Reactions of Strained Organosilicon Heterocycles with Nonacarbonyldi-iron(0). Part I. Reactivity and Mechanism †

By **Colin S. Cundy** and **Michael F. Lappert,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ
(in part) **Jacques Dubac** and **Pierre Mazerolles,** Laboratoire des Organométalliques, Université P. Sabatier, 118 route de Narbonne, 31-Toulouse, France

The formation of 2,2,2,2-tetracarbonyl-1-sila-2-ferracyclopentanes by the reaction of silacyclobutanes with nonacarbonyldi-iron is described, and the nature of the process discussed. Completely regioselective reactions are found with $Me_2\overline{SiCH_2CH_2C}(Me)H$ [Si–CH$_2$ and not Si–C(Me)H cleavage] and with two silabenzocyclobutenes $R_2\overline{Si(o\text{-}C_6H_4)C}H_2$ (R = Me or Ph) [C(aryl)–Si and not C(alkyl)–Si cleavage]. With mixtures of the two isomers of $XMe\overline{SiCH_2C(Me)HC}H_2$ (X = Bu^n, isomer ratio 4:1; X = MeO, isomer ratio 7:3) the reaction is stereospecific, there being no significant change in isomer ratio between the reactant and product. It is concluded that this facile [Fe(CO)$_4$] insertion is probably an electrophilic C–Si cleavage reaction and that the process, using the term broadly, is concerted.

ALTHOUGH the very low volatility and virtual insolubility of nonacarbonyldi-iron(0) have long seemed anomalous for a binuclear molecular metal carbonyl,[1] a recent single-crystal *X*-ray study [2] has vindicated all the main points of the structure originally [3] deduced. The complex [Fe$_2$(CO)$_9$] has been much used as a source of carbonyliron in the preparation of complexes with two-electron donors (L), *e.g.* [Fe(CO)$_4$L] or [Fe(CO)$_3$L$_2$],[4] and with more complex species;[5] however, numerous interesting reactions have been recently reported in which [Fe$_2$(CO)$_9$] undergoes oxidative-elimination reactions with strained-ring systems to produce complexes containing σ-bonded endocyclic iron.[6,7] We briefly reported that silacyclobutane (I; R^1 = R^2 = Me) undergoes ring expansion to furnish the silaferracyclopentane, (II).[7] In this paper we deal with the problems of reactivity and mechanism, mainly by consideration of substituent effects and hence of regio- and stereo-

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† No reprints available.

[1] *Cf.*, E. W. Abel and F. G. A. Stone, *Quart. Rev.*, 1969, **23**, 325.

[2] F. A. Cotton and J. M. Troup, *J.C.S. Dalton*, 1974, 800.

[3] R. Brill, *Z. Krist.*, 1927, **65**, 85; H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 1939, 286.

[4] 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.

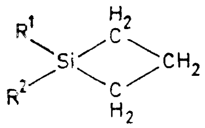
[5] See, for example, E. Koerner von Gustorf and R. Wagner, *Angew. Chem. Internat. Edn.*, 1971, **10**, 910; B. L. Barnett and C. Kruger, *ibid.*, p. 910.

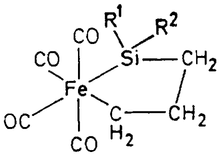
[6] See, for example, (*a*) R. Aumann, *J. Organometallic Chem.*, 1973, **47**, C29; (*b*) J. L. Flippen, *Inorg. Chem.*, 1974, **13**, 1054; (*c*) R. M. Moriarty, Chin-Lung Yeh, Kan-Nan Chen, and R. Srinivasan, *Tetrahedron Letters*, 1972, 5325.

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

selectivity. In Part II, we shall report details of reactions on a wider range of silicon heterocycles.[8] There is much current interest in the transition metal-promoted valence isomerisation of strained polycyclic hydrocarbons,[9] and the present studies are a natural extension. The most topical question is that of mechanism, and of the role of the transition metal which in the widest sense is to provide a low-activation energy path which is otherwise inaccessible, due to the constraints of orbital symmetry. An originally attractive hypothesis required appropriate empty and filled metal *d* orbitals to participate in a transition state involving a concerted bond-making–bond-breaking process.[10] This has fallen into some disfavour as evidence has accumulated for stepwise reaction paths, including the formation of intermediate metallocycles. We show here for the strained silicon rings that the formation of such a metallocycle is itself an essentially concerted process.

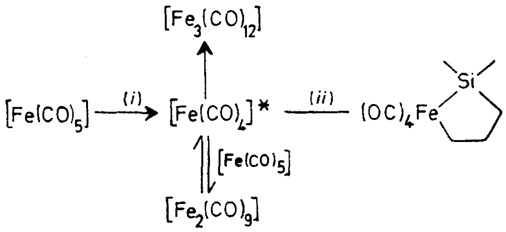
RESULTS AND DISCUSSION


(I)


(II)

When a suspension of $[Fe_2(CO)_9]$ was stirred at 21 °C in benzene, the complex decomposed slowly and cleanly over many hours to give soluble $[Fe(CO)_5]$ and $[Fe_3(CO)_{12}]$. However, when at least 1 mol equivalent {per$[Fe_2(CO)_9]$} of 1,1-dimethyl-1-silacyclobutane (I; $R^1 = R^2 =$ Me) was initially included in the reaction mixture, $[Fe_3(CO)_{12}]$ formation was suppressed and a quantitative yield of 2,2,2,2-tetracarbonyl-1,1-dimethyl-1-sila-2-ferracyclopentane (II; $R^1 = R^2 =$ Me) was produced. This reaction has been carried out on a large number of similar silicon heterocycles.[8] It appears to be general for substituents R = alkyl, aryl, alkoxy, or chloro, but not for R = hydrido or an organometallic group. The driving force for the reaction is presumably that of relief of organosilicon ring strain,[11] while Si–C bond polarity and the strengths of the two new bonds (Fe–Si and Fe–C) formed must assist kinetically and thermodynamically in providing a favourable reaction profile. Thus, strain energies have been calculated for $Me_2SiCH_2CH_2CH_2$ (*ca.* 52—62), $Me_2SiCH_2SiMe_2CH_2$ (62—72), and $Me_2SiCH_2CH_2CH_2CH_2$ (24—31 kJ mol^{-1}) from heats of formation obtained by rotating-bomb combustion calorimetry.[12] While the two heterocyclobutanes reacted readily with $[Fe_2(CO)_9]$ to form stable cyclic complexes, no reaction occurred with the silacyclopentane under identical conditions. However, there was also no reaction with cyclobutanone, which must have a strain energy in excess of that for cyclobutane (*ca.* 110 kJ mol^{-1} [13]). The reactivity of silacycloalkanes towards $[Fe_2(CO)_9]$ is most certainly not governed by unusual values for the vertical ionisation potentials (i.p.s) of the filled ring orbitals of highest energy since, for example, the i.p.s for these orbitals (a_1 and b_1) for $Me_2SiCH_2CH_2CH_2$, $Cl_2SiCH_2CH_2CH_2$, and $Me_2SiCH_2CH_2CH_2CH_2$ (as determined from photoelectron spectra [14]) are respectively 9.40 and 10.00, 10.50 and 10.70, and 9.75 and 10.10 eV.*

For the silicon heterocyclobutanes which form silaferracyclopentanes with $[Fe_2(CO)_9]$, a gradation in reactivity was found, with the most reactive heterocycles requiring short reaction times and giving no, or very little, $[Fe_3(CO)_{12}]$ as a by-product, whereas the less reactive compounds were consumed very slowly, considerable amounts of $[Fe_3(CO)_{12}]$ also being formed. Any excess of heterocycle remained unchanged at the end of the experiment, showing that no reaction occurred with $[Fe(CO)_5]$ or $[Fe_3(CO)_{12}]$ under these conditions, and also that polymerisation[15] of the silicon compounds was negligible. Using (I; $R^1 = R^2 =$ Me) as a model, reaction with $[Fe(CO)_5]$ in hexane or benzene solution gave (II; $R^1 = R^2 =$ Me) but only on irradiation with ultraviolet light. {No $[Fe_2(CO)_9]$ was formed in these systems.} However, $[Fe_3(CO)_{12}]$ was much less reactive, only a trace amount of (I) being detectable after 8 h. Reaction between $[Fe_2(CO)_9]$ and (I; $R^1 = R^2 =$ OMe), the most reactive heterocycle, in an atmosphere of CO gave a greatly reduced yield of (II; $R^1 = R^2 =$ OMe) with a corresponding increase in $[Fe(CO)_5]$ production.



Scheme 1 (i), U.v.; (ii), $>SiCH_2CH_2CH_2$

We rationalise these findings by Scheme 1. The silicon heterocycle is envisaged as competing for $[Fe(CO)_4]^*$. However, the real situation is undoubtedly more complex, since the nature of the active entity

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* 1 eV ≈ 1.60×10^{-19} J.

[8] Part II, C. S. Cundy and M. F. Lappert, to be published.

[9] *Cf.*, D. J. Cardin, B. Çetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

[10] *Cf.*, F. D. Mango and J. H. Schachtschneider, in ' Transition Metals in Homogeneous Catalysis,' ed. G. N. Schrauzer, Marcel Dekker, New York, 1971, p. 223.

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

[12] B. Iseard, D.Phil. Thesis, University of Sussex, 1973.

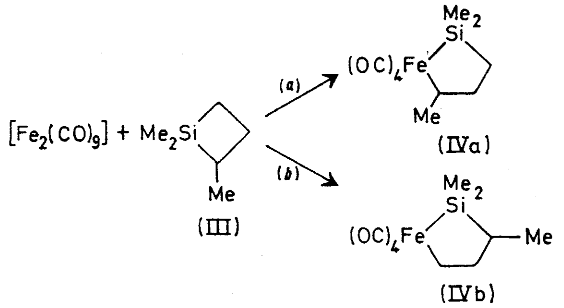
[13] *Cf.*, J. D. Cox and G. Pilcher, ' Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970, p. 571.

[14] C. S. Cundy, M. F. Lappert, J. B. Pedley, W. Schmidt, and B. T. Wilkins, *J. Organometallic Chem.*, 1973, **51**, 99.

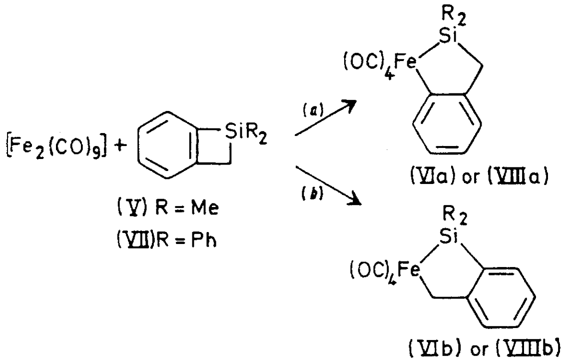
[15] C. S. Cundy, C. Eaborn, and M. F. Lappert, *J. Organometallic Chem.*, 1972, **44**, 291.

derived from $[Fe_2(CO)_9]$ is unknown, although recent work[16] suggests the possibility of a binuclear species such as $[(OC)_4Fe{=}Fe(CO)_4]$. Although this point remains obscure, it was possible to gain further insight into the reaction mechanism and the timing of the covalency changes by study of a range of silicon substrates.

Reaction of $[Fe_2(CO)_9]$ *with the Unsymmetrical Silacyclobutane* (III).—The reaction between $[Fe_2(CO)_9]$ and (III) could proceed in two ways, (*a*) or (*b*). Exclusive formation of a single isomer occurred, (IVb) being indicated by spectroscopic properties and confirmed by degradation experiments. (The latter involve the facile reaction[8] of the silaferracyclopentane with water to give the corresponding silanol, which was identified by independent synthesis. The positive identification of the product also ruled out the slight possibility of silacyclobutane endocyclic C–C bond cleavage, of which one example is known,[17] or of exocyclic C–Si cleavage.) It thus appears that the ring-opening reaction is highly regioselective, as in the case of SO_3 insertion.[18] It seems likely that the reason for the selection for (IVb) rather than (IVa) is due to a steric rather than to an electronic effect.

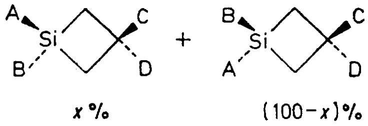


Reaction of $[Fe_2(CO)_9]$ *with the Silabenzocyclobutene* (V) *or* (VII).—This represents a second case in which isomeric products are possible. With the dimethyl substrate (V) the reaction yielded exclusively isomer (VIa). In this case, the possible alternative sites for insertion of $[Fe(CO)_4]$ differ markedly both sterically and electronically. The site chosen is the more sterically hindered, but involves phenyl– rather than benzyl–silicon cleavage. Interestingly, for protic systems (protodesilylation) it is the phenyl–silicon bond which is attacked by electrophiles and the benzyl–silicon bond by nucleophiles, as expected from electronic considerations.[19a] This is supporting evidence for the proposal that the attacking transition-metal unit is acting as an electrophilic reagent,[15] a premise further substantiated by the observation that electron-releasing groups at silicon tend to enhance, and electron-attracting groups to decrease, the rate of reaction in the various derivatives prepared.[8] Formation of a phenyl–iron rather than a benzyl–iron bond may be an additional incentive for the chosen reaction path. The reaction has also been carried out with (VII), the diphenyl analogue of (V). A single product, assumed to be of analogous structure, (VIIIa), was formed.



The $[Fe(CO)_4]$–H^+ analogy was examined further. Although the C–Si bond in 1,3,5-trimethoxy-2-trimethylsilylbenzene readily undergoes protolytic cleavage,[19b] no reaction was found with $[Fe_2(CO)_9]$ in benzene; however, the cause may be steric in origin.

Reaction of $[Fe_2(CO)_9]$ *with Mixtures of Stereoisomeric Silacyclobutanes.*—It has recently become possible to obtain various silacyclobutanes as non-equimolar mixtures of stereoisomers.[20] Such mixtures may be used to obtain mechanistic information about reactions of silacyclobutanes in which there is the possibility of loss of stereochemical integrity at either silicon or carbon, since a concerted reaction, or one in which any ' open ' intermediate is very short lived, will cause no change in the isomer ratio $x : (100 - x)$ of the product. This procedure has been already applied to reactions at silicon substituents[20,21] and to the insertion of dichlorocarbene[22] or oxides of sulphur.[23]



Reaction of $[Fe_2(CO)_9]$ with each of the silacyclobutanes (IX) or (X) having isomer ratios of $Z:E$ 4 : 1 and 7 : 3, respectively {as deduced from ^1H n.m.r. spectroscopy [(IX) or (X)] or g.l.c. measurements [(X)]} gave mixtures, (XI) or (XII), of stereoisomeric 2,2,2,2-tetracarbonyl-1-sila-2-ferracyclopentanes in which the isomer ratios were (within experimental error) unchanged from those of the starting materials. The isomer ratios of the products (XI) or (XII) were deter-

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[16] I. Fischler, K. Hildenbrand, and E. Koerner von Gustorf, *Angew. Chem. Internat. Edn.*, 1975, **14**, 54.

[17] H. Schmidbaur and W. Wolf, *Angew. Chem. Internat. Edn.*, 1973, **12**, 320.

[18] J. Dubac, P. Mazerolles, M. Lesbre, and M. Joly, *J. Organometallic Chem.*, 1970, **25**, 367.

[19] (*a*) C. Eaborn, D. R. M. Walton, and M. Chan, *J. Organometallic Chem.*, 1967, **9**, 251; (*b*) C. Eaborn, Z. S. Salih, and D. R. M. Walton, *ibid.*, 1972, **36**, 47.

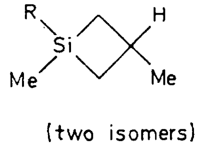
[20] J. Dubac, P. Mazerolles, and B. Serres, *Tetrahedron Letters*, 1972, 525, 3495; *Tetrahedron*, 1974, **30**, 749, 759.

[21] B. G. McKinnie, N. S. Bhacca, F. K. Cartledge, and J. Fayssoux, *J. Amer. Chem. Soc.*, 1974, **96**, 2637, 6819.

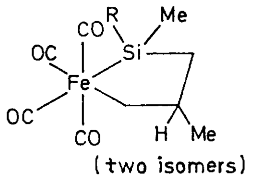
[22] D. Seyferth, Houng-Min Shih, J. Dubac, P. Mazerolles, and B. Serres, *J. Organometallic Chem.*, 1973, **50**, 39.

[23] J. Dubac, P. Mazerolles, B. Serres, and M. Joly, *Compt. rend.*, 1902, **C275**, 1049.

mined from their ^1H n.m.r. spectra in which the separate Si*Me* singlets of either (XI) or (XII) and also the SiO*Me* singlets of (XII) were clearly separated (*ca.* 4 Hz at 60 MHz). The C*Me*H methyl doublets from the predominant isomers of (XI) or (XII) could be located, but other features were less easy to distinguish. ^1H N.m.r. spectroscopic assignments to particular isomers cannot be made with certainty. However, in each case the more intense of the Si*Me* ^1H signals was at high field as in (IX) or (X), as had also been the case in the isomeric mixture of 2,2-dichloro-1,4-dimethyl-1-n-butyl-1-silacyclopentane obtained by $\ddot{C}Cl_2$ insertion, attributed to the *Z* isomer;[22] hence the stereochemical composition of the $[Fe(CO)_4]$ and $\ddot{C}Cl_2$ insertion products into (IX) or (X) is identical and is obtained with retention of configuration.

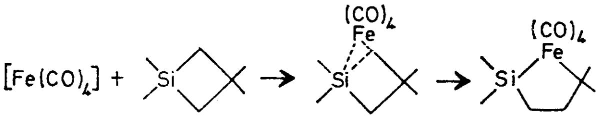


(IX) R = Bu^n; (X) R = MeO

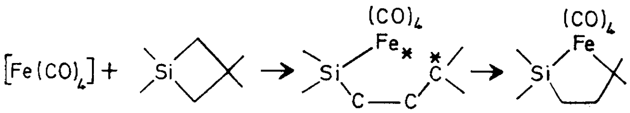


(XI) R = Bu^n; (XII) R = MeO

It is thus apparent that either a concerted reaction



path is followed or that any dipolar or diradical intermediate (represented schematically with two asterisks) must have a lifetime which is short compared with the duration of a racemising bond rotation. {The illustration



of $[Fe(CO)_4]$ as the attacking electrophile is subject to the reservations discussed earlier.}

EXPERIMENTAL

The compounds (III),[14,18] (V),[18] and (VII)[24] were prepared by published procedures. ^1H N.m.r. spectra [benzene solvent and reference (τ 2.73) unless otherwise stated] were recorded on Varian Associates T60 or HA100 spectrometers, and i.r. spectra (metal carbonyls in cyclohexane, otherwise as indicated) on a Perkin-Elmer 457 spectrometer. Molecular weights were measured either cryoscopically in benzene, or mass spectrometrically (m.s.) (A.E.I. MS9). All reactions were carried out under pure nitrogen using dried solvents. All the silaferracyclopentanes decompose slowly at room temperature and should be stored at −30 °C.

Decomposition of $[Fe_2(CO)_9]$ (cf. *Ref.* 25).—A suspension of $[Fe_2(CO)_9]$ (0.109 g, 0.300 mmol) in benzene (30 cm^3) was stirred at 21 °C, and the decomposition was followed by monitoring the change in the i.r. spectrum of the solution component with time. After 21 h no $[Fe_2(CO)_9]$ remained and the homogeneous green solution contained only $[Fe(CO)_5]$ and $[Fe_3(CO)_{12}]$, as shown by comparison with authentic spectra. The half-life for $[Fe_2(CO)_9]$ under these conditions was estimated graphically to be 1.6 h.

Reaction of $[Fe_2(CO)_9]$ *with* $\mathrm{Me_2\overline{SiCH_2CH_2C}(Me)H}$, (III).—To a stirred suspension of $[Fe_2(CO)_9]$ (1.091 g, 3.000 mmol) in benzene (30 cm^3) held just above its freezing point was added the silacyclobutane (III) (0.457 g, 4.000 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 three-quarters of the silacyclobutane into a single new product. Solvent, $[Fe(CO)_5]$, and excess of (III) 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 at low temperature from the filtrate *in vacuo*. Distillation (0 °C probe, 10^{-3} mmHg pressure) of the residue gave the colourless oily *2,2,2,2-tetracarbonyl-1,1,5-trimethyl-1-sila-2-ferracyclopentane*, (IVb) {0.600 g, 71% based on $[Fe_2(CO)_9]$}, m.p. 15—18 °C [Found: C, 42.6; H, 5.1; Fe, 20.0; O (by difference), 22.5; Si, 9.8%; *M* 282 (m.s.). $C_{10}H_{14}FeO_4Si$ requires C, 42.6; H, 5.0; Fe, 19.8; O, 22.7; Si, 9.95%; *M* 282]; ν(CO) at 2 082, 2 020, 1 999(sh), and 1 996 cm^{-1}; ^1H n.m.r. spectrum τ 7.8—9.2 (8 H, complex multiplets) (ring CH_2, CH, and CMe), 9.44 (3 H, s) (SiMe), and 9.57 (3 H, s) (SiMe).

Hydrolytic Degradation of (IVb).—Water (1 cm^3) was added to (IVb) (0·049 g, 0.174 mmol) in diethyl ether (10 cm^3) under nitrogen. The vessel was then opened to the air and the contents stirred vigorously for 1 h. The diethyl ether portion was separated, dried (Mg[SO$_4$]), and the ether removed *in vacuo* at low temperature. Distillation of the residue gave a colourless liquid, identified by g.l.c., ^1H n.m.r., and i.r. comparison with an authentic sample (see below) as pure Bu^sMe_2SiOH (0·016 g, 70%).

Preparation of Dimethyl-n-butylsilanol.—A 1 mol dm^{-3} solution of n-butyl-lithium (10 cm^3, 10.0 mmol) in diethyl ether was added dropwise with stirring to dichlorodimethylsilane (1.29 g, 10.0 mmol) in diethyl ether (10 cm^3) at 0 °C. G.l.c. investigation of the supernatant separated from the precipitated lithium chloride showed (besides diethyl ether) a single product (chlorodimethyl-n-butylsilane). The ether solution was added dropwise to a very vigorously stirred mixture of water (20 cm^3) and diethyl ether (10 cm^3). The water contained a trace of phenolphthalein and a 1 mol dm^{-3} solution of KOH was added dropwise, the rate of addition being controlled so that the aqueous component was always just alkaline. After all the chlorosilane had been hydrolysed in this way, the diethyl ether layer was separated, dried (Mg[SO$_4$]), and the solvent removed at low temperature *in vacuo*. Distillation gave dimethyl-n-butylsilanol (0·993 g, 75%), shown to be pure by g.l.c., i.r., and ^1H n.m.r. analyses; τ 8.3—9.7 (*ca.* 9 H, complex multiplets) (Bu^nSi) and 9.84 (3 H, s) (Me_2Si). [All the silanols described in this paper

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[24] H. Gilman and W. H. Atwell, *J. Amer. Chem. Soc.*, 1964, **86**, 5589.

[25] H. G. Cutforth and P. W. Selwood, *J. Amer. Chem. Soc.*, 1943, **65**, 2414.

displayed the expected volatility and g.l.c. retention times. I.r. spectra as thin films showed the strong broad hydrogen-bonded SiO–H stretch (3 280 cm^{-1} for $BuMe_2SiOH$; 3 350 cm^{-1} for $PhCH_2Me_2SiOH$) with the unassociated vibration visible in dilute CCl_4 solution (3 690 cm^{-1} for $BuMe_2SiOH$; 3 670 cm^{-1} for $PhCH_2Me_2SiOH$). Broad strong Si–O–Si absorption at *ca.* 1 060 cm^{-1} was absent. The hydroxyl proton was not in general located unequivocally in the ^1H n.m.r. spectra, but in one instance its presence was specifically checked: for $PhCH_2Me_2SiOH$ in dimethyl sulphoxide, Si*OH* appeared as a singlet at τ 4.47, vanishing when shaken with D_2O (*cf.* ref. 26).]

Preparation of Dimethyl-s-butylsilanol.—A similar procedure to that described above, but using $SiMe_2Cl_2$ (1.29 g, 10.0 mmol) and s-butyl-lithium (10.0 mmol) in n-pentane (20 cm^3 total volume) gave $SiMe_2Bu^sCl$. After substitution of diethyl ether for pentane, the previous hydrolysis procedure gave dimethyl-s-butylsilanol (0.542 g, 41%); τ 8.0—9.7 (*ca.* 6 H) (CH_3CH_2CH), 8.97 (3 H, d) {CMe[*J*(H–C–H_3) 6.5 Hz]}, and 9.88 (6 H, s) ($SiMe_2$).

Reaction of $[Fe_2(CO)_9]$ *with* $Me_2\overline{Si(o\text{-}C_6H_4)C}H_2$, (V).—Following a similar procedure to that described for (III), $[Fe_2(CO)_9]$ (1.009 g, 2.770 mmol) was treated in benzene (30 cm^3) with the silabenzocyclobutene (V) (0.340 g, 2.299 mmol). After 24 h, none of (V) remained in the solution (^1H n.m.r.). The mixture was worked up as before to yield the liquid 1,1,1,1-*tetracarbonyl*-2,2-*dimethyl*-2-*sila*-1-*ferra-indane*, (VIa) (0.611 g, 84% based on silabenzocyclobutene), m.p. *ca.* −55 °C [Found: C, 49.55; H, 3.8; Fe, 17.35; O (by difference), 20.1; Si, 9.1%; *M* 297 (in benzene), 316 (m.s.). $C_{13}H_{12}FeO_4Si$ requires C, 49.4; H, 3.8; Fe, 17.7; O, 20.2; Si, 8.9%; *M* 316]; ν(CO) at 2 089, 2 030, 2 013, and 2 008 cm^{-1}; ^1H n.m.r. spectrum in CH_2Cl_2 (τ 4.70) τ 2.77 (4 H, m) (Ph), 7.32 (2 H, s) (ring CH_2), and 9.32 (6 H, s) ($SiMe_2$). (Resonances at τ 7.40 and 9.43 occurred in benzene solution.)

Hydrolytic Degradation of (VIa).—Following a procedure similar to that described for (IVa), the iron complex was degraded to a single silanol, found to be benzyldimethylsilanol from its ^1H n.m.r. spectrum, and by g.l.c., ^1H n.m.r., and i.r. comparison with an authentic specimen.

Preparation of Benzyldimethylsilanol.—Benzylchlorodimethylsilane was prepared as in the following sequence and

$$SiMe_3Cl \xrightarrow[h\nu]{Cl_2} SiMe_2(CH_2Cl)Cl \xrightarrow{MgBrPh}$$

$$SiMe_2(CH_2Cl)Ph \xrightarrow[C_6H_6]{AlCl_3} SiMe_2(CH_2Ph)Cl$$

hydrolysed, as described above for the aliphatic silanols, to yield benzyldimethylsilanol, shown to be pure by g.l.c., ^1H n.m.r., and i.r. analyses; ^1H n.m.r. spectrum in CH_2Cl_2 τ 2.6—3.3 (5 H, complex m) (Ph), 7.86 (2 H, s) (CH_2), and 9.90 (6 H, s) ($SiMe_2$).

Reaction of $[Fe_2(CO)_9]$ *with* $Ph_2\overline{Si(o\text{-}C_6H_4)C}H_2$, (VII).—As for (III), $[Fe_2(CO)_9]$ (0·182 g, 0.500 mmol) and the silabenzocyclobutene (VII) (0.091 g, 0.333 mmol) were allowed to react in benzene (5 cm^3). After 48 h, all the original organosilicon heterocycle had been consumed (^1H n.m.r.). After removal of material volatile at room temperature, the residue was extracted with hexane (2 × 0.5 cm^3) and the extract stored at −30 °C. Crystallised $[Fe_3(CO)_{12}]$ was removed at −30 °C and the solvent was removed from the remaining solution to give a white gum. Addition of hexane (1.5 cm^3) and storage at −30 °C for several weeks with occasional agitation gave the white crystalline 1,1,1,1-*tetracarbonyl*-2,2-*diphenyl*-2-*sila*-1-*ferra-indane* (VIIIa), m.p. 78—79 °C (Found: C, 63.2; H, 3.6. $C_{23}H_{16}FeO_4Si$ requires C, 62.7; H, 3.7%); ν(CO) at 2 093, 2 037, 2 019, and 2 011 cm^{-1}; ^1H n.m.r. spectrum in CH_2Cl_2, τ 2.2—3.1 (14 H, complex m) (2Ph + C_6H_4), 6.80 (2 H, s) (ring CH_2). (In benzene a resonance at τ 6.80 was observed.)

Reaction of $[Fe_2(CO)_9]$ *with* $Bu^nMe\overline{SiCH_2C(Me)HC}H_2$,(IX),. *Isomer Ratio* 4 : 1.—As for (III), $[Fe_2(CO)_9]$ (1.310 g, 3.600 mmol) and the silacyclobutane isomer mixture[20] were allowed to react in benzene (30 cm^3). After 40 h, no $[Fe_2(CO)_9]$ remained but the silacyclobutane (IX) was not totally consumed (^1H n.m.r.). Solvent and $[Fe(CO)_5]$ were removed *in vacuo* and more $[Fe_2(CO)_9]$ (0.200 g, 0.550 mmol) and benzene (10 cm^3) were added. After a further 40 h, only a trace amount of (IX) remained. Using the work-up procedure as described previously for (III), an isomeric mixture of 2,2,2,2-*tetracarbonyldimethyl-n-butyl*-1-*sila*-2-*ferracyclopentanes*, (XI), was obtained [0.603 g, 62% based on (IX)], liquid at 0 °C, immobile resin at −78 °C [Found: C, 48.4; H, 6.4; Fe, 17.1; O (by difference) 19.3; Si, 8.8%; *M* 324 (m.s.). $C_{13}H_{20}FeO_4Si$ requires C, 48.2; H, 6.2; Fe, 17.2; O, 19.7; Si, 8.7%; *M* 324]; ν(CO) at 2 082, 2 019, 1 998(sh), and 1 996 cm^{-1}; τ 7.6—9.3 (14 H, complex m) (Bu^nSi, two ring CH_2 + ring CH), 8.82 (80% 3 H, d) {CMe, [*J*(H–C–H_3) 5.3 Hz]}, 9.40 (20%) + 9.47 (80%), and (3 H, two singlets) (SiMe) (Δν 4.3 Hz).

Reaction of $[Fe(CO)_9]$ *with* $(MeO)(Me)\overline{SiCH_2C(Me)HC}H_2$, (X), *Isomer Ratio* 7 : 3.—From $[Fe_2(CO)_9]$ (0.872 g, 2.400 mmol) and the silacyclobutane (X)[20] (0.260 g, 2.000 mmol) in benzene (20 cm^3) the procedure as for (III) gave an isomeric mixture of 2,2,2,2-*tetracarbonyl*-1-*methoxy*-1,4-*dimethyl*-1-*sila*-2-*ferracyclopentanes*, (XII) [0.366 g, 61% based on (X)], liquid at 0 °C, immobile resin at −78 °C [Found: C, 40.45; H, 4.9; Fe, 18.5; O (by difference), 27.1; Si, 9.1%; *M* 298 (m.s.). $C_{10}H_{14}FeO_5Si$ requires C, 40.3; H, 4.7; Fe, 18.7; O, 26.8; Si, 9.4%; *M* 298]; ν(CO) at 2 084, 2 024, 2 006(sh), 2 001, and 1 995(sh) cm^{-1}; τ 6.58 (70%) + 6.63 (30%) (3 H, two singlets) [MeOSi (Δν 2.8 Hz)], 7.7—9.2 (5 H, complex m) (two ring CH_2 + ring CH), 8.84 (70% 3 H, d) {CMe, [*J*(H–C–H_3) 4.5 Hz]}, and 9.31 (30%) + 9.36 (70%) (3 H, two singlets) [MeSi(Δν 3.4 Hz)].

We thank the S.R.C. for support.

[5/1788 *Received*, 18*th September*, 1975]

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