Reactions of Strained Organosilicon Heterocycles with Nonacarbonyldi-iron(0). Part 2.[1] Preparation and Reactions of Silaferracyclopentanes

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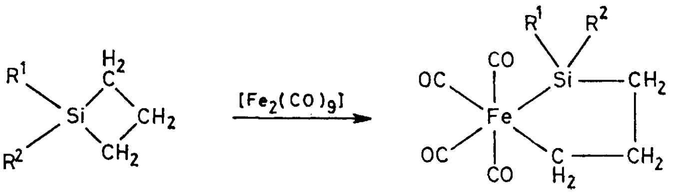
The formation of silaferracyclopentanes, by the reaction of silacyclobutanes with iron carbonyls, is described and their properties and reactions are discussed. The parent complex, 2,2,2,2-tetracarbonyl-1,1-dimethyl-1-sila-2-ferracyclopentane, has been prepared by the reaction of $Me_2\overline{SiCH_2CH_2CH_2}$ with $[Fe_2(CO)_9]$ (the preferred route) or, under u.v. irradiation, with $[Fe(CO)_5]$ or $[Fe_3(CO)_{12}]$; it has also been synthesised from $Na_2[Fe(CO)_4]$ and $SiMe_2(CH_2CH_2CH_2Cl)Cl$. Analogues having aryl, alkoxy-, or chloro-substituents at silicon are described, together with derivatives of 1,1,3,3-tetramethyl-1,3-disilacyclobutane and two silabenzocyclobutenes. Infrared, ^1H and ^{13}C n.m.r., and mass spectroscopic data are discussed. Chemical properties of the silaferracyclopentanes are contrasted with those of the parent silacyclobutanes. The complex $[\overline{Fe(CH_2CH_2CH_2SiMe_2})(CO)_4]$ shows some activity as a hydrosilylation catalyst.

FOLLOWING our original report[2] of the synthesis of silaferracyclopentanes by the reaction of silacyclobutanes[3] with nonacarbonyldi-iron, we published[1] our findings on reactivity and mechanism in these systems. We now present details of the preparation and reactions of a wider range of cyclic iron–silicon complexes. (In Part 1,[1] we referred to the possibility[4a] of endocyclic C–C cleavage of a silacyclobutane; this has now been discounted.[4b])

RESULTS AND DISCUSSION

When a suspension of $[Fe_2(CO)_9]$ was stirred at 21 °C in benzene containing at least 1 mol equivalent per $[Fe_2(CO)_9]$ of 1,1-dimethyl-1-silacyclobutane (1a) a quantitative yield of 2,2,2,2-tetracarbonyl-1,1-dimethyl-1-sila-2-ferracyclopentane (2a) was produced. The product (2a) is a volatile, white, crystalline solid, m.p. 87.5—88.5 °C, very soluble in non-polar solvents. As with $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiMe_3)]$,[5] the crystals are readily deformed by pressure. The proposed structure (2a) was confirmed by elemental analysis, molecular-weight measurement (mass spectrometrically, and cryoscopically in benzene), spectroscopic data, and alternative syntheses. Thus, reaction between (1a) and $[Fe(CO)_5]$ gave (2a) in fair yield, but only on irradiation with u.v. light.



(1a)	$R^1 = R^2 = Me$	(2a)
(1b)	$R^1 = Me, R^2 = Cl$	(2b)
(1c)	$R^1 = Me, R^2 = OMe$	(2c)
(1d)	$R^1 = R^2 = Cl$	(2d)
(1e)	$R^1 = R^2 = OMe$	(2e)

Dodecacarbonyltri-iron was much less reactive, only a trace amount of (2a) being detectable after 8-h irradiation. More significantly, from a structural standpoint, complex (2a) was also formed in the reaction of $SiMe_2(CH_2CH_2CH_2Cl)Cl$ with $Na_2[Fe(CO)_4]$, the disiloxane $O[SiMe_2(CH_2CH_2CH_2Cl)]_2$ being a major by-product.

Preparation of Other Silaferracyclopentanes.—The reaction of silacyclobutane (1) with $[Fe_2(CO)_9]$ to give the silaferracyclopentane (2) was found to be general for substituents R = alkyl, aryl, alkoxy, or chloro, although rates of reaction and yields varied considerably.[1] The same type of reaction occurred with the α-substituted silacyclobutane (3), and with the silabenzocyclobutenes (4), giving completely regioselectively the products (5) and (6), respectively.[1] The disilacyclobutane (7) reacted analogously to give the disilaferracyclopentane (8). The difunctional disiloxane (9) underwent $[Fe(CO)_4]$ insertion first in one then in both silacyclobutane rings, as was clearly shown by following changes in the ^1H n.m.r. spectrum of the solution component of the reaction mixture with time. The monosubstituted product was formed in too small a quantity to permit recovery, but the disubstituted material (10) was isolated, albeit in an impure state due to its high solubility and low volatility.

All the SiFe heterocycles are colourless when pure but tend to become green at room temperature, due to decomposition to $[Fe_3(CO)_{12}]$. They are stable when stored at −30 °C.

When at least one of the silicon substituents was hydrogen or an organometallic group the above pattern of reactivity was not followed. With hydridosilicon compounds the labile Si–H bond also reacted at iron.[6a] In the series of iron-substituted silacyclobutanes $[Fe(\eta\text{-}C_5H_5)(CO)_x(PMePh_2)_{2-x}\{\overline{Si(Me)CH_2CH_2CH_2}\}]$[6b] a gradation in reactivity was found: for $x = 2$ no reaction

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[1] Part 1, C. S. Cundy, M. F. Lappert, J. Dubac, and P. Mazerolles, *J.C.S. Dalton*, 1976, 910.

[2] C. S. Cundy and M. F. Lappert, *J.C.S. Chem. Comm.*, 1972, 445.

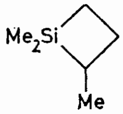
[3] R. Damrauer, *Organometallic Chem. Rev.*, 1972, **A8**, 67.

[4] (*a*) H. Schmidbaur and W. Wolf, *Angew. Chem. Internat. Edn.*, 1973, **12**, 320; (*b*) *Chem. Ber.*, 1976, **108**, 2834.

[5] T. S. Piper, D. Lemal, and G. Wilkinson, *Naturwiss.*, 1956, **43**, 129.

[6] (*a*) C. S. Cundy and M. F. Lappert, *J. Organometallic Chem.*, 1978, **144**, 317; (*b*) C. S. Cundy, M. F. Lappert, and Choi-Kwan Yuen, *J.C.S. Dalton*, 1978, 427; (*c*) *Inorg. Chem.*, 1978, in the press.

of the heterocycle occurred after 16 h under the usual conditions; for $x = 1$, 30% remained unchanged while 70% had apparently (^1H n.m.r.) been converted into polymeric material; for $x = 0$, 100% conversion into polymer occurred. With the germanium-substituted silacyclobutane $Ph_3Ge\overline{Si(Me)CH_2CH_2CH_2}$ [6c] a slow reaction occurred: after 3 d, 20% of the initial heterocycle remained unchanged and the presence of some non-polymeric product was indicated; however, none was isolated.



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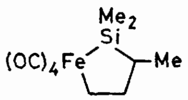

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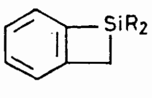
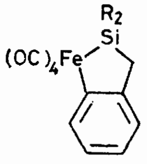
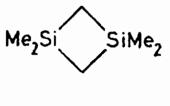


(4a) R=Me
(4b) R=Ph



(6a) R = Me
(6b) R = Ph



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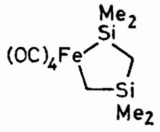

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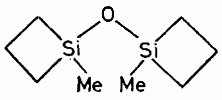

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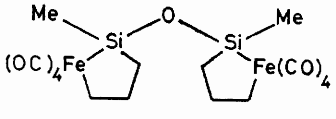

(10)

It has recently been found that stannacyclopentanes behave as strained-ring compounds and that they afford stannaferracyclohexanes with $[Fe_2(CO)_9]$.[7]

Attempted Syntheses of Silametallapentane Analogues containing Another Transition Metal in Place of Iron.—No transition-metal–silicon complex was isolated from attempted reactions between the silacyclobutane (1a) and $[Cr(CO)_6]$, $[Mo(CO)_6]$, $[Mo(CO)_4(\text{norbornadiene})]$, $[Mn_2(CO)_{10}]$, $[Ru_3(CO)_{12}]$, $[Co_2(CO)_8]$, $[Co(\eta\text{-}C_5H_5)(CO)_2]$, $[Pt(PPh_3)_3]$, $[Pt(PEt_3)_3]$, $[Pt(PPh_3)_2(\textit{trans}\text{-stilbene})]$, $[Pt(C_2H_4)(PPh_3)_2]$, $[Pt(PPh_3)_2O_2]$, *trans*-$[Ir(CO)Cl(PPh_3)_2]$, or $[Zr(CH_2SiMe_3)_4]$: in most cases no appreciable reaction took place. As described elsewhere,[8] silacyclobutanes are generally polymerised by transition-metal complexes $[M^nL_x(R)]$ when R is a mobile alkyl or halide leaving group and where the metal M (possessing an accessible $n + 2$ oxidation state) in the complex can achieve co-ordinative unsaturation. Furthermore, silametallacyclopentanes of type (2) represent a model for proposed intermediates in the catalytic polymerisation.

Infrared Spectra.—The characteristic i.r. absorption bands associated with the silacyclobutane ring system have been well studied:[3] the three bands at *ca.* 1 190, 1 130, and 930 cm^{-1} are particularly useful diagnostically. As expected, such a pattern of bands was absent from the spectra of the silaferracyclopentane products (2), which instead are dominated by vibrations associated with metal carbonyl ligands, characteristic substituent groups (*e.g.* Si–Me or aryl), and some new features. Four strong metal–carbonyl absorptions in the 2 000 cm^{-1} region were usually observed, as required for C_s symmetry, but in some cases the two vibrations of lowest energy (probably $A_1{}^2$ and B_2) were unresolved. When the substituents at silicon were different (*i.e.* $R^1 \neq R^2$) more than four carbonyl peaks were seen, indicating the presence of conformers in solution. Groups of strong bands due to ν(Fe–CO) at *ca.* 600 cm^{-1} appeared in the spectra of all the complexes. A band at *ca.* 300m cm^{-1} may represent ν(Fe–Si),[9] but was not seen in all cases. A group of CH_2 vibrations (1 250m, 1 215w, 1 170m, 1 070m, 1 015w, and 920m cm^{-1}) appeared in the spectra of all the silaferracyclopentanes (2) (some bands were occasionally obscured), and thus are probably characteristic of the $\overline{FeCH_2CH_2CH_2SiR_2}$ ring system. Further details are in the Table, and, for (2a), in the Experimental section.

N.M.R. Spectra.—The ^1H n.m.r. spectra of the silaferracyclopentanes (2), although useful diagnostically, are complex (even at 220 MHz) and do not readily lead to helpful structural conclusions. In general, the spectra show distinctive features due to substituent groups (*e.g.* SiMe), together with two multiplets in a 2 : 1 ratio which represent the ring methylene protons. It was not possible to make assignments for the ring protons. Attempts to synthesise derivatives containing additional nuclei with spin were all unsuccessful (see below), and use of the shift reagent $[Eu(fod)_3]$ (fod = $CF_3CF_2CF_2COCHCOBu^t$) at concentrations of from 2 to 200% had no effect on the spectrum of silaferracyclopentane (2a). Although the presence of solution conformers of the 1-chloro-1-methyl derivative (2b) was indicated by i.r. spectroscopy, interconversion was far too rapid to cause any significant change in the ^1H n.m.r. spectrum on cooling to −70 °C. The ^1H n.m.r. spectrum of the disilacyclopentane adduct (8) was unusual in showing (at 60 MHz) only two signals (singlets in a 6 : 10 ratio) for a total of 16 protons in four apparently different environments. Close examination (at 100 MHz) showed that the stronger high-field signal possessed a shoulder and it is assumed that the peak represents one $SiMe_2$ group together with both ring methylenes at nearly coincident chemical shifts. The bis(silaferracyclopentyl) ether (10) may exist in two

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[7] E. J. Bulten, 2nd International Conference on The Organometallic Chemistry of Germanium, Tin, and Lead, Nottingham, July 1977.

[8] C. S. Cundy, C. Eaborn, and M. F. Lappert, *J. Organometallic Chem.*, 1972, **44**, 291.

[9] C. S. Cundy, B. M. Kingston, and M. F. Lappert, *Adv. Organometallic Chem.*, 1973, **11**, 253.

stereoisomeric forms but no deduction can be made from the ^1H n.m.r. spectrum as to posible regioselectivity [1] for the second insertion, since although the Fe–SiMe signal was a singlet its chemical shift differed even from that of the monosubstituted material by only 1.6 Hz. Details of the ^1H n.m.r. spectra are in the Table.

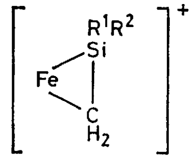
Spectroscopic data for silaferracyclopentanes

Complex	I.r. (cm^{-1}) ν(CO) [a]								ν(Fe–Si) [b]	^1H N.m.r. (τ) Absorption [c]	Assignment
(2a)	2 083	2 021		2 000 (sh)			1 998		302	8.0—8.3 (4 H, complex m) 9.0—9.3 (2 H, complex m) 9.44 (6 H, s)	2 ring CH_2 1 ring CH_2 $Si(CH_3)_2$
(2b)	2 093	2 037		2 017		2 010		2 007	314	8.0—8.7 (4 H, complex m) 8.7—9.3 (2 H, complex m) 9.13 (3 H, s) 6.58 (3 H, s)	2 ring CH_2 1 ring CH_2 $SiCH_3$ $SiOCH_3$
(2c)	2 085	2 024		2 007 (sh)			2 000	1 995 (sh)	325	7.9—8.4 (4 H, complex m) 8.5—*ca.* 9.3 (2 H, complex m) 9.72 (3 H, s)	2 ring CH_2 1 ring CH_2 $SiCH_3$
(2d)	2 105	2 050		2 034		2 031			321	8.1—8.9 (complex m) 6.41 (6 H, s)	3 ring CH_2 $Si(OCH_3)_2$
(2e)	2 090		2 028			2 008			*d*	7.9—8.4 (4 H, complex m) 8.8—9.0 (2 H, complex m)	2 ring CH_2 1 ring CH_2
(5)	2 082		2 020		1 999 (sh)		1 996		304	7.8—9.2 (8 H, complex m) 9.44 (3 H, s) 9.57 (3 H, s)	ring CH_2, CH, and $C(CH_3)$ 2 inequivalent $SiCH_3$
(6a)	2 089	2 030		2 013		2 008			310	2.77 (4 H, m) [e] 7.32 (2 H, s) 9.32 (6 H, s)	C_6H_4 ring CH_2 $Si(CH_3)_2$
(6b)	2 093	2 037		2 019		2 011				2.2—3.1 (14 H, complex m) [e] 6.80 (2 H, s)	2Ph + C_6H_4 ring CH_2
(8j)	2 082	2 023		2 000		1 996			297	9.34 (6 H, s) 9.77 + 9.79 (10 H, asymmetric s)	$Si(CH_3)_2$ $Si(CH_3)_2$ + 2 ring CH_2
(10) [g]	2 087 (sh)	2 084		2 023	2 006		1 999	1 997 (sh)	*f*	7.9—8.3 (8 H, complex m) 8.7—*ca.* 9.1 (4 H, complex m) 9.23 (6 H, s)	2 × 2 ring CH_2 2 × 1 ring CH_2 2 × $Si(CH_3)_2$

[a] In cyclohexane. [b] Tentative assignment (Nujol or thin film). [c] In benzene (τ 2.73). [d] Not observed. [e] In CH_2Cl_2 (τ 4.70). [f] Not recorded. [g] Impure.

The ^{13}C n.m.r. spectra at *ca.* 30 °C of complexes (2a), (8), and, especially, (5) provide convincing evidence for the proposed structures, as is shown in the Experimental section. The shifts for (8) were not significantly different when measured at 77 °C.

Mass Spectra.—These (detailed in the Experimental section) were obtained for all but the least volatile complexes, (6b) and (10), where decomposition before sufficient volatilisation precluded measurement. All the compounds, except (1d), gave molecular ions M^+, although that from (1e) was extremely weak. The fragmentation patterns support the proposed structures; loss of carbonyl groups and substituents at silicon, and ring fragmentation being observed. Interestingly, a dominant peak in the spectra of all the silaferracyclopentanes (2) was that corresponding to $[M - 140]^+$, *i.e.* loss of all the CO groups and C_2H_4. {Complex (5) showed both $[M - 4CO - C_2H_4]^+$ (17%) and $[M - 4CO - C_3H_6]^+$ (100%).} This parallels the behaviour found [10] for the parent silacyclobutanes [although with (3) loss of C_2H_4 or C_3H_6 were equally favoured] and



(I)

suggests the description of the fragment concerned as an iron-bound Si–C species as in (I). Only complex (2d) showed an ion corresponding to $[M - 4CO - C_2H_4 - CH_2]^+$: the case of $R^1 = R^2 = Cl$ seems the most likely to favour a metal-bound silylene, $[Fe(SiCl_2)]^+$.

Attempted X-Ray Studies.—Crystals of (2a) or (6b) suitable for single-crystal *X*-ray studies could not be prepared, and a brief study of (2d) gave only very poor data.

Chemical Reactions.—For the silaferracyclopentane ring system these are exemplified (see Scheme) by those of the dimethyl derivative (2a). Any significant variations with other compounds, where examined, are noted.

Complex (2a) showed considerable thermal stability: after 2.5 d at 80 °C approximately half the original sample condensed on cooling to room temperature. After 5 d no complex remained; the involatile residue was an intractable tar, while volatile products consisted of $[Fe(CO)_5]$ together with trace amounts of unidentified organosilanes. Very similar behaviour was observed for decomposition in solution: after 5.3 h in refluxing toluene only a trace amount of the silaferracyclopentane remained, and $[Fe(CO)_5]$ represented the only tractable product.

Reaction with excess of hydrogen chloride in benzene at 21 °C slowly (and incompletely) yielded $SiMe_2Pr^nCl$ as the sole condensable product; $FeCl_2$ was precipitated.

In a dinitrogen atmosphere, complex (2a) in diethyl ether was rapidly (<5 min) and quantitatively cleaved by excess of water at 21 °C to give $SiMe_2Pr^n(OH)$ in an unstable air-sensitive deep red solution. The solution showed a resonance attributable [11] to FeH at τ 24.81, but the intensity was only *ca.* 6% of that expected for a stoicheiometric reaction giving '$[Fe(CO)_4H(OH)]$.' No tractable organometallic material was isolated from this

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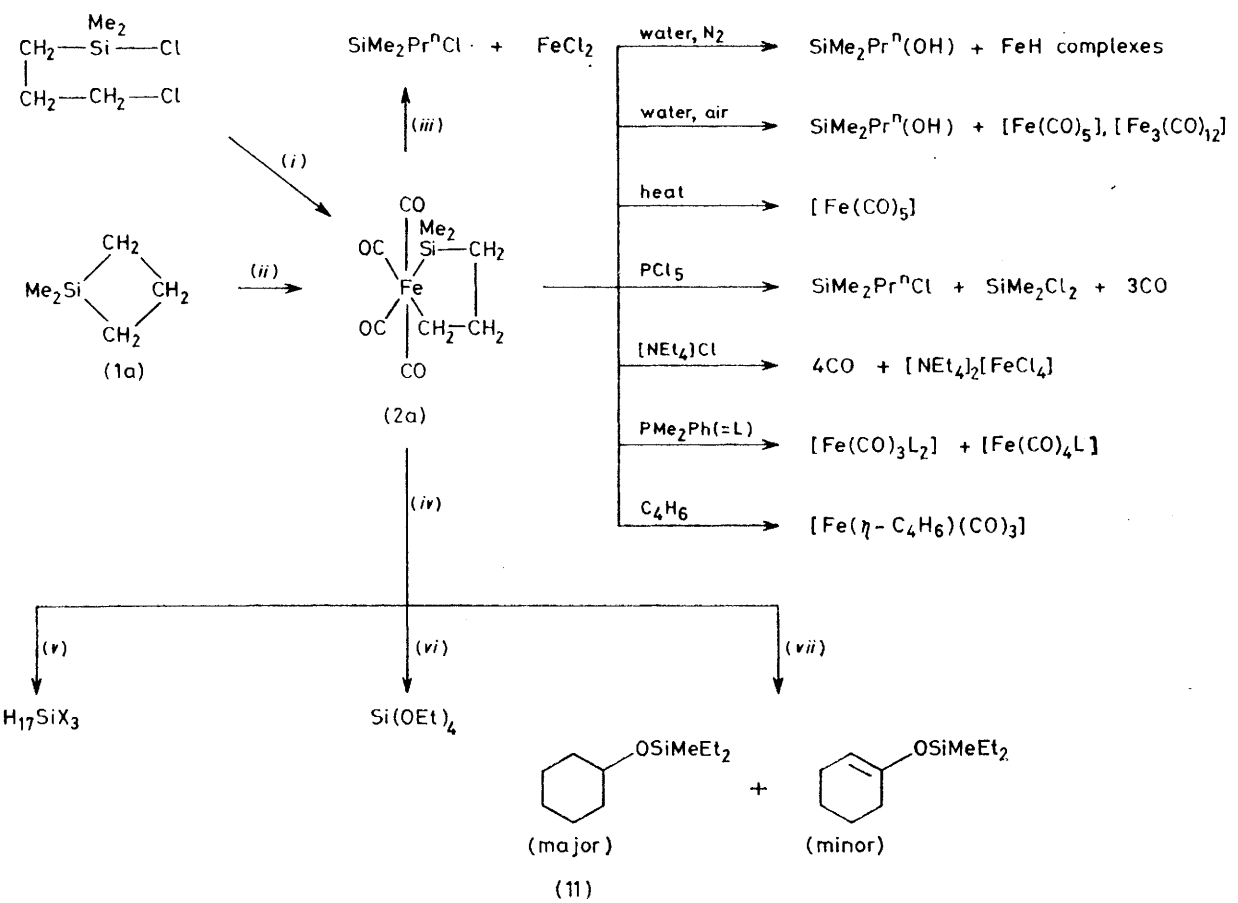
[10] C. S. Cundy, M. F. Lappert, and T. R. Spalding, *J.C.S. Dalton*, 1976, 558.

[11] K. M. Mackay, 'Hydrogen Compounds of the Metallic Elements,' Spon, London, 1966, p. 158.

solution. Exposure to air caused the red solution to decompose, yielding [Fe(CO)$_5$], [Fe$_3$(CO)$_{12}$], and an intractable light brown solid containing OH and M–CO groups. This behaviour is similar to that reported [12] for [Fe$_3$(CO)$_{11}$H$_2$], and undoubtedly involves carbonylhydridoiron species.



SCHEME Synthesis and reactions of 2,2,2,2-tetracarbonyl-1,1-dimethyl-1-sila-2-ferracyclopentane (2a). (*i*) Na$_2$[Fe(CO)$_4$] (*ii*) [Fe$_2$(CO)$_9$], or [Fe(CO)$_5$] and $h\nu$; (*iii*) HCl; (*iv*) (2a) as hydrosilylation catalyst; (*v*) CH$_2$=CHC$_6$H$_{13}$-n, SiX$_3$H; (*vi*) CH≡CPr^n, SiH(OEt)$_3$; (*vii*) cyclohexanone, SiHMeEt$_2$

Addition of water to a diethyl ether solution of complex (2a) in air caused instant decomposition to SiMe$_2$Pr^n(OH), [Fe(CO)$_5$], [Fe$_3$(CO)$_{12}$], and '[Fe(CO)$_y$(OH)$_x$].' (Conversion of the silanol into the corresponding disiloxane occurred slowly on standing.). This rapid reaction is very valuable in analytical degradation studies [1] of silaferracyclopentanes, since the otherwise preferred HCl reaction takes place far less readily. The reactions of HCl (electrophilic) and water (nucleophilic) with silaferracyclopentane (2a) contrast markedly with those of the parent silacyclobutane (1a) (which were run as controls), where the water reaction is slow and incomplete even at reflux, but the HCl reaction is rapid and total at 10 °C.

Dichlorine in carbon tetrachloride reacted readily with complex (2a) to produce a brown precipitate with slow evolution of gas. After the addition of 1 mol equivalent of Cl$_2$, 75% of the original complex remained; after 2 mol, 33% (by ^{1}H n.m.r.). Distillation *in vacuo* gave a trace of an unidentified high-boiling product which was not SiMe$_2$(CH$_2$CH$_2$CH$_2$Cl)Cl. The brown precipitate gave an aqueous solution containing Fe^{2+}, Fe^{3+}, and Cl$^-$ ions.

Phosphorus(v) chloride reacted cleanly with the related tetracarbonyliron complex [Fe(CF$_2$CF$_2$CF$_2$CF$_2$)(CO)$_4$] to release Cl[CF$_2$]$_4$Cl,[13] but the results were less clear cut with silaferracyclopentane (2a). After 18 h at 88 °C a quantity of non-condensable gas (assumed to be CO), equivalent to 70% of the CO contained in the starting complex, had been released, while SiMe$_2$Pr^{n}Cl and SiMe$_2$Cl$_2$ were also formed (24 and 9% yield, respectively). No benzene-soluble carbonyliron species remained (i.r.).

Excess of [NEt$_4$]Cl in chloroform reacted rapidly with (2a) to evolve CO quantitatively. The colourless solution became orange and was shown by n.m.r. and g.l.c. analysis to contain no tractable organosilicon products. A white crystalline precipitate which formed was identified as [NEt$_4$]$_2$[FeCl$_4$]. This unusual reaction

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[12] W. Hieber and G. Brendell, *Z. anorg. Chem.*, 1957, **289**, 324.

[13] R. Fields, M. M. Germain, R. N. Haszeldine, and P. W. Wiggans, *J. Chem. Soc.* (*A*), 1970, 1964.

is probably best considered together with the Lewis-base interactions described below in which the organosilicon ring is displaced from iron as some type of polymer. In the present instance, even the weakly nucleophilic chloride ion is apparently sufficient to bring about this reaction.

The silaferracyclopentane (2b) was recovered essentially quantitatively from excess of refluxing tetramethyltin after 1 h. The reagents MgBrMe in diethyl ether, LiMe in diethyl ether–hexane, or $AlEt_3$ in benzene all reacted over a few minutes; however, only starting material (32—85% recovery) was isolated from the residue. Presumably, nucleophilic ring opening (see below) followed by decomposition was the dominating reaction.

Addition of a Lewis base L (*e.g.* a tertiary phosphine) to a solution of complex (2a) caused a change from colourless through orange to brown, the rate of change depending on the donor employed. Following the reaction by ^1H n.m.r. or i.r. spectroscopy showed that, although both L and (2a) were being consumed, only the adducts[14] $[Fe(CO)_4L]$ and $[Fe(CO)_3L_2]$ were apparent as products. A series of experiments aimed at shedding further light on the processes involved yielded only gums and tars, no discrete intermediates or products being isolated or detected spectroscopically. The products appeared to consist largely of polymeric organosilicon material; however, they probably incorporated at least some of the added ligand since often more ligand L disappeared than subsequently reappeared in carbonyl-iron complexes. Further elucidation of these interesting reactions will have to accommodate the following additional facts. (*i*) The rate and extent of the reaction depended on the ligand employed, the activity order in benzene solvent being: $PhNC \gg PMe_2Ph > PMePh_2 > P(OMe)_3 >$ 4-methylpyridine $> PF_3 \sim NEt_3$. One mol equivalent of PhNC destroyed all the starting complex in 10 min at 21 °C; NEt_3 and PF_3 did not react. (*ii*) With $L = P(OMe)_3$, some added $SiCl_3H$ was consumed in the reaction. (The mixture was stable before addition of L.) (*iii*) With $L = PMe_2Ph$, added $Me_2SiCH_2CH_2CH_2$ was unaffected by the reaction. (Ligands L do not usually react with silacyclobutanes.) (*iv*) Complex (2b) showed a similar pattern of behaviour to (2a). (*v*) Addition of (2a) in CH_2Cl_2 to excess of $Ph_2PCH_2CH_2PPh_2$ at −20 °C gave the usual displacement reaction. No silacyclobutane (1a), or other simple species, was detected.

Complex (2a) did not react with *trans*-stilbene or diphenylacetylene under reflux in benzene nor with PhC≡CPh or norbornadiene in benzene under u.v. irradiation. The complex in pentane reacts on u.v. irradiation with butadiene to give $[Fe(C_4H_6)(CO)_3]$, and some unidentified organosilicon compound; some starting material was also recovered.

Complex (2a) did not react with dihydrogen or carbon monoxide in benzene up to reflux temperature. Some evidence for CO dissociation as a first step in the thermal decomposition of (2a) was provided by the observation that, unusually, no decomposition of the complex occurred on heating in solution when a CO atmosphere was employed. No reaction occurred in benzene at room temperature with carbon disulphide, sulphur dioxide, or in pentane with hexafluoroacetone (even under u.v. irradiation). Only very slight decomposition occurred on vigorously stirring a solution of (2a) in benzene under pure dioxygen for 1 h.

In view of our interest[15] in the hydrosilylation reaction and the known[16] catalytic activity of $[Fe(CO)_5]$, some tests were carried out to compare $[Fe(CO)_5]$ with silaferracyclopentane (2a). Under the conditions chosen (solution in refluxing benzene), $[Fe(CO)_5]$ and (2a) showed similar patterns of behaviour in reactions of $SiEt_3H$, $SiMeEt_2H$, or $SiH(OEt)_3$ with the unsaturated substrates oct-1-ene, pent-1-yne, or 2,3-dimethylbuta-1,3-diene: small quantities (<10% yield) of mixtures of products were formed, except for the case of pent-1-yne–$SiH(OEt)_3$ where $Si(OEt)_4$ appeared in >50% yield. More interesting were the reactions with cyclohexanone: with $SiH(OEt)_3$ both (2a) and $[Fe(CO)_5]$ gave $Si(OEt)_3(OC_6H_{11})$ in 40% yield after 6 h. However, with $SiMeEt_2H$ the products (11) and (12) (see Scheme) (in the ratio 4 : 1) were formed after 6 h in 40% yield using (2a). When $[Fe(CO)_5]$ was used as catalyst the yield was <3%. [The reaction with complex (2a) gave a similar result in the absence of solvent.] In no case was reaction observed when complex (2a) was used together with PPh_3 (1 : 1 mol ratio).

To our knowledge, these cyclic complexes containing both a M–Si and a M–C σ bond (M = transition metal) are unique. However, related species are known, and the comparative results described below may be of interest.

An early result in fluorocarbon–transition-metal chemistry was the discovery that C_2F_4 reacted with iron carbonyls to give $[Fe(CF_2CF_2CF_2CF_2)(CO)_4]$.[17] This complex has been investigated further.[13] A clear case of the insertion of an $[Fe(CO)_4]$ unit into a C_3 ring of a polycyclic hydrocarbon is known, and other similar structures have been found, or postulated, in intermediates.[18] Platinacyclobutanes are formed in the ring-opening reaction of cyclopropanes by Pt^{II},[19]

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[14] See, for example, A. Reckziegel and M. Bigorgne, *J. Organometallic Chem.*, 1965, **3**, 341 and refs. therein; G. Cardaci and V. Narciso, *J.C.S. Dalton*, 1972, 2289 and refs. therein.

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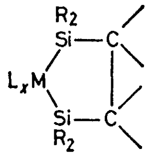
[16] E. Y. Lukevits and M. G. Voronkov, 'Organic Insertion Reactions of Group IVB Elements,' Consultants Bureau, New York, 1966; J. F. Harrod and A. J. Chalk, in 'Organic Syntheses *via* Metal Carbonyls,' vol. 2, eds. I. Wender and P. Pino, Wiley, New York, 1977, p. 673.

[17] P. M. Treichel and F. G. A. Stone, *Adv. Organometallic Chem.*, 1964, **1**, 143.

[18] See, for example, R. Aumann, *J. Organometallic Chem.*, 1973, **47**, C29; J. L. Flippen, *Inorg. Chem.*, 1974, **14**, 1054; R. M. Moriarty, Chin-Lung Yeh, Kan-Nan Chen, and R. Srinivasan, *Tetrahedron Letters*, 1972, 5325.

[19] R. J. Pudephatt and C. F. H. Tipper, *J. Organometallic Chem.*, 1974, **81**, 423; 1975, **84**, 407, and refs. therein.

while other platinocycles and titanocycles containing $M-(CH_2)_x$ ($x = 4$—6) have been prepared by Grignard or alkyl-lithium reactions.[20] More closely related to the silaferracyclopentanes are various compounds containing an $MSiC_2Si$ ring as in (II) where $ML_x = [Fe(CO)_4]$,[21,22]



(II)

$[Ru(CO)_4]$,[22] $[Os(CO)_4]$,[22] or $[Pt(PMe_2Ph)_2]$.[23] Compounds with $ML_x = [Ni(CO)_2]$ or $[Ni(CO)_4]$ have also been claimed.[24] Of special interest, in view of the alternative synthesis of complex (2a) from $SiMe_2(CH_2CH_2CH_2Cl)Cl$ and $Na_2[Fe(CO)_4]$, is the reaction of the latter with $Br[CH_2]_3Br$ in the presence of a tertiary phosphine, L, yielding the complexes *cis*-$[Fe(COCH_2CH_2CH_2)(CO)_3L]$.[25] In the PPh_3 complex the methylenes were clearly separated in the ^1H n.m.r. spectrum with chemical shifts at τ 8.09 (α to Fe), 8.27 (β), and 7.59 (γ). Since the methylene group α to iron does not give the highest-field signal, this suggests that in the spectrum of complex (2a) the 2 H multiplet centred at τ 9.09 is due to CH_2–Si and the 4 H multiplet at τ 8.13 to CH_2CH_2Fe.

Reactions between transition-metal carbonyl anions and silyl halides are complicated by nucleophilic attack at silicon from carbonyl oxygen.[9] The presence of a Si–O–C linkage in complex (2a) is considered unlikely because of (*a*) the mild conditions used for the alternative synthesis from compound (1a) and $[Fe_2(CO)_9]$ and (*b*) the weight of chemical and physical data supporting the illustrated structure.

EXPERIMENTAL

Experimental procedures and instrumentation were as described previously.[1] Carbon-13 n.m.r. spectra were recorded in deuteriobenzene on a Bruker HFX 90 Fourier-transform spectrometer at 22.63 MHz; chemical shifts were measured relative to C_6D_6 but are reported relative to $SiMe_4$. Organosilicon heterocycles were prepared by published methods [3] except for the disiloxane (9) which was synthesised from (1b) as described below. Molecular weights were determined cryoscopically or by mass spectrometry (m.s.).

Preparations.—$[Fe(CH_2CH_2CH_2SiMe_2)(CO)_4]$ (2a) *from* $Me_2SiCH_2CH_2CH_2$ (1a) *and* $[Fe_2(CO)_9]$. To a stirred suspension of $[Fe_2(CO)_9]$ (1.100 g, 3.024 mmol) in benzene (30 cm^3) held just above its freezing point was added the silacyclobutane (1a) (0.606 g, 6.048 mmol). The mixture was allowed to warm to 21 °C and was stirred until no $[Fe_2(CO)_9]$ remained (24 h). Monitoring the ^1H n.m.r. spectrum of the solution component throughout the course of the reaction showed the conversion of one half of the silacyclobutane into a single new product. Solvent, $[Fe(CO)_5]$, and excess of (1a) were then removed *in vacuo* at a rate which maintained the lowest temperature possible without allowing the reaction mixture to freeze (to minimise loss of the volatile product). The resulting green gum was taken up in n-hexane (10 cm^3) and the mixture was maintained at -30 °C for several days. Filtration at -30 °C removed most of the relatively insoluble, crystalline, green $[Fe_3(CO)_{12}]$ by-product. Hexane was removed *in vacuo* at low temperature from the filtrate. Sublimation (0 °C probe, 10^{-3} mmHg pressure *) of the residue gave colourless waxy crystals of 2,2,2,2-*tetracarbonyl*-1,1-*dimethyl*-1-*sila*-2-*ferracyclopentane* (2a) {0.696 g, 86% based on $[Fe_2(CO)_9]$}, m.p. 87.5—88.5 °C [Found: C, 40.05; H, 4.7; Fe, 20.5; O, 24.5 (by difference); Si, 10.25%; *M* 268 (in benzene), 268 (m.s.). $C_9H_{12}FeO_4Si$ requires C, 40.3; H, 4.5; Fe, 20.8; O, 23.9; Si, 10.5%; *M* 268]. Infrared spectrum (Nujol mull and thin film): 2 950w, 2 920w, 2 890w, 2 837w, 2 795w, 2 084vs, 2 022vs, 1 990vs,br, 1 918m, 1 455w, 1 434w, 1 406w, 1 260w(sh), 1 250s, 1 214vw, 1 171m, 1 071w, 1 040vw, 1 015vw, 970vw, 925w, 881vw, 848s, 827s, 780s, 767w, 750vw, 726vw, 708w, 693m, 638vs, 624vs, 608vs, 540w, 515vw, 468w, 441w, 433w, 425w, 390w, 380vw, 310w(sh), 302m, 295w(sh), and 284w cm^{-1}. Carbon-13 n.m.r. spectrum (p.p.m. upfield from $SiMe_4$): 211.54 (2 *trans* CO), 207.49 (1 CO), 206.13 (1 CO), 31.28 (ring CH_2), 26.12 (ring CH_2), 22.55 (ring CH_2), 4.20 ($SiMe_2$). Mass spectrum [*m*/*e* (assignment, rel. percentage abundance)]: 268 (M^+, 8), 253 ($[M - Me]^+$, 3), 240 ($[M - CO]^+$, 18), 225 ($[M - CO - Me]^+$, 1), 212 ($[M - 2CO]^+$, 26), 184 ($[M - 3CO]^+$, 34), 168 ($[M - C_5H_{12}Si]^+$, 38), 156 ($[M - 4CO]^+$, 51), 140 ($[M - CO - C_5H_{12}Si]^+$, 31), and ($[M - 4CO - C_2H_4]^+$, 100).

Complex (2a) *from* (1a) *and* $[Fe(CO)_5]$ *or* $[Fe_3(CO)_{12}]$. A solution of compound (1a) (0.050 g, 0.500 mmol) and $[Fe(CO)_5]$ (0.098 g, 0.500 mmol) in hexane (5 cm^3) was irradiated in a quartz tube with u.v. light (Hanovia 125-W medium-pressure lamp). After 6 h an appreciable quantity of complex (2a) had been formed (i.r.). Hexane and excess of reagents were removed *in vacuo* at low temperature, when sublimation gave pure complex (2a) (0.047 g, 35%). A similar experiment with a stirred suspension/solution of $[Fe_3(CO)_{12}]$ gave only a trace amount of (2a) together with $[Fe(CO)_5]$ and solid decomposition products after 8 h.

Complex (2a) *from* $Na_2[Fe(CO)_4]$ *and* $SiMe_2(CH_2CH_2CH_2Cl)Cl$. Sodium tetracarbonylferrate(2−) was prepared from $[Fe_3(CO)_{12}]$ (0.504 g, 1.000 mmol), sodium amalgam (Na, 0.207 g, 9.000 mmol; Hg, 27.2 g), and tetrahydrofuran (thf) (20 cm^3). Diethyl ether (20 cm^3) was then substituted for the thf. A solution of chloro(3-chloropropyl)-dimethylsilane (0.514 g, 3.000 mmol) in diethyl ether (10 cm^3) was added dropwise over 2.5 h to the stirred ether suspension of $Na_2[Fe(CO)_4]$ at 0 °C, whereafter the brown

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* Throughout this paper: 1 mmHg $\approx 13.6 \times 9.8$ Pa.

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[24] C. W. Cheng and C. S. Liu, *J.C.S. Chem. Comm.*, 1974, 1013.

[25] Y. Watanabe, T. Mitsudo, M. Yamashita, M. Tanaka, and Y. Takegami, *Chem. Letters*, 1973, 475.

suspension was stirred at room temperature for 16 h. Solvent was removed *in vacuo* to leave a red-brown oil from which 0.110 g of a faintly green $\{[\mathrm{Fe_3(CO)_{12}}]\}$ oil distilled at *ca.* 100 °C (0.01 mmHg) (−78 °C probe). The residue was extracted with hexane (10 cm^3), filtered, and the hexane removed *in vacuo*. Distillation as before gave another 0.171 g of similar oil. G.l.c., ^{1}H n.m.r., and i.r. analysis of the combined oily products showed the presence of $\mathrm{SiMe_2(CH_2CH_2CH_2Cl)Cl}$ (0.28 mmol, 9% recovery), $\mathrm{O[SiMe_2(CH_2CH_2CH_2Cl)]_2}$ (1.31 mmol, 44%), and (2a) (0.54 mmol, 18%).

$[\mathrm{Fe(CH_2CH_2CH_2SiMeCl)(CO)_4}]$ (2b). Following a similar procedure to that described for (2a), $[\mathrm{Fe_2(CO)_9}]$ (1.091 g, 3.000 mmol) was treated in benzene (30 cm^3) with 1-chloro-1-methyl-1-silacyclobutane (1b) (0.723 g, 6.000 mmol). The mixture was worked up as before to yield crystalline 2,2,2,2-*tetracarbonyl*-1-*chloro*-1-*methyl*-1-*sila*-2-*ferracyclopentane* (2b) (0.588 g, 68%), m.p. 93—94 °C [Found: C, 33.2; H, 3.1; Cl, 12.1; Fe, 19.0; O (by difference), 23.0; Si, 9.65%; *M* 288 (m.s.). $\mathrm{C_8H_9ClFeO_4Si}$ requires C, 33.3; H, 3.1; Cl, 12.3; Fe, 19.35; O, 22.2; Si, 9.7%; *M* 288]. Mass spectrum: 288 (M^+, 6), 260 ($[M-\mathrm{CO}]^+$, 27), 232 ($[M-2\mathrm{CO}]^+$, 27), 204 ($[M-3\mathrm{CO}]^+$, 67), 176 ($[M-4\mathrm{CO}]^+$, 100), 168 ($[M-\mathrm{C_4H_9ClSi}]^+$, 12), 148 ($[M-4\mathrm{CO}-\mathrm{C_2H_4}]^+$, 96), and 140 ($[M-\mathrm{CO}-\mathrm{C_4H_9ClSi}]^+$, 24).

$[\mathrm{Fe(CH_2CH_2CH_2SiCl_2)(CO)_4}]$ (2d). As for complex (2a), $[\mathrm{Fe_2(CO)_9}]$ (0.364 g, 1.000 mmol) was treated in benzene (10 cm^3) with 1,1-dichloro-1-silacyclobutane (1d) (0.155 g, 1.100 mmol). After 48 h the mixture was worked up as before (hexane, 10 cm^3) to yield crystalline 2,2,2,2-*tetracarbonyl*-1,1-*dichloro*-1-*sila*-2-*ferracyclopentane* (2d) (0.114 g, 37%), m.p. 110—111 °C. The complex was readily recrystallised from n-hexane [Found: C, 27.35; H, 1.9; Cl, 22.7; Fe, 18.1; O (by difference), 21.0; Si, 8.9. $\mathrm{C_7H_6Cl_2FeO_4Si}$ requires C, 27.2; H, 2.0; Cl, 22.95; Fe, 18.1; O, 20.7; Si, 9.1%]. Mass spectrum: 280 ($[M-\mathrm{CO}]^+$, 17), 252 ($[M-2\mathrm{CO}]^+$, 33), 224 ($[M-3\mathrm{CO}]^+$, 100), 196 ($[M-4\mathrm{CO}]^+$, 72), 168 ($[M-4\mathrm{CO}-\mathrm{C_2H_4}]^+$, 56), 154 ($[M-4\mathrm{CO}-\mathrm{C_2H_4}-\mathrm{CH_2}]^+$, 22), and 140 ($[M-\mathrm{C_3H_6Cl_2Si}]^+$, 28).

$[\mathrm{Fe\{CH_2CH_2CH_2SiMe(OMe)\}(CO)_4}]$ (2c). As for (2a), $[\mathrm{Fe_2(CO)_9}]$ (0.728 g, 2.000 mmol) was treated in benzene (20 cm^3) with 1-methoxy-1-methyl-1-silacyclobutane (1c) (0.256 g, 2.200 mmol). Hexane (7.5 cm^3) treatment followed by molecular distillation (0 °C probe, 10^{-3} mmHg) gave the liquid 2,2,2,2-*tetracarbonyl*-1-*methoxy*-1-*methyl*-1-*sila*-2-*ferracyclopentane* (2c) (0.455 g, 80%), m.p. −9 to −7 °C [Found: C, 37.7; H, 4.2; Fe, 19.3; O (by difference), 28.7; Si, 10.1%; *M* 284 (m.s.). $\mathrm{C_9H_{12}FeO_5Si}$ requires C, 38.05; H, 4.3; Fe, 19.7; O, 28.2; Si, 9.9%; *M* 284]. Mass spectrum: 284 (M^+, 7), 269 ($[M-\mathrm{Me}]^+$, 8), 256 ($[M-\mathrm{CO}]^+$, 25), 228 ($[M-2\mathrm{CO}]^+$, 50), 200 ($[M-3\mathrm{CO}]^+$, 100), 172 ($[M-4\mathrm{CO}]^+$, 33), 144 ($[M-4\mathrm{CO}-\mathrm{C_2H_4}]^+$, 50), and 140 ($[M-\mathrm{CO}-\mathrm{C_5H_{12}OSi}]^+$, 17).

$[\mathrm{Fe\{CH_2CH_2CH_2Si(OMe)_2\}(CO)_4}]$ (2e). As for (2a), $[\mathrm{Fe_2(CO)_9}]$ (0.364 g, 1.000 mmol) was treated in benzene (15 cm^3) with 1,1-dimethoxy-1-silacyclobutane (1e) (0.264 g, 2.000 mmol). After 7 h all the $[\mathrm{Fe_2(CO)_9}]$ had been consumed to give a light yellow solution. After another 5 h (no further change), solvent, $[\mathrm{Fe(CO)_5}]$, and unchanged (1e) were removed *in vacuo* to give a pale brown oil. Molecular distillation (30 °C; 0 °C probe, 0.01 mmHg) gave the liquid 2,2,2,2-*tetracarbonyl*-1,1-*dimethoxy*-1-*sila*-2-*ferracyclopentane* (2e) (0.287 g, 96%), m.p. 7—9 °C [Found: C, 35.8; H, 4.1; Fe, 18.2; O (by difference), 32.2; Si, 9.6%; *M* 300 (m.s.). $\mathrm{C_9H_{12}FeO_6Si}$ requires C, 36.0; H, 4.0; Fe, 18.6; O, 32.0; Si, 9.4%; *M* 300]. Mass spectrum: 300 (M^+, 0.002), 272 ($[M-\mathrm{CO}]^+$, 4), 244 ($[M-2\mathrm{CO}]^+$, 30), 216 ($[M-3\mathrm{CO}]^+$, 100), 188 ($[M-4\mathrm{CO}]^+$, 55), 168 ($[M-\mathrm{C_5H_{12}O_2Si}]^+$, 6), 160 ($[M-4\mathrm{CO}-\mathrm{C_2H_4}]^+$, 66), and 140 ($[M-\mathrm{CO}-\mathrm{C_5H_{12}O_2Si}]^+$, 6).

$[\mathrm{Fe\{CH_2CH_2CH(Me)SiMe_2\}(CO)_4}]$ (5). The method was similar to that for compound (2a) (for details see ref. 1), m.p. 15—18 °C. Carbon-13 n.m.r. spectrum (partially decoupled; CO signals not located; p.p.m. from $\mathrm{SiMe_4}$): 39.10 (d, ring CH), 32.49 (t, ring $\mathrm{CH_2}$), 16.99 (t, ring $\mathrm{CH_2}$), 14.03 (q, $\mathrm{CH_3}$ ring substituent), 2.16 (q), +0.00 (q)(2 inequivalent $\mathrm{SiCH_3}$). Mass spectrum: 282 (M^+, 11), 26 ($[M-\mathrm{Me}]^+$, 4), 254 ($[M-\mathrm{CO}]^+$, 26), 239 ($[M-\mathrm{CO}-\mathrm{Me}]^+$, 1), 226 ($[M-2\mathrm{CO}]^+$, 38), 211 ($[M-2\mathrm{CO}-\mathrm{Me}]^+$, 2), 198 ($[M-3\mathrm{CO}]^+$, 46), 170 ($[M-4\mathrm{CO}]^+$, 62), 168 ($[M-\mathrm{C_6H_{14}Si}]^+$, 54), 142 ($[M-4\mathrm{CO}-\mathrm{C_2H_4}]^+$, 17), 140 ($[M-\mathrm{CO}-\mathrm{C_6H_{14}Si}]^+$, 38), and 128 ($[M-4\mathrm{CO}-\mathrm{C_3H_6}]^+$, 100).

$[\mathrm{Fe\{(\mathit{o}\text{-}C_6H_4)CH_2SiMe_2\}(CO)_4}]$ (6a). The method was similar to that for compound (2a), but using excess of $[\mathrm{Fe_2(CO)_9}]$ (for details see ref. 1). M.p. *ca.* −55 °C. Mass spectrum: 316 (M^+, 5), 267 (18), 260 ($[M-2\mathrm{CO}]^+$, 41), 232 ($[M-3\mathrm{CO}]^+$, 55), 204 ($[M-4\mathrm{CO}]^+$, 100), and 133 (73).

$[\mathrm{Fe\{(\mathit{o}\text{-}C_6H_4)CH_2SiPh_2\}(CO)_4}]$ (6b). The method was similar to that for compound (2a) but using excess of $[\mathrm{Fe_2(CO)_9}]$ (for details see ref. 1), m.p. 78—79 °C.

$[\mathrm{Fe(CH_2SiMe_2CH_2SiMe_2)(CO)_4}]$ (8). As for compound (2c), $[\mathrm{Fe_2(CO)_9}]$ (0.364 g, 1.000 mmol) was treated in benzene (15 cm^3) with 1,1,3,3-tetramethyl-1,3-disilacyclobutane (7) (0.289 g, 2.000 mmol). After 24 h, work-up (hexane, 5 cm^3) gave liquid 2,2,2,2-*tetracarbonyl*-1,1,4,4-*tetramethyl*-1,4-*disila*-2-*ferracyclopentane* (8) (0.119 g, 38%), m.p. 10—11 °C [Found: C, 38.6; H, 5.1; Fe, 17.7; O (by difference), 20.9; Si, 17.7%; *M* 300 (in benzene); 312 (m.s.). $\mathrm{C_{10}H_{16}FeO_4Si_2}$ requires C, 38.5; H, 5.2; Fe, 17.9; O, 20.5; Si, 18.0%; *M* 312]. Carbon-13 n.m.r. spectrum: 210.80 (2 *trans* CO), 207.03 (1 CO), 205.14 (1 CO), 12.03 (ring $\mathrm{CH_2}$), 7.17 (ring $\mathrm{CH_2}$), 1.78 $[\mathrm{Si(CH_3)_2}]$, and −3.08 p.p.m. $[\mathrm{Si(CH_3)_2}]$. Mass spectrum: 312 (M^+, 5), 284 ($[M-\mathrm{CO}]^+$, 11), 256 ($[M-2\mathrm{CO}]^+$, 27), 228 ($[M-3\mathrm{CO}]^+$, 49), and 200 ($[M-4\mathrm{CO}]^+$, 100).

Bis(1-*methyl*-1-*silacyclobutyl*) *Ether* (9). Compound (1b) (2.96 g, 24.6 mmol) was added dropwise to vigorously stirred distilled water (28 cm^3). After the mixture had been stirred for 1.5 h it was extracted with diethyl ether (45 cm^3 in three portions). After drying ($\mathrm{Mg[SO_4]}$), ether was removed at 10 cmHg. Molecular distillation of the resulting liquid (0 °C probe) gave colourless pure (g.l.c.) *compound* (9) (1.355 g, 63%) (Found: C, 51.5; H, 9.6. $\mathrm{C_8H_{18}OSi_2}$ requires C, 51.5; H, 9.7%); τ 7.6—9.1 (12 H, complex m) and 9.65 (6 H, s). Infrared spectrum: SiO–H absent; 1 040vs,br (SiOSi); 1 185m, 1 120s, and 920s cm^{-1} [characteristic silacyclobutane vibrations (see Discussion section)].

$\mathrm{O[Si(Me)CH_2CH_2CH_2Fe(CO)_4]_2}$ (10). As for compound (2a), $[\mathrm{Fe_2(CO)_9}]$ (0.727 g, 2.000 mmol) in benzene (20 cm^3)

was treated with compound (9) (0.186 g, 1.000 mmol). After 24 h, all the $[Fe_2(CO)_9]$ had been consumed and ^1H n.m.r. spectroscopy showed SiMe peaks at τ 9.23 (FeSiOSiFe), 9.26 (FeSiOSi), and 9.68 (FeSiOSi and possibly also some coincident SiOSi) in the ratio 4 : 1 : 1. Another 0.500 g (1.373 mmol) of $[Fe_2(CO)_9]$ was then added and the stirring continued. After 24 h some $[Fe_2(CO)_9]$ remained but the SiMe peaks at τ 9.26 and 9.68 had disappeared. The usual work-up procedure (hexane, 5 + 2.5 cm^3) yielded an involatile gum. The gum was taken up in hexane (10 cm^3) and filtered through a short Florisil column. Solvent was then removed *in vacuo* and the residue dissolved in hexane (2 cm^3). The mixture was set aside at −30 °C, which allowed crystallisation of most of the remaining $[Fe_3(CO)_{12}]$. Volatile material was then removed from the separated supernatant to leave impure bis[2,2,2,2-tetracarbonyl-1-methyl-1-sila-2-ferracyclopentyl] ether as a pale green, very viscous, oil (0.350 g) (Found: C, 39.1; H, 4.2. Calc. for $C_{16}H_{18}Fe_2O_9Si_2$: C, 36.8; H, 3.5%).

Pyrolysis of (2a).—(*a*) *Gas phase.* A sample of (2a) (0.022 g) was heated under a dinitrogen atmosphere in a vessel (100 cm^3) at 80 °C. After 2.5 d a brown-black deposit had formed on the vessel sides and approximately half the original material condensed on cooling. After another 2.5 d at 80 °C no condensate of (2a) formed on cooling. Examination by g.l.c., i.r., and n.m.r. methods of volatile material distilled *in vacuo* from the dark intractable residue showed only $[Fe(CO)_5]$ and trace amounts of an unidentified organosilicon material.

(*b*) *In solution.* A sample of (2a) (0.047 g, 0.175 mmol) was heated under reflux in toluene (5 cm^3), and its decomposition was monitored by g.l.c. The mixture rapidly darkened and became heterogeneous. After 5.3 h almost all the complex had been destroyed. G.l.c., n.m.r., and i.r. analysis of volatile material distilled *in vacuo* revealed only $[Fe(CO)_5]$ (0.1 mmol, 70%) and a trace amount of (2a). No (1a) was detected.

Reactions of Complex (2a).—*With hydrogen chloride.* A solution of complex (2a) (0.075 g, 0.280 mmol) in benzene (7.5 cm^3) was sealed into a Carius tube (25 cm^3) with hydrogen chloride (2.80 mmol) and left at 21 °C for 7 weeks, shaking occasionally. After opening the tube, g.l.c. and ^1H n.m.r. analysis of the clear colourless benzene solution showed unchanged (2a) (80%) and $SiMe_2Pr^nCl$ (20%). A small white precipitate (*ca.* 5 mg) was insoluble in chloroform but soluble in water; the solution contained Fe^{2+} and Cl^-. Exposure of a stirred benzene solution of (2a) to 600 mmHg pressure of HCl for 5 min caused no detectable change, whereas (1a) was quantitatively[26] converted into $SiMe_2Pr^nCl$ under these conditions.

With water. Deoxygenated water (0.050 cm^3, 2.78 mmol) was added to a shaken solution of (2a) (0.096 g, 0.358 mmol) in diethyl ether (0.75 cm^3) under dinitrogen in an n.m.r. tube. The colourless solution immediately became deep red and slowly deposited a dark red precipitate. The ^1H n.m.r. spectrum of the solution showed quantitative conversion of (2a) into $SiMe_2Pr^n(OH)$ while an FeH signal appeared at τ 24.81 {*cf.*[11] $[Fe_3(CO)_{11}H_2]$, τ 24.9}. Exposure to air caused the red solution to decompose, yielding $[Fe(CO)_5]$, $[Fe_3(CO)_{12}]$, and a light brown precipitate (insoluble in all the common solvents) showing strong broad hydroxyl and carbonylmetal absorptions in its i.r. spectrum. In a separate experiment, no tractable product was isolated from the red solution in an inert atmosphere. Heterocycle (1a) does not react with water under these conditions. Very much more vigorous treatment[26] was required to synthesise $SiMe_2Pr^n(OH)$ for comparison purposes.

With dichlorine. To a solution of (2a) (0.034 g, 0.126 mmol) in CCl_4 (1.5 cm^3) containing a trace amount of $CHCl_3$ was added at −10 °C a solution of dichlorine in CCl_4 (0.25 mol dm^{-3}). Addition of 0.126 mmol of Cl_2 produced a brown precipitate. The supernatant showed (^1H n.m.r.) 75% of the original amount of (2a) to remain. After 0.252 mmol of Cl_2 had been added 33% of (2a) remained. No clearly defined product was seen and only a trace amount of a high-boiling material was detected by g.l.c. analysis; $SiMe_2(CH_2CH_2CH_2Cl)Cl$ was definitely absent. A solution of the brown precipitate in water contained Fe^{2+}, Fe^{3+}, and Cl^-.

With phosphorus(V) *chloride.* A solution of (2a) (0.231 g, 0.862 mmol) in pentane (5 cm^3) was run on to powdered PCl_5 (0.200 g, 0.961 mmol) in a Carius tube (25 cm^3). After removal of the pentane *in vacuo* the tube was sealed and heated to 88 °C for 18 h. On opening the cooled tube 2.4 mmol of non-condensable gas was found. The brown product was extracted with benzene (2.5 cm^3, in portions) and the resulting solution examined by g.l.c., ^1H n.m.r., and i.r. methods. No carbonyliron complex was present but $SiMe_2Pr^nCl$ (0.21 mmol, 24%) and $SiMe_2Cl_2$ (0.078 mmol, 9%) were found.

With tetraethylammonium chloride in chloroform. Solid $[NEt_4]Cl$ (0.241 g, 1.450 mmol) was added to a solution of (2a) (0.039 g, 0.145 mmol) in chloroform (5 cm^3) in a flask connected to a gas burette. A gas (13 cm^3 at n.t.p.) shown (by i.r.) to be CO was rapidly evolved (99% yield), the colourless solution became orange, and a white crystalline precipitate appeared. The separated solid was washed ($CHCl_3$) and dried (Found: C, 42.2; H, 9.2; N, 6.1. Calc. for $C_{16}H_{40}Cl_4FeN_2$: C, 41.95; H, 8.8; N, 6.1%). Solvent was removed from the filtered $CHCl_3$ solution *in vacuo* and the residue extracted with benzene (2 cm^3). G.l.c. and ^1H n.m.r. analyses of these solutions showed no tractable product except for trace amounts of $SiMe_2Pr^n(OH)$ and $O(SiMe_2Pr^n)_2$ presumably formed by adventitious hydrolysis.

With Lewis bases. These reactions were generally run in n.m.r. tubes and followed by changes in ^1H n.m.r. and i.r. spectra. For example, to a solution of (2a) (0.018 g, 0.067 mmol) in benzene (0.5 cm^3) was added dimethylphenylphosphine (L) (0.009 g, 0.067 mmol). The colourless solution rapidly became orange. After 1 min, n.m.r. signals due to (2a) had lost 50% of their intensity and a new broad SiMe resonance at τ *ca.* 9.5—9.8 had appeared; 50% of L had been converted into $[Fe(CO)_4L]$. After 10 min, 85% of (2a) had been converted, giving $[Fe(CO)_3L_2] : [Fe(CO)_4L] : L = 1 : 6 : 1$. After 25 min, 100% of (2a) had been converted and $[Fe(CO)_3L_2] : [Fe(CO)_4L] : L = 1 : 7 : 0$.

With butadiene. A solution of (2a) (0.078 g, 0.289 mmol) in pentane (10 cm^3) was sealed in a Pyrex Carius tube (25 cm^3) with butadiene (2.89 mmol). After 24 h at 21 °C no obvious reaction had occurred, and the mixture was irradiated for 6 h with u.v. light. After opening the tube, material volatile at 21 °C was distilled *in vacuo* from the yellow solution to give a colourless distillate and an orange-yellow residual gum. The distillate contained (i.r.) a small amount of $[Fe(CO)_5]$. The residue contained (n.m.r.

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[26] N. S. Nametkin, V. M. Vdovin, and P. L. Grinberg, *Proc. Acad. Sci.* (*U.S.S.R.*), 1964, **155**, 320.

and i.r.) unchanged (2a) (*ca.* 25% recovery), [Fe(CO)$_3$-(butadiene)],[27] and some unidentified organosilicon material.

Hydrosilylation Reactions using [Fe(CO)$_5$] *or* (2a) *as Catalyst.*—The unsaturated substrate (3—4 mmol) and an equimolar quantity of silane together with the catalyst (1 mol %) in benzene (to give a total volume of 2.0 cm^3) were heated under reflux for 5—7 h (exceptionally, 16 h for 2,3-dimethylbuta-1,3-diene). The reaction mixtures were then analysed by m.s. and g.l.c. methods, as described in the Discussion section.

We thank the S.R.C. for support, Dr. D. J. Cardin for running the ^{13}C n.m.r. spectra, and Miss C.-K. Yuen for performing the hydrosilylation reactions.

[7/1561 *Received*, 1*st September*, 1977]

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[27] R. B. King, ' Organometallic Syntheses,' Academic Press, New York, 1965, p. 128.