Transition-metal Silacyclohexyl Derivatives. Crystal and Molecular Structure of Carbonyl(η-cyclopentadienyl)(1-phenyl-1-silacyclohex-1-yl)-(triphenylphosphine)iron(II)†

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Synthesis of transition-metal silacyclohexyl complexes (1-metallo-1-silacyclohexanes) is reported *via* two established preparative routes: (a) reaction of 1-chloro-1-silacyclohexanes with

[Fe(η^5 -C₅H₅)(CO)₂]⁻ to give Si-Fe compounds [Fe(η^5 -C₅H₅)(CO)₂{Si(R²)(CH₂)₄CH₂}] R² = H, (8); R² = Me, (9); R² = Ph (10)] followed by photochemical substitution with PPh₃ to give the corresponding complexes [Fe(η^5 -C₅H₅)(CO)(PPh₃){Si(R²)(CH₂)₄CH₂}] [R² = H, (11); R² = Me, (12); R² = Ph (13)] which are chiral at Fe; (b) hydrosilylation at the metal to give mononuclear complexes [Co(CO)₄{Si(R²)(CH₂)₄CH₂}] [R² = Me, (14); R² = Ph, (15), R² = Cl (16)] and [Mn(CO)₅{Si(R²)(CH₂)₄CH₂}] [R² = Me, (17); R² = Ph (18)] from [Co₂(CO)₈] or [Mn₂(CO)₁₀], binuclear complexes [{M(CO)₄[Si(R²)(CH₂)₄CH₂]₂] [M = Ru, R² = Me, (19), or Ph, (20); M = Os, R² = Me, (21)] with linear Si-M-M-Si skeletons from [Ru₃(CO)₁₂] or [Os₃(CO)₁₂], or [Os(CO)₄{Si(Ph)(CH₂)₄CH₂}] (22). Infrared and ¹H, ¹³C, and ³¹P n.m.r. spectral data are reported, including resolution of diastereotopic shifts in ¹³C n.m.r. spectral for compounds (12) and (13) arising from asymmetry at the iron centre. The crystal and molecular structure of the title compound (13) has been determined using single-crystal X-ray diffraction; the silacyclohexyl substituent adopts a flattened chair conformation with Si-Fe = 2.366(2) Å. Angles at Fe between the three

different unidentate ligands are markedly distorted from 90° [97.2(2), 98.43(6), and 83.2(2)°]; this is interpreted in terms of steric congestion about the asymmetric metal centre and accordingly moderated reactivity of complex (15) towards a variety of reagents is observed compared with $[Co(CO)_4(SiMe_3)]$.

A vast range of complexes in which silicon is bound to a transition metal centre is known.¹ Recently a further subgroup has been characterized the members of which are metallosilacyclobutanes,² attention in these compounds being focused on ring-opening reactions of the strained fourmembered unit occurring in close proximity to a transitionmetal atom and more generally reflecting current interest in metallacycle chemistry. We have investigated the formation of related silacyclohexane derivatives, the rationale being somewhat different: to expand the scope of silacyclohexane chemistry to include structural characterization by X-ray methods of such a molecule incorporating a spatially demanding substituent in the form of a metal-containing fragment; and to investigate the effect on Si⁻M bond reactivity in such an arrangement in relation to that encountered ¹ previously.

The first examples of silacyclohexanes (I) were prepared in 1954 by West ³ and corresponding germanium and tin compounds have subsequently been added to the array of Group 4 element-containing heterocycles.⁴ Stereochemically these molecules have been defined by analogy with the cyclohexane family, assuming a ground-state chair conformation,

Non-S.I. unit employed: $1 \text{ mmHg} \approx 13.6 \times 9.8 \text{ Pa.}$

and it has been reported ⁵ that in 1,1-dimethyl-1-silacyclohexane (I; $R^1 = R^2 = Me$) the barrier to ring inversion is very low, the methyl resonances in ¹H n.m.r. spectra being isochronous at temperatures as low as -150 °C. No compound of type (I) appears to have been structurally characterized although two 1-silacyclohex-3-enes (II, X = Y = Ph; ⁶



 $X = \alpha$ -naphthyl, $Y = F^{7}$) have been the subject of X-ray studies. Included in the present paper are ¹³C n.m.r. data for seven known representatives having structure (I), although the main emphasis here is concerned with the synthesis and spectroscopic properties of fifteen novel examples in which R² is bonded to Si through a transition-metal atom. The latter is a chiral iron centre in three of these complexes, leading to diastereotopic effects discernible in ¹³C n.m.r. spectra, and it is for one such compound [Fe(η -C₅H₅)(CO)(PPh₃)-

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 $^{\{}Si(Ph)(CH_2)_4CH_2\}\$ that an X-ray structure determination has been completed.

Table 1. Calobi-15 II.II.I. data Tol Shacyclohexan	Table 1	m.r. data " for silacy.	clohexane
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	δ/p.p.m.*			
Compound	Cα	Cβ	Сү	C(SiMe)
(1) $Me_2Si(CH_2)_4CH_2$	14.3 "	24.4	30.1	-3.3
(2) Me(Cl) $\dot{Si}(CH_2)_4CH_2$	17.1	23.8	29.5	0.9
(3) Me(Br) $\overset{1}{\text{Si}}(CH_2)_4CH_2$	17.6	24.7	30.2	1.7
(4) $Ph(Cl)Si(CH_2)_4CH_2$	15.8	23.7	29.4	
(5) $Ph(H)Si(CH_2)_4CH_2$	10.4	24.6	25.2	
(6) $Cl(H)Si(CH_2)_4CH_2$	15.4	23.7	29.7	
(7) $Cl_2Si(CH_2)_4CH_2$	20.4	24.1	28.7	

^a CDCl₃ used as solvent and internal reference throughout. ^b High frequency relative to δ 77.2 p.p.m. for CDCl₃ (central component of triplet).

Table 2. Synthesis of silacyclohexyl complexes (8)-(22)

Compound a

supplied by Canadian Microanalytical Service Ltd., Vancouver.

Synthesis of Transition-metal Complexes.—Several representative reactions are described fully below, while preparative details for all the complexes (8)—(22) are summarized in Table 2 and analytical data are presented in Table 3.

(*i*) $[Fe(\eta^{5}-C_{s}H_{s})(CO)_{2}{Si(Ph)(CH_{2})_{4}CH_{2}}]$ (10). 1-Chloro-1phenyl-1-silacyclohexane (3.0 g, 14.3 mmol) was added to a solution of Na[Fe($\eta^{5}-C_{s}H_{s}$)(CO)₂] in tetrahydrofuran (45 cm³) prepared from [{Fe($\eta^{5}-C_{s}H_{s}$)(CO)₂]₂] (4.0 g, 11.3 mmol) and 1% sodium amalgam. After stirring (72 h) the volatiles were removed *in vacuo* and the residue extracted with hexane. Filtration and evaporation of solvent gave a yellow-brown oil. Chromatography (Florisil, 2.5 × 30 cm) with elution with hexane gave first colourless disiloxane (identified by i.r.) and then a pale yellow oil. This was pumped (10⁻² mmHg, 4 d) then warmed *in vacuo* to 30 °C, subliming the pale yellow *product* (1.2 g, 3.76 mmol, 24%) onto a water-cooled probe.

~		R ²	Reactants	Conditions ^b	Yield (%)
(8)	Fe	Н	[{Fe(η^5 -C ₅ H ₅)(CO) ₂ }] (3.0 g, 8.48 mmol); Cl(H)Si(CH ₂),CH ₂ (2.0 g, 8.6 mmol)	(anion); thf, 20 °C, 48 h	15.8
(9)	Fe	Me	[{Fe(η^{5} -C ₃ H ₅)(CO) ₂ } ₂] (4.0 g, 11.3 mmol); Me(Cl)Si(CH ₂) ₄ CH ₂ (2.0 g, 13.5 mmol)	(anion); thf, 20 $^{\circ}$ C, 72 h	21.5
(10)	Fe	Ph	$[\{Fe(n^{5}-C_{5}H_{5})(CO)_{2}\}_{2}]$ (4.0 g, 11.3 mmol); Ph(Cl)Si(CH ₂) ₄ CH ₂ (3.0 g, 14.3 mmol)	(anion); thf, 20 °C, 72 h	23.9
(11)	Fe′	н	(8) (1.99 g, 7.2 mmol); $P(C_6H_5)_3$ (3.4 g, 13.0 mmol)	hexane, 25 °C, u.v., 5 h	21.2
(12)	Fe'	Me	(9) (0.27 g, 0.93 mmol); $P(C_6H_5)_3$ (0.375 g, 1.43 mmol)	hexane, 25 °C, u.v., 3 h	22.5
(13)	Fe'	Ph	(10) (0.317 g, 1.37 mmol); P(C ₆ H ₅) ₃ (0.462 g, 1.76 mmol)	hexane, 25 °C, u.v., 6 h	32.2
(14)	Со	Me	$[Co_2(CO)_8]$ (0.684 g, 2.0 mmol); Me(H)Si(CH ₂) ₄ CH ₂ (0.456 g, 4.0 mmol)	20 °C, 24 h	52.6
(15)	Co	Ph	$[Co_2(CO)_8]$ (0.685 g, 2.0 mmol); Ph(H)Si(CH ₂) ₄ CH ₂ (0.704 g, 4.0 mmol)	20 °C, 18 h	35.8
(16)	Co	Cl	$[Co_2(CO)_8]$ (3.25 g, 9.5 mmol); Cl(H)Si(CH ₂) ₄ CH ₂ (2.56 g, 19.0 mmol)	20 °C, 24 h	46.0
(17)	Mn	Me	$[Mn_2(CO)_{10}]$ (2.0 g, 5.1 mmol); Me(Cl)Si(CH ₂) ₄ CH ₂ (2.0 g, 9.5 mmol)	(anion); thf, 25 °C, 18 h	с
(18)	Mn	Ph	$[Mn_2(CO)_{10}]$ (2.22 g, 5.7 mmol); Ph(H)Si(CH ₂) ₄ CH ₂ (1.94 g, 14.4 mmol)	170 °C, 17 h	67.0
(19)	Ru ^d	Me	$[Ru_3(CO)_{12}]$ (0.090 g, 0.14 mmol); Me(H)Si(CH ₂) ₄ CH ₂ (0.18 g, 1.58 mmol)	130 °C, 15 h	31.8
(20)	Ru ^d	Ph	$[Ru_3(CO)_{12}]$ (0.090 g, 0.14 mmol); Ph(H)Si(CH ₂) ₄ CH ₂ (0.20 g, 1.14 mmol)	130 °C, 8 h	28.6
(21)	Os ^d	Me	$[Os_3(CO)_{12}]$ (0.160 g, 0.18 mmol); Me(H)Si(CH ₂) ₄ CH ₂ (0.20 g, 1.75 mmol)	145 °C, 45 h	28.0
(22)	Os °	Ph	[Os ₃ (CO ₁₂] (0.160 g, 0.18 mmol); Ph(H)Si(CH ₂) ₄ CH ₂ (0.30 g, 1.70 mmol)	145 °C, 12 h	37.0

^{*a*} R¹, R² of structure (I): Fe = Fe(η^5 -C₅H₅)(CO)₂; Fe' = Fe(η^5 -C₅H₅)(CO)(PPh₃); Co = Co(CO)₄; Mn - Mn(CO)₅; Ru = Ru(CO)₄; O_S = O_S(CO)₄. ^{*b*} thf = Tetrahydrofuran. ^{*c*} Yellow oil, contaminated with [Mn₂(CO)₁₀]. ^{*d*} Bis(silacyclohexyl) compound, binuclear structure (III). ^{*e*} Bis(silacyclohexyl) compound, mononuclear structure (IV).

Experimental

Synthetic manipulations were carried out using standard inert atmosphere techniques. Solvents were dried and distilled under dry dinitrogen gas. Infrared spectra were recorded using a Perkin-Elmer 283 spectrometer; ¹H n.m.r. spectra were obtained at 90 MHz using a Perkin-Elmer R32 instrument while Fourier-transform ¹³C and ³¹P data were measured with a Nicolet TT-14 spectrometer operating at 15.09 or 24.3 MHz as appropriate. The compounds (1)—(7) were prepared by the method of West ³ and characterized by i.r., ¹H n.m.r., and ¹³C n.m.r. spectra (Table 1). Microanalytical data were

(*ii*) [Fe(η^{5} -C₅H₅)(CO)(PPh₃){Si(Ph)(CH₂)₄CH₂}] (13). Compound (10) (0.317 g, 1.37 mmol), PPh₃ (0.462 g, 1.76 mmol), and hexane (10 cm³) were cooled *in vacuo* to -196 °C in a quartz tube, sealed, and irradiated with a medium-pressure u.v. lamp (6 h). The reaction mixture was taken up in the minimum of diethyl ether-hexane mixture (1 : 4) from which after 5 h crystallized the orange *product* (0.17 g, 0.44 mmol, 32.2%).

(*iii*) $[Co(CO)_4(\dot{Si}(Me)(CH_2)_4\dot{C}H_2)]$ (14). Octacarbonyldicobalt (0.684 g, 2.0 mmol) was placed in a 100 cm³ two-neck

Table 3. Analytical data

		Analysis	^b (%)			
Compound ^a	Colour	C	H	M.p./°C	$v(CO) c/cm^{-1}$	
(8)	Yellow	52.40 (52.15)	5.80 (5.85)	28	1 948s, 1 998s	
(9)	Yellow	53.85 (53.80)	6.35 (6.20)	Oil	1 935s, 1 995s	
(10)	Yellow	61.75 (61.35)	5.65 (5.75)	75—77	1 941s, 1 997s	
àn	Pale	68.20 (68.25)	6.35 (6.10)	165—167	1 902s	
. ,	yellow					
(12)	Orange	68.45 (68.70)	6.20 (6.30)	139-141	1 903s	
(13)	Red-	71.55 (71.65)	6.05 (5.95)	169—171	1 907s	
	orange					
(14)	White	42.05 (42.25)	4.55 (4.60)	31-32	1 980s, 2 015m, 2 079m	
(15)	White	52.00 (52.00)	4.45 (4.35)	62	1 997s, 2 025m, 2 089m	
(19)	Yellow	36.65 (36.80)	3.90 (4.00)	126	1 969w, 1 992w, 2 016s, 2 041m	
(20)	Yellow	46.55 (46.40)	3.80 (3.85)	135-136	1 991m, 2 007m (sh), 2 015s, 2 041w, 2 051w	
(21)	Yellow	29.45 (28.90)	3.05 (3.15)	147—151	2 013s, 2 053w	
(22)	Yellow	47.55 (47.85)	4.70 (4.60)	112-115	2 010s, 2 041w	

"Numbering key as in Table 2. ^b Calculated values in parentheses. ^c KBr disc.

flask and 1-methyl-1-silacyclohexane (0.456 g, 4.0 mmol) added under an atmosphere of N₂. The mixture was kept at ambient temperature (24 h) after which time volatile material was sublimed *in vacuo* from the reaction mixture to yield the white crystalline *product* (0.60 g, 2.2 mmol, 55%).

(*iv*) [{Ru(CO)₄[Si(Ph)(CH₂)₄CH₂]}₂] (20). Dodecarbonyltriruthenium (0.090 g, 0.14 mmol) was placed in a small reaction tube and 1-phenyl-1-silacyclohexane (0.20 g, 1.14 mmol) syringed into the reaction tube. After evacuation the tube was sealed *in vacuo* and heated at 130 °C (8 h). The resulting yellow mixture was taken up in hexane, the solvent reduced and bright yellow crystals of the *product* (0.047 g, 0.06 mmol, 28.6%) were isolated on cooling to -78 °C.

(v) $[Os(CO)_4{Si(Ph)(CH_2)_4CH_2}_2]$ (22). To dodecarbonyltriosmium (0.16 g, 0.18 mmol) in a small reaction tube was added 1-phenyl-1-silacyclohexane (0.30 g, 1.70 mmol), the tube was evacuated then sealed and heated to 145 °C (12 h). The resulting solid was taken up in pentane and filtered (Florisil column, 10 × 0.7 cm). Removal of solvent *in vacuo* gave a white solid which on recrystallization from pentane at -78 °C afforded the *product* (0.081 g, 0.20 mmol, 37%).

Results and Discussion

The silacyclohexanes (1)-(7) were prepared via reactions of the di-Grignard compound formed by 1,5-dibromopentane according to the procedure described by West.³ These materials were used as precursors to the 1-metallo-1-silacyclohexanes (silacyclohexyl complexes) (8)-(22) by employing two well established ^{1,8} synthetic routes: (a) reaction of the chloro compounds (2), (4), or (6) with an anionic transitionmetal complex {e.g., Na[Fe(η^{5} -C₅H₅)(CO)₂]}, or (b) photochemical or thermal addition of the Si-H bond in (5), (6), or (I, $R^1 = Me$, $R^2 = H$) (hydrosilylation) with a polynuclear metal carbonyl, e.g. $[Co_2(CO)_8]$. Reactions of the second type involving [M₃(CO)₁₂] afforded binuclear products of known ⁹ structural type (III) (when M = Ru); for M = Os from one reaction an osmium analogue of (III) was obtained while the other afforded a carbonylbis(silacyclohexyl)osmium compound (IV) for which a trans geometry has subsequently been identified. Photochemically induced substitution of CO by PPh_3 in the iron complexes (8)—(10) yielded compounds (11)— (12) which ¹⁰ are chiral at the transition-metal atom. With the exception of the pentacarbonylmanganese derivatives for which separation from unreacted starting material was found



to be problematic (parallelling the situation described 2 for silacyclobutyl manganese analogues), the products were isolable as yellow-orange or colourless thermally stable crystalline materials. No decomposition in air was apparent in the solid state although solutions of the complexes appeared to be somewhat air-sensitive.

The dicarbonyliron complexes (8)-(10) each show two strong i.r. absorptions due to v(CO) modes with roughly equal intensity in the 1 935-2 000 cm⁻¹ range. On replacement of one CO group with the poorer π -acceptor, PPh₃, to give (11)-(13), a single band is observed at lower energy (ca. 1 900 cm⁻¹). For the cobalt derivatives (14)—(16) a strong band near 1 990 cm⁻¹ together with two medium-intensity components above 2 000 cm⁻¹ correspond to e and $2a_1$ fundamentals respectively of a Co(CO)₄ unit following predictions based on local C_{3v} symmetry,¹¹ and the data for the manganese compounds can likewise be related to earlier work.^{11,12} The analytical figures for the Ru complexes substantiate the binuclear formulation (III; M = Ru), other examples of which have been extensively investigated by Knox and Stone.¹³ Accordingly for (19) and (20) the i.r. frequencies for v(CO) conform to the pattern identified earlier¹³ and the i.r. spectrum of the carbonylosmium analogue (21) is similar. The single strong i.r. absorption at 2010 cm^{-1} for the mononuclear Os derivative (22) is consistent ¹⁴ with a trans geometry, (IV).

Nuclear magnetic resonance data for the complexes are collected in Table 4 (¹H and ¹³C chemical shifts); compounds (11)---(13) showed singlet ³¹P resonances at -62.8, -60.6, and -60.0 p.p.m. respectively relative to external trimethyl phosphite. The ¹³C parameters may also be compared with those given for compounds (1)---(7) in Table 1. In the proton n.m.r. spectra (90 MHz) the 10 silacyclohexyl ring hydrogens appear as a complex, poorly resolved non-first-order contour consistently in the τ 8--9.2 region. The η^5 -C₅H₅ ring protons for the iron compounds (8)--(13) give rise to sharp re-

		¹ H Chemical shift	(τ) ^{<i>a</i>}	¹³ C Che	mical shift (δ/p.	p.m.) ^ø	
Compound	η ⁵ -C₅H₅	C ₅ H ₁₀	Others	Ca	Cβ	Cγ	C _{Me} ^c
(8)	5.38	7.7-9.0		19.1	28.3	30.3	
(9)	5.21	7.8-9.2	9.95 ^d	21.7	25.8	30.4	2.3
(10)	5.52	8.0-9.2	2.3—2.8 °	19.8	26.2	30.7	
(11)	5.75	7.79.1	2.6–2.9 ^r	20.6	30.0	31.7	
(12)	5.31 ^g	9.0	9.83, ^d	23.0,	26.4	30.8	2.0
			2.6—2.9 ^f	20.9			
(13)	5.92 %	8.39.2	2.6-2.9 e,s	20.6,	26.1	30.5	
				18.1			
(14)		7.8-9.1	9.82 ^d	22.0	26.0	29.6	2.5
(15)		7.9-9.2	2.7—2.9 °	20.0	25.5	29.5	
(16)		7.7-9.0		25.1	26.6	29.2	
(17)		7.8-9.1	2.7-2.9 °				
(18)		7.79.0		24.2	24.7	29.5	
(19)		8.1-9.2	9.55 ^d	22.4	25.7	30.6	3.6
(20)		8.0-9.2	2.6—2.9 °	20.1	25.8	30.6	
(21)		8.09.2	9.47 ⁴	20.8	25.1	29.9	2.7
(22)		8.1-9.1	2.6-2.9	19.1	25.6	30.5	

Table 4. N.m.r. data

^{*a*} CDCl₃ solvent, CH₂Cl₂ internal reference. ^{*b*} High frequency relative to δ (CDCl₃) = 77.2 p.p.m. (central component of triplet). ^{*c*} Carbon atoms of methyl substituent at Si. ^{*d*} Methyl substituent at Si. ^{*e*} Phenyl substituent at silicon. ^{*f*} Phenyl substituent at phosphorus. ^{*g*} Doublet with ³J(PH) = 1.5 Hz.

sonances near τ 5.5, split by coupling to phosphorus (J = 1.5 Hz) in (12) and (13). A slight shift to low field in τ CH₃ in (I; R² = Me) is evident, varying from τ 9.95 (Fe) to 9.47 (Os) with R¹ in the order Fe > Fe' > Co > Ru > Os (see Table 2, footnote *a*).

The ¹³C data are more informative. Tables 1 and 4 illustrate that resonant frequencies for C^{α} , C^{β} , and C^{γ} of the silacyclohexyl ring system are well separated and only C^{α} is substantially influenced by the substituents R^1 and R^2 at Si. The assignment given here agrees with that proposed for the only compound (I) examined previously 15 which is the 1,1-dimethyl (1). Replacement of H at Si by Ph, Me, Cl, and a transition-metal atom results in a shift of C^{α} to high frequency of approximately 0.5, 2.0, 4.2, and 9.3 p.p.m. respectively, and Tables 1 and 4 indicate that these relationships are additive. The differences may be attributed to changes in electron density due to σ -type inductive effects transmitted by the heteroatom, increasing in importance in the order $M(CO)_x \gg Cl > Me > Ph \gg H$. In compounds (12) and (13) the ¹³C resonance assigned to C^{α} is split into two components (see Figure 1), separation 2.1 and 2.5 p.p.m. respectively. These diastereotopic shifts result from magnetic nonequivalence induced by the chirality of the central iron atom; no corresponding splitting of the C^{β} pair was resolved.

Crystal and Molecular Structure of [Fe(n⁵-C₅H₅)(CO)(PPh₃)-

{Si(Ph)(CH₂)₄CH₂] (13).—(*i*) Crystal data. C₃₅H₃₅FeOPSi, M = 586.6, Monoclinic, a = 9.632(4), b = 35.645(9), c = 9.529(4) Å, $\beta = 115.36(4)^{\circ}$, U = 2.956.3 Å³, Z = 4, $D_c = 1.32$ g cm⁻³, μ (Mo- K_{α}) = 6.47 cm⁻¹, F(000) = 1.232, λ (Mo- K_{α}) = 0.710 69 Å, space group $P2_1/c$. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 40^{\circ}$) accurately centred on an Enraf-Nonius CAD-4 diffractometer.

(ii) X-Ray data collection. A crystal of dimensions $0.35 \times 0.40 \times 0.40$ mm was sealed in a thin-walled glass capillary under a nitrogen atmosphere. Data were taken on the diffractometer using graphite-monochromated molybdenum radiation. The diffracted intensities were collected by the θ -2 θ scan technique in the usual manner.¹⁶ All the reflections in one independent quadrant out to $2\theta \leq 50^{\circ}$ were measured;



Figure 1. Carbon-13 n.m.r. spectrum (15.09 MHz) of compound (13) in the range δ 15—40 p.p.m.

2 622 were considered observed $[I \ge 3\sigma(I)]$. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Full-matrix least-squares refinement was carried out using the SHELX system of programs.¹⁷ Atomic scattering factors for Fe, P, Si, O, and C were taken from Cromer and Waber,¹⁸ and the scattering for Fe was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.¹⁹ Scattering factors for H were from ref. 20.

(iii) Structure determination and refinement. Inspection of a Patterson map revealed the position of the iron atom, and the calculation of a difference-Fourier map phased on the metal atom led to the co-ordinates of the remaining non-hydrogen atoms. Several cycles of least-squares refinement with isotropic temperature factors, followed by more cycles with anisotropic thermal parameters for non-hydrogen atoms (hydrogen atoms in calculated positions), led to final values of $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|) = 0.048$ and $R' = [\Sigma w(|F_o| - |F_c|)/\Sigma(|F_o|)]^{\frac{1}{2}} = 0.051$. Unit weights were used at all stages

Table 5. Fractional atomic co-ordinates for compound (13)

2	A	C	5
- 2	4	o	Э

Atom	X a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Fe	0.326 01(9)	0.336 08(2)	0.595 85(9)	H(1)	0.6048	0.3357	0.8769
Р	0.263 8(1)	0.350 74(4)	0.353 0(2)	H(2)	0.3537	0.3023	0.8743
Si	0.3984(2)	0.396 51(4)	0.706 0(2)	H(3)	0.2208	0.2602	0.6151
0	0.0382(5)	0.353 4(1)	0.606 1(6)	H(4)	0.3842	0.2722	0.4499
C(1)	0.169 9(6)	0.396 0(1)	0.275 3(5)	H(5)	0.6212	0.3167	0.6129
C(2)	0.022 5(6)	0.401 0(2)	0.266 0(7)	H(6)	0.4570	0.4590	0.5282
C(3)	-0.054 7(7)	0.434 0(2)	0.214 6(7)	H(7)	0.6862	0.4818	0.5002
C(4)	0.012 7(8)	0.463 7(2)	0.173 2(7)	H(8)	0.9377	0.4548	0.6555
C(5)	0.158 8(8)	0.459 2(2)	0.181 2(7)	H(9)	0.9656	0.4044	0.8422
C(6)	0.237 0(7)	0.425 3(2)	0.231 5(6)	H(10)	0.7398	0.3804	0.8695
C(7)	0.119 1(5)	0.320 5(1)	0.202 9(6)	H(11)	-0.0313	0.3799	0.3004
C(8)	0.051 4(6)	0.290 3(2)	0.243 2(6)	H(12)	-0.1715	0.4361	0.2005
C(9)	-0.059 5(7)	0.268 5(2)	0.125 1(7)	H(13)	-0.0478	0.4902	0.1377
C(10)	-0.101 0(6)	0.276 6(2)	-0.027 7(7)	H(14)	0.2131	0.4830	0.1507
C(11)	- 0.033 7(7)	0.306 7(2)	-0.066 3(7)	H(15)	0.3485	0.4219	0.2347
C(12)	0.074 8(6)	0.328 4(2)	0.047 6(6)	H(16)	0.0833	0.2844	0.3631
C(13)	0.428 0(5)	0.345 9(1)	0.303 5(6)	H(17)	-0.1096	0.2445	0.1553
C(14)	0.443 7(6)	0.314 8(1)	0.224 3(6)	H(18)	-0.1890	0.2606	-0.1177
C(15)	0.579 3(7)	0.308 3(2)	0.210 0(7)	H(19)	-0.0651	0.3125	-0.1874
C(16)	0.698 5(6)	0.333 0(2)	0.270 5(7)	H(20)	0.1251	0.3520	0.0144
C(17)	0.684 8(6)	0.364 6(2)	0.348 0(7)	H(21)	0.3493	0.2954	0.1746
C(18)	0.551 0(6)	0.370 6(2)	0.365 6(7)	H(22)	0.5898	0.2841	0.1479
C(19)	0.152 8(7)	0.347 6(2)	0.597 8(6)	H(23)	0.8039	0.3275	0.2606
C(20)	0.526 3(7)	0.317 6(2)	0.786 3(7)	H(24)	0.7782	0.3848	0.3931
C(21)	0.395 0(8)	0.299 5(2)	0.786 3(7)	H(25)	0.5420	0.3956	0.4280
C(22)	0.321 9(7)	0.278 7(2)	0.648 3(8)	H(26)	0.5445	0.3795	0.9823
C(23)	0.408 7(7)	0.283 6(2)	0.562 6(7)	H(27)	0.3467	0.3835	0.9339
C(24)	0.534 5(7)	0.307 6(2)	0.647 9(7)	H(28)	0.5631	0.4490	0.9747
C(25)	0.442 0(7)	0.395 8(2)	0.919 8(7)	H(29)	0.4940	0.4352	1.1109
C(26)	0.467 3(7)	0.436 1(2)	0.989 0(7)	H(30)	0.2299	0.4472	0.9059
C(27)	0.329 1(7)	0.461 8(2)	0.908 0(7)	H(31)	0.3454	0.4876	0.9723
C(28)	0.295 8(7)	0.470 5(1)	0.739 8(7)	H(32)	0.2037	0.4912	0.6959
C(29)	0.250 9(6)	0.435 3(1)	0.633 2(6)	H(33)	0.3985	0.4830	0.7400
C(30)	0.577 9(6)	0.417 1(1)	0.696 9(6)	H(34)	0.1427	0.4250	0.6257
C(31)	0.568 3(7)	0.446 5(1)	0.597 1(7)	H(35)	0.2372	0.4437	0.5185
C(32)	0.697 5(8)	0.459 9(2)	0.582 1(8)				
C(33)	0.839 4(8)	0.444 2(2)	0.669(1)				
C(34)	0.852 6(7)	0.415 8(2)	0.771(1)				
C(35)	0.724 8(7)	0.402 5(2)	0.786 8(8)				

of the refinement, and unobserved reflections were not included. The largest parameter shifts in the final cycle were less than 0.05 of their estimated standard deviation. A final difference-Fourier map showed no unaccounted electron density. The standard deviation of an observation of unit weight was 1.55. No systematic variation of $w(|F_o| - |F_c|)$ against $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 5.

(*iv*) Discussion. The molecular structure with atom numbering scheme and the unit-cell packing diagram are depicted in Figures 2 and 3 respectively. Important bond distances and angles are listed in Table 6.

The co-ordination at the asymmetric iron centre may be viewed ¹⁰ as distorted tetrahedral, derived from octahedral by collapse of three facial points to a position occupied by the centroid of the η^5 -C₅H₅ ring. In keeping with this argument, in other compounds [M(η^5 -C₅H₅)L¹L²L³] each of the angles between the three σ -ligands have proved to be close to 90°, *e.g.* in [Fe(η^5 -C₅H₅)(PPh₃)(CO)(COOC₁₀H₁₉)] the largest deviation ¹⁰ was P-Fe-C(carbonyl) = 91.7°. By contrast the distortion in compound (13) is very pronounced, with P-Fe-C(carbonyl) = 97.2(2), Si-Fe-P = 98.43(6), and Si-Fe-C-(carbonyl) = 83.2(2)°; we attribute this effect to the strong repulsive interactions between the silyl and phosphine ligands in the sterically congested vicinity of the metal centre. The Fe-Si bond length at 2.366(2) Å is elongated compared with 2.249(1) and 2.252(3) Å respectively²¹ in the related [Fe-(η^5 -C₅H₅)(CO)(H)(SiX₂Y)₂] (X = F, Y = Me; X = Y = Cl), although under the influence of competing electron withdrawal from the metal by strong π -acceptor ligands this distance can be²² as long as 2.456(2) Å, in *cis*-[Fe(CO)₄-(SiMe₃)₂].

The most significant feature of the structure however is the clear demonstration that the silacyclohexane framework does indeed adopt a chair conformation (Figures 2 and 3) with the more spatially demanding substituent $-Fe(\eta^5-C_5H_5)(PPh_3)$ -(CO) occupying the equatorial site. The planar substituent phenyl group is attached to Si in the axial position with an orientation which is rotated about the Si-C (phenyl) bond to minimize interaction with the iron-containing unit and the silacyclohexyl hydrogens. The Si-C(phenyl) distance (1.914 Å) is only marginally different from Si-C(silacyclohexyl) (mean 1.893 Å) but since the latter is more than 0.3 Å longer than the C-C distances in the silacyclohexyl ring the angle at Si within the cyclic unit contracts to 100.9°. The geometry at Si is therefore considerably distorted from tetrahedral and the C-C-C angles respond by increasing slightly to a mean of 113°, corresponding to a somewhat flattened chair.

Although no other silacyclohexanes appear to have been structurally characterized, X-ray data are available ^{6,7} for two silacyclohexenes possessing structure (II) (X = Y = Ph; X = F, Y = α -naphthyl). Compared with that in (13), in



Figure 2. Molecular structure of $[Fe(\eta^5-C_5H_5)(CO)(PPh_3)(Si(Ph)(CH_2)_4CH_2)]$ (13)



Figure 3. Unit-cell packing diagram for $[Fe(\eta^5-C_5H_5)(CO)(PPh_3)\{\dot{Si}(Ph)(CH_2)_4CH_2]$ (13)

Table 6. Bond leng	ths (Å) and a	ngles (°) for compound	(13)
Fe-P	2.191(2)	Fe-Si	2.366(2)
Fe = C(19)	1 725(6)	Fe-C(20)	2 109(5)
$Fe^{-C(21)}$	2 098(6)	$Fe^{-C(22)}$	2 111(6)
$Fe^{-C(23)}$	2.000(0)	$F_{e} = C(24)$	2.111(0) 2.111(5)
Fe C(23)	2.110(3)	P = C(1)	1.842(5)
re-Cent	1.733	P = C(1)	1.043(3)
P = C(7)	1.856(5)	P = C(13)	1.842(5)
S1-C(25)	1.896(6)	S1-C(29)	1.889(5)
$S_1 - C(30)$	1.914(6)	C(1) - C(2)	1.395(7)
C(1) - C(6)	1.383(7)	C(2) - C(3)	1.364(7)
C(3) - C(4)	1.386(9)	C(4) - C(5)	1.386(8)
C(5) - C(6)	1.396(8)	C(7)-C(8)	1.394(7)
C(7) - C(12)	1.383(7)	C(8)-C(9)	1.409(8)
C(9) - C(10)	1.365(8)	C(10) - C(11)	1.383(8)
C(11)-C(12)	1.377(8)	C(13) - C(14)	1.386(7)
C(13) - C(18)	1.389(7)	C(14) - C(15)	1.389(7)
C(15) - C(16)	1.366(8)	C(16) - C(17)	1.382(8)
C(17) - C(18)	1 385(7)	C(19)-O	1 1 59(6)
C(20) - C(21)	1.505(7) 1.419(3)	C(20) - C(24)	1 401(8)
C(21) = C(22)	1.409(0)	C(20) = C(24)	1 407(8)
C(21) C(22) C(22) C(24)	1.400(9)	C(22) = C(23)	1.407(0)
$C(23)^{-}C(24)$	1.420(8)	C(23) - C(20)	1.534(6)
C(26) = C(27)	1.526(8)	C(27) - C(28)	1.525(8)
C(28) - C(29)	1.555(7)	C(30) - C(31)	1.394(7)
C(30) - C(35)	1.403(8)	C(31)-C(32)	1.396(8)
C(32) - C(33)	1.377(9)	C(33)-C(34)	1.38(1)
C(34)-C(35)	1.385(9)		
D-Fo-Si	08 43(6)	$\mathbf{P}_{-}\mathbf{F}_{\mathbf{e}} = C(10)$	07 2(2)
$\mathbf{S}_{i} = \mathbf{F}_{0} = \mathbf{C}(10)$	90.45(0) 93.2(2)	$C(10) = E_0 = C_{opt}$	125 400
$D = E_0 = C_{out}$	122 100	C(19) Fe Cent	120.100
$\mathbf{F} = \mathbf{P} \cdot \mathbf{C}(1)$	123.100	$\Sigma_{r} P C(7)$	116 9(2)
re-P-C(1)	119.9(2)	Fe-P-C(7)	110.0(2)
C(1) - P - C(7)	97.0(2)	Fe-P-C(13)	111.8(2)
C(1) - P - C(13)	107.8(2)	C(7) - P - C(13)	101.1(2)
Fe-Si-C(25)	110.7(2)	Fe-Si-C(29)	118.1(2)
C(25)-Si-C(29)	100.9(2)	Fe-Si-C(30)	115.4(2)
C(25)-Si-C(30)	105.4(3)	C(29)-Si-C(30)	104.8(2)
P - C(1) - C(2)	116.7(4)	P-C(1)-C(6)	124.7(4)
C(2) - C(1) - C(6)	118.6(5)	C(1)-C(2)-C(3)	121.1(5)
C(2)-C(3)-C(4)	120.8(5)	C(3) - C(4) - C(5)	118.9(5)
C(4) - C(5) - C(6)	120.4(6)	C(1) - C(6) - C(5)	120.2(5)
P-C(7)-C(8)	1214(4)	P-C(7)-C(12)	119.5(4)
C(8) - C(7) - C(12)	119 1(5)	C(8) - C(9) - C(10)	120.7(6)
C(7) - C(8) - C(9)	119 3(5)	C(9) - C(10) - C(11)	119 5(5)
C(1) = C(1) = C(12)	120.6(5)	C(7) - C(12) - C(11)	120.8(5)
$P_{-C(12)-C(14)}$	120.0(3)	$P_{-C}(12) = C(18)$	120.0(3)
C(14) = C(13) = C(14)	121.3(4)	$F^{-}C(13)^{-}C(16)$	120.1(4)
C(14) = C(15) = C(16)	117.9(4)	C(13) - C(14) - C(13)	120.9(3)
C(14) = C(15) = C(10)	120.4(5)	C(13) - C(10) - C(17)	119.7(5)
C(16) - C(17) - C(18)	119.9(5)	C(13) - C(18) - C(17)	121.2(5)
Fe-C(19)-O	175.4(5)	C(21) - C(20) - C(24)	107.1(5)
C(20)-C(21)-C(22)	109.2(6)	C(21)-C(22)-C(23)	107.0(6)
C(22)-C(23)-C(24)	108.5(5)	C(20)-C(24)-C(23)	108.2(6)
Si-C(25)-C(26)	111.5(4)	C(25)-C(26)-C(27)	113.3(5)
C(26)-C(27)-C(28)	113.5(5)	C(27)-C(28)-C(29)	113.4(5)
Si-C(29)-C(23)	113.3(4)	Si-C(30)-C(31)	121.5(4)
Si-C(30)-C(35)	121.6(4)	C(31)-C(30)-C(35)	116.8(5)
C(30)-C(31)-C(32)	121.7(6)	C(31)-C(32)-C(33)	120.0(6)
C(32)-C(33)-C(34)	119.4(6)	C(33)-C(34)-C(35)	120.8(6)
C(30)-C(35)-C(34)	121.2(6)	-(, -(-, -(-))	

these compounds the Si⁻C distances are marginally shorter within the heterocycle (1.88 and 1.86 Å respectively); C⁻C⁻C angles are 100° except at the C⁵ and C⁶ carbons which are planar.

Nature of the Si-M bond in Silacyclohexyl Transition-metal Complexes.—Apparent congestion at Fe in complex (13) led us to compare the properties of a representative from among compounds (8)—(22) with those of a simple trimethylsilylmetal analogue. The cobalt complex (15) was chosen for study. The central component in the i.r. absorption due to v(CO) modes, that at 2 025 cm⁻¹ (Table 3), can be assigned ¹¹ to the $a_1^{(1)}$ vibration predicted assuming approximation to C_{3v} selection rules; the intensity of this band was found to be equal to that of the higher-frequency (2 089 cm⁻¹) $a_1^{(2)}$ mode, unlike the situation for [Co(CO)₄(SiMe₃)] where the $a_1^{(1)}$ vibration is much the stronger of the two in the i.r. spectrum.²³ On the basis of earlier results,¹¹ this observation is consistent with bending of the three CO groups in the equatorial plane away from the silicon centre as a consequence of the steric demands of the phenylsilacyclohexane unit.

The reactivity of complex (15) also seems to be moderated compared with that for triorganosilyl relatives; we tentatively ascribe this effect to inhibition of attack on the Si-Co bond through steric restriction. Thus no significant deterioration of the solid compound was observed when handled in air over periods up to 1 h, in contrast with $[Co(CO)_4(SiMe_3)]$ which is thermally unstable and quickly decomposes on exposure to the atmosphere.²⁴ In reactions followed using i.r. spectroscopy, compound (15) was unaffected by CCl4 (24 h) or 1,2-dibromoethane (5 h, 25 °C) although the latter has been suggested as a general reagent for cleavage of the metal-metal bond in related complexes.²⁵ Partial recovery (ca. 40–50%) of compound (15) was also possible after stirring in liquid NEt₃, in contrast ^{11,24} to $[Co(CO)_4(MMe_3)]$ (M = Si or Ge). Reaction with HgCl₂ was slower than that encountered ^{11,25} in related systems, and unlike the latter reduction to Hg was noted with formation of some $[Co_2(CO)_8]$. The complex did react rapidly with SnHMe₃ to give [Co(CO)₄(SnMe₃)] quantitatively while with MeOH, formation of a yellow solution was accompanied by deposition of a purple solid identified ²⁶ (i.r.) as [Co₄(CO)₁₂]. These last three reactions yielded oily products having i.r. spectra consistent with the presence of species with structure (I).

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References

- 1 F. Glockling and S. R. Stobart, M.T.P. Internat. Rev. Sci., Inorg. Chem. Ser. 1, 1972, 6, 63.
- 2 C. S. Cundy, M. F. Lappert, and C. Yuen, J. Chem. Soc., Dalton Trans., 1978, 427.
- 3 R. West, J. Am. Chem. Soc., 1954, 76, 6012.
- 4 'The Organic Compounds of Germanium,' eds M. Lesbre, P. Mazerolles, and J. Satge, J. Wiley and Sons, London, 1971.
- 5 F. R. Jensen and C. H. Bushweller, Tetrahedron Lett., 1968, 2825.
- 6 J. P. Vidal, J. Lapasset, and J. Falqueirettes, Acta Crystallogr., Sect. B, 1972, 28, 3137.
- 7 J. P. Vidal and J. Falqueirettes, Acta Crystallogr., Sect. B, 1973, 29, 2833.
- 8 J. F. Harrod and A. J. Chalk, J. Am. Chem. Soc., 1965, 87, 1133;
 A. J. Chalk and J. F. Harrod, *ibid.*, 1967, 89, 1640.
- 9 J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, Chem. Commun., 1967, 965.
- 10 G. M. Reisner, I. Bernal, H. Brunner, and M. Muschiol, *Inorg. Chem.*, 1978, 17, 783.
- 11 G. F. Bradley and S. R. Stobart, J. Chem. Soc., Dalton Trans., 1974, 264.
- 12 R. A. Burnham and S. R. Stobart, J. Chem. Soc., Dalton Trans., 1973, 1269.
- 13 S. A. R. Knox and F. G. A. Stone, J. Chem. Soc. A, 1969, 2559.
- 14 S. A. R. Knox and F. G. A. Stone, J. Chem. Soc. A, 1970, 3147.
- 15 J. B. Lambert, D. A. Netzel, H. Sun, and K. K. Lilianstrom, J. Am. Chem. Soc., 1976, 98, 3778.
- 16 J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, J. Chem. Soc., Dalton Trans., 1979, 45.

- 17 G. M. Sheldrick, SHELX 76, Programs for Crystal Structure Determination, University of Cambridge, 1976.
- 18 D. T. Cromer and J. T. Waber, Acta Crystallogr., 1965, 18, 104.
- 19 D. T. Cromer and D. Liberman, J. Chem. Phys., 1970, 53, 1891.
- 20 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
- 21 L. Manojlović-Muir, K. W. Muir, and J. A. Ibers, *Inorg. Chem.*, 1970, 9, 447.
- 22 R. V. Parish and B. F. Riley, J. Chem. Soc., Dalton Trans., 1979, 482.
- 23 J. R. Durig, S. J. Meischen, S. E. Hannum, R. R. Hitch, S. K. Gondal, and C. T. Sears, *Appl. Spectrosc.*, 1971, 25, 182.
- 24 Y. L. Baay and A. G. MacDiarmid, Inorg. Chem., 1969, 8, 986.
 25 R. A. Burnham, F. Glockling, and S. R. Stobart, J. Chem. Soc., Dalton Trans., 1972, 1991.
- 26 F. A. Cotton and R. R. Monchamp, J. Chem. Soc., 1960, 1882.

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