical Shift Difference, $\Delta\delta = \delta(LMSi_n) - \delta(MeSi_n)$

	$LMSi_n$	Si_α	Si_β
Ia	$(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_3$	47.5	
Ib	$(\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)SiMe_3$	41.7	
IIa	$(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_2SiMe_3$	44.6	7.6
IIb	$(\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)SiMe_2SiMe_3$	37.4	9.5
IIIa	$(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe(SiMe_3)_2$	35.9	7.4
IIIb	$(\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)SiMe(SiMe_3)_2$	28.1	8.9

phosphine ligand, while $Me_3Si(3)$ is directed away from the bulky ligand. The various Si–Si bond lengths also exhibit a significant increase as a function of the substitution of CO by PPh_3. In the case of IIa and IIIa the Si–Si bonds are 2.361 (3) and 2.354 (2) Å (2.361 (2) Å), respectively; i.e., the bond lengths are equivalent. Substitution of the CO by PPh_3 lengthens these bonds to 2.393 (2) (IIb) and 2.377 (2) Å (2.378 (2) Å) (IIIb). There is no simple relationship to these various bond lengths, and certainly they do not change in the same incremental fashion as the Fe–Si bonds in the series I–III. The problem of variation of Si–Si bond lengths in transition-metal complexes is currently under investigation in our laboratories.

It is instructive to study the various geometrical considerations relating to the η^5-indenyl ligand in the complexes Ia,b–IIIa,b. The various ring bond lengths and angles of the indenyl group itself do not alter significantly; however, the distance between the Fe atom and the center of the η^5 ring does show interesting variations among the complexes. For the three dicarbonyl complexes Ia–IIIa, this distance averages 1.747 (6) Å, while in the phosphine-substituted complexes Ib–IIIb, this value increases to 1.780 (6) Å. This change reflects the steric bulk of the complexes and reinforces the idea that it is such steric features that dominate the structural aspects of the six complexes studied. The coordination of the η^5 ring to Fe is asymmetric in all cases, exhibiting the previously observed "slipfold" distortion for π-indenyl ligands, in which the Fe atom shifts away from the central C–C bond of the indenyl group; the three Fe–C bond lengths to the outside C atoms are between 0.16 and 0.10 Å shorter than those to the central C atoms.[14] As the overall bulk around the Fe atom increases, this distortion increases; in Ia the av-

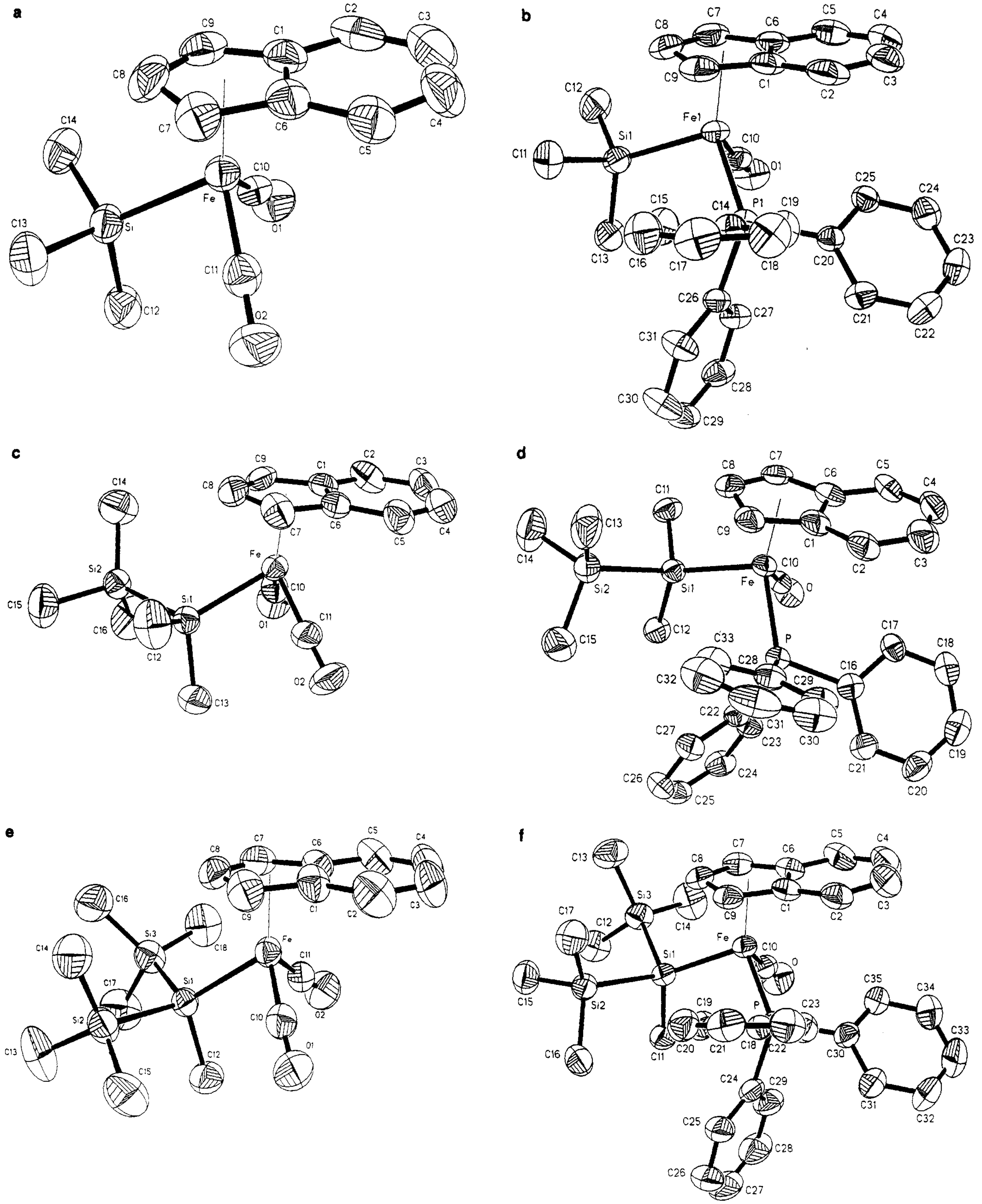

Figure 1. Structures of the (η^5-C_9H_7)Fe(CO)(L)–oligosilane complexes: (a) (η^5-C_9H_7)Fe$(CO)_2$$SiMe_3$ (Ia); (b) (η^5-C_9H_7)Fe(CO)(PPh_3)$SiMe_3$ (Ib); (c) (η^5-C_9H_7)Fe$(CO)_2$$SiMe_2SiMe_3$ (IIa); (d) (η^5-C_9H_7)Fe(CO)(PPh_3)$SiMe_2SiMe_3$ (IIb); (e) (η^5-C_9H_7)Fe$(CO)_2$SiMe$(SiMe_3)_2$ (IIIa); (f) (η^5-C_9H_7)Fe(CO)(PPh_3)SiMe$(SiMe_3)_2$ (IIIb).

erage difference between the inner and outer Fe–C bond lengths is 0.096 Å, while in the bulkiest of the new complexes, IIIb, this has increased significantly to 0.13 Å. The fold angles, i.e. the angle between the planes of the allyl group and the six-membered ring of the η^5-indenyl group, vary from 3.9 to 11.1°. There are no clear trends except that substitution of a CO group by PPh_3 significantly increases these angles: Ia, 6.7°; Ib, 8.5°; IIa, 3.9°; IIb, 11.1°; IIIa, 3.2°; IIIb, 8.9°. In all cases the phenyl ring points away from the coordinated metal atom, which is displaced from the center of the η^5 ring by between 0.1 and 0.2 Å: Ia, 0.10 Å; Ib, 0.15 Å; IIa, 0.12 Å; IIb, 0.18 Å; IIIa, 0.07 Å;

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IIIb, 0.15 Å. These distortions are in line with those noted for other η^5-indenyl complexes and show a distinct increase upon phosphine substitution.[14b,c] Finally, it is noteworthy that the phenyl portion of the indenyl group always points away from the silyl group, even when this means it must be close to the bulky PPh_3 ligand. It seems that the silyl or methyl groups on the Fe-bonded silicon pose a greater steric impediment than the phenyl groups of the phosphine ligand. This is perhaps not surprising due to the capacity of the phenyl groups of the phosphine to take on a propeller type conformation, permitting a type of intercalation of the planar indenyl phenyl region.

A final example of the dominant steric factors in the phosphine complexes is the slight elongation of the Fe–P bonds on changing from Ib (2.207 (1) Å) to IIb (2.210 (1) Å) to IIIb (2.220 (1) Å).

In summary, the data presented in this study suggest that the role of π-bonding between the Fe and Si atoms in complexes of the type $(\eta^5\text{-}C_9H_7)Fe(CO)(L)$–silyl (L = CO, PPh_3) is minimal. The "expected" shortening of the Fe–Si bond upon replacement of CO by PPh_3 is not apparent. Of the three ligands involved in the complexes upon substitution of a CO ligand by PPh_3, only the CO ligand exhibits any bond length contraction expected for increased π-bonding with the metal atom. Both the silyl and η^5-indenyl groups exhibit bond length increases, reflecting the steric changes occurring. The changes in the Fe–Si bond lengths are similar for the dicarbonyl and carbonyl phosphine complexes upon changing from $SiMe_3$ to Si_2Me_5 to 2-Si_3Me_7. It is of course possible that any π-bonding is being overwhelmed by the increasing steric demand of the silyl and phosphine ligands at the iron atom. Further, it is possible that the Fe–Si bond lengths already are short in the $(\eta^5\text{-}C_9H_7)Fe(CO)_2$ system due to π-bonding and, therefore, increases in such bonding due to the phosphine substitution are not significant. Structural analysis of complexes involving smaller phosphine ligands may provide evidence to reinforce, or counter, the first possibility, while previous spectroscopic results would seem to rule out the second.[10,12]

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Supplementary Material Available: Tables of crystal data, complete bond lengths and bond angles, anisotropic thermal parameters, and H atom parameters for Ia,b, and IIa,b, and IIIa,b (45 pages); listings of observed and calculated structure factors (85 pages). Ordering information is given on any current masthead page.

Solid-State Structure and Dynamics of a Chiral Metallacyclic (Zirconoxycarbene)tungsten Complex

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The reaction of the (π-allyl)zirconoxycarbene complex $Cp_2ZrOC[{=}W(CO)_5]CH_2C_3H_4$ (**3a**) with pinacolone affords the chiral nine-membered metallacyclic carbene complex $Cp_2Zr(OC[{=}W(CO)_5]CH_2CH{=}CHCH_2CMe(CMe_3)O)$ (**5**), featuring a trans C=C double bond in the ring. In solution only one diastereoisomer is detected, being characterized by *relative* configurations of R^* and p-S^* at the chiral center and at the adjacent planar chirality element within the ring system, respectively. In contrast, the diastereomer **5′**, having relative configurations R^* and p-R^*, is detected as a minor component of the **3a**/pinacolone addition product in the solid state by ^{13}C CP/MAS NMR spectroscopy. Complex **5** crystallizes in space group $P\bar{1}$ with cell parameters a = 8.447 (2) Å, b = 11.257 (3) Å, c = 15.224 (3) Å, α = 102.78 (2)°, β = 103.16 (2)°, γ = 99.69 (2)°, and Z = 2. Temperature-dependent ^{13}C CP/MAS NMR spectroscopy revealed hindered rotation of the W=C(carbene) bond of **5** in the crystalline state ($\Delta G^{\ddagger}_{rot}(350\ K) \approx 16.5$ kcal/mol). The corresponding nine-membered metallacyclic (zirconoxycarbene)tungsten complex $Cp_2Zr(OC[{=}W(CO)_5]CH_2CH{=}CHCH_2CMe_2O)$ (**4**), formed by treatment of **3a** with 1 molar equiv of acetone, exhibits a W=C(carbene) rotational barrier of $\Delta G^{\ddagger}_{rot}(260\ K) \approx 13.5$ kcal/mol in the solid state.

Introduction

Metaloxycarbene complexes are obtained by reacting (η^2-olefin) metallocene type reagents with metal carbonyls.[1] Typically, treatment of $L_nM(CO)_m$ compounds with an equilibrium mixture of (*s-cis*-butadiene)- and (*s-trans*-butadiene)zirconocene at 25 °C affords the corresponding (π-allyl)zirconoxycarbene complexes in good yield.[2] Zirconoxycarbene complexes such as $(C_5H_4R)_2Zr(OC[{=}W(CO)_5]CH_2C_3H_4)$ (**3a**, R = H; **3b**, R = CH_3) further react with ketones,[3] aldehydes,[4a] and nitriles[4b] by means of CC

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