Metal–Silacyclobutane Complexes. Part 1. Derivatives of Iron and Manganese †

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The complexes $[M\{\overline{Si(Me)CH_2CH_2CH_2}\}]$ [$M = Fe(\eta\text{-}C_5H_5)(CO)_2$, $Fe(\eta\text{-}C_5H_5)(CO)(PMePh_2)$, $Fe(\eta\text{-}C_5H_5)(PMePh_2)_2$, or $Mn(CO)_5$] have been prepared and their reactions (substitution at Si or Fe, Fe–Si bond cleavage, or ring opening) studied. The complex $[Fe(\eta\text{-}C_5H_5)(CO)_2\{\overline{Si(Me)CH_2CH_2CH_2}\}]$ reacts with hydrogen chloride to give $[Fe(\eta\text{-}C_5H_5)(CO)_2H]$ and $Cl(Me)\overline{SiCH_2CH_2CH_2}$ (minor reaction) together with $[Fe(\eta\text{-}C_5H_5)(CO)_2\{SiMe(Pr^n)Cl\}]$ (major product), and with Cl_2 to afford $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ and $Cl(Me)\overline{SiCH_2CH_2CH_2}$, methanolic K[OH] cleaves first the Fe–Si bond and then the displaced silacyclobutane ring; catalytic polymerisation gives $\{-Si(Me)[Fe(\eta\text{-}C_5H_5)(CO)_2]CH_2CH_2CH_2-\}_n$. Hydrogen-1 n.m.r. and mass spectrometric data are presented.

ALTHOUGH the chemistry of both silacyclobutanes[1] and compounds containing metal–silicon bonds[2] is well established, there are no reports on silacyclobutanes substituted at silicon by metals. Our reasons for undertaking such a study were two-fold: first, since the two principal structural features under consideration (namely the strained organosilicon ring and the M–Si bond) were separately of interest, we wished to examine compounds in which their properties might be interdependent; secondly, since silaolefins[3] are not readily accessible we regarded the silacyclobutane function in these derivatives as a potential source of unsaturation at silicon, so that a silacyclobutylmetal group might be considered as analogous to a vinylmetal group. Primary interest derived from our earlier studies[4,5] of reactions between a transition-metal complex and a silacyclobutane. This paper is concerned with some transition-metal-substituted silacyclobutanes. The reactions of hydridosilacyclobutanes with transition-metal complexes, and silacyclobutanes substituted at silicon by iron or platinum arising from such reactions, are described elsewhere.[6] A preliminary account of some of the work has appeared.[7]

RESULTS AND DISCUSSION

Representative transition-metal-substituted 1-methyl-1-silacyclobutanes and some related compounds have been prepared (see Table and Scheme). Complex (7), $[Mn(CO)_5\{\overline{Si(Me)CH_2CH_2CH_2}\}]$, could not be entirely freed from contamination with the by-product $[Mn_2(CO)_{10}]$. Reactions, possibly competing, were expected to occur at (*i*) the transition metal, (*ii*) the transition-metal–silicon bond, and (*iii*) the silacyclobutane ring.

Preparation and Properties of Complexes $[Fe(\eta\text{-}C_5H_5)L(L')\{\overline{Si(Me)CH_2CH_2CH_2}\}]$ (1)—(3).—Sodium dicarbonyl(η-cyclopentadienyl)ferrate(–I) reacted with 1-chloro-1-methyl-1-silacyclobutane in tetrahydrofuran (thf) to eliminate sodium chloride and give $[Fe(\eta\text{-}C_5H_5)(CO)_2\{\overline{Si(Me)CH_2CH_2CH_2}\}]$ (1) in 56% yield. This result is noteworthy in two respects: first, since it illustrates once again[2] that $[Fe(\eta\text{-}C_5H_5)(CO)_2)]^-$, alone among transition-metal carbonyl anions, consistently gives silyltransition-metal products when treated with chlorosilanes in thf (see below); secondly, since the yield of complex (1) is greater than that (42,[8] 41%[9]) reported for the corresponding acyclic complex $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiMe_3)]$, prepared similarly, it is clear that (1) is not cleaved by $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$, present in excess under the conditions employed, although nucleophilic cleavage[1] is a common occurrence with silacyclobutanes. Complex (1) is an aromatic amber liquid at ambient temperature and shows all the characteristics expected from the constituent groups present. Diagnostic silacyclobutane i.r. absorptions[1,5] are at 1 183w, 1 114s, and 930m cm^{-1} (thin film) and a weak band at 281 cm^{-1} may be assigned to ν(Fe–Si).[2,5] (Other physical and spectroscopic properties of this and other transition-metal complexes will be found either in the Table or in the Experimental section.) The pure complex is sensitive to light, darkening considerably over 1 h in daylight; eventually, crystals of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ are precipitated. Irradiation of a n-hexane solution of complex (1) with u.v. light in the cavity of an e.s.r. spectrometer produced only a very weak and ill defined e.s.r. signal.

Ultraviolet irradiation of a mixture of complex (1) and methyldiphenylphosphine in n-hexane enabled replacement of either one or both carbonyl groups at iron to be effected, yielding the crystalline complexes $[Fe(\eta\text{-}C_5H_5)(PMePh_2)L\{\overline{Si(Me)CH_2CH_2CH_2}\}]$ [$L = CO$ (2) or $PMePh_2$ (3)]. This parallels the substitution pattern

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† No reprints available.

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

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

[3] L. E. Gusel'nikov, N. S. Nametkin, and V. M. Vdovin, *Accounts Chem. Res.*, 1975, **8**, 18.

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

[5] C. S. Cundy, M. F. Lappert, J. Dubac, and P. Mazerolles, *J.C.S. Dalton*, 1976, 910; C. S. Cundy and M. F. Lappert, *ibid.*, 1978, in the press

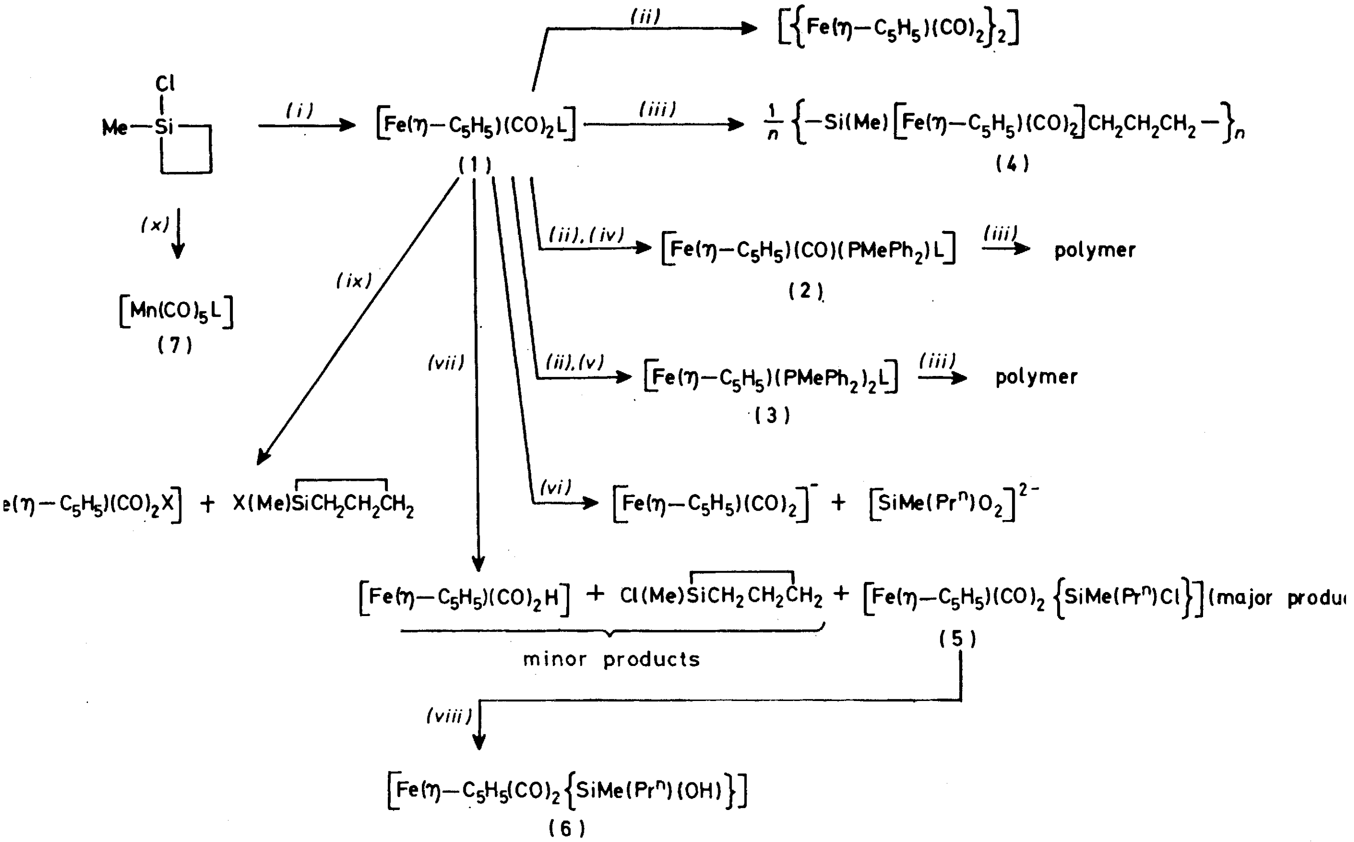
[6] C. S. Cundy, M. F. Lappert, and Choi-Kwan Yuen, *Inorg. Chem.*, in the press.

[7] C. S. Cundy and M. F. Lappert, *J. Organometallic Chem.*, 1973, **57**, C72.

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

[9] R. B. King and K. H. Pannell, *Inorg. Chem.*, 1968, **7**, 1510.

found[9] for the acyclic analogue $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)_2(SiMe_3)}]$, but contrasts with the behaviour of the related endocyclic iron complex $[\mathrm{Fe(CH_2CH_2CH_2SiMe_2)(CO)_4}]$,[5] where loss of the organosilicon function occurred on treatment with similar donors. Only monosubstituted products were reported from the reactions between $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)_2(SiMe_3)}]$ and $\mathrm{PPh_3}$ or $\mathrm{P(OPh)_3}$. In order to distinguish between phosphine ligand differences and possible enhanced steric accessibility of the iron atom in complex (1) compared with its acyclic Fe–Si counterpart, triphenylphosphine substitution in complex (1) was followed by ^{1}H n.m.r. spectroscopy under similar reaction conditions: no trace of disubstituted product was detected. Further n.m.r. experiments in benzene showed the formation of a monosubstituted derivative as the major product also with tri-n-butylphosphine, and a more complex mixture from 1,2-bis(diphenylphosphino)ethane. 2,2′-Bipyridine (bipy) gave an immediate red-purple precipitate. The yellow supernatant solution showed only unchanged complex (1) by ^{1}H n.m.r. spectroscopy, while an acetone extract of the precipitate appeared to show only resonances due to bipy.



SCHEME Synthesis and some reactions of $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)_2L}]$ (1) and preparation of $[\mathrm{Mn(CO)_5L}]$ (7) [L = $\mathrm{Si(Me)CH_2CH_2CH_2}$]. (*i*) $\mathrm{Na[Fe(\eta\text{-}C_5H_5)(CO)_2]}$; (*ii*) $h\nu$, $\mathrm{n\text{-}C_6H_{14}}$; (*iii*) trace amount of $[\{\mathrm{Pt(C_2H_4)Cl_2}\}_2]$; (*iv*) $\mathrm{PMePh_2}$; (*v*) 2 $\mathrm{PMePh_2}$; (*vi*) K[OH]–MeOH; (*vii*) HCl; (*viii*) $\mathrm{H_2O}$; (*ix*) $\mathrm{X_2}$ (X = Cl or Br), $\mathrm{CCl_4}$; (*x*) $\mathrm{Na[Mn(CO)_5]}$, $\mathrm{n\text{-}C_6H_{14}}$

Physical data for the complexes

Complex	Colour	M.p. (θ_c/°C)	ν(CO) (cm^{-1})[a]	N.m.r. spectrum (τ)		
				Si*Me*[b,c]	$(CH_2)_3$ or Pr^n[b]	Other resonances[b]
(1) $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)_2\{Si(Me)CH_2CH_2CH_2\}}]$	Amber	−17 to −15	2 002vs, 1 950vs	9.20	7.46 (2 H, qnt), 8.51 (4 H, t), ^3J(HH) 8.0 Hz	5.84 (5 H, s, $\mathrm{C_5H_5}$)
(2) $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)(PMePh_2)\{Si(Me)CH_2CH_2CH_2\}}]$	Yellow	106—107	1 916	9.30	6.8—7.9 (2 H, br m), 8.1—*ca.* 9.1 (4 H, br m)	5.80 (5 H, d, $\mathrm{C_5H_5}$)[^3J(PH) 1.5 Hz], 8.31 (3 H, d, $\mathrm{PCH_3}$) [^2J(PH) 8.0 Hz]
3) $[\mathrm{Fe(\eta\text{-}C_5H_5)(PMePh_2)_2\{Si(Me)CH_2CH_2CH_2\}}]$	Orange	176—177		9.41	6.4—7.6 (2 H, br m), *ca.* 8.2—8.7 (4 H, br m)	5.90 (5 H, t, $\mathrm{C_5H_5}$)[^3J(PH) 1.8 Hz], 8.30 (3 H, virtual t, $\mathrm{PCH_3}$) [^2J(PH) (between outer lines) 7.2 Hz]
(4) $\{\mathrm{\text{-}Si(Me)[Fe(\eta\text{-}C_5H_5)(CO)_2]CH_2CH_2CH_2\text{-}}\}_n$	Pale grey-brown	110—115	1 931vs,br,[d] 1 990vs,br	9.21br	7.6—9.6 (6 H, br)	5.31 (5 H, br s, $\mathrm{C_5H_5}$)
(5) $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)_2\{SiMe(Pr^n)Cl\}}]$	Amber	17—18	2 019, 1 969w, 2 012, 1 958s	9.08	7.9—9.2 (7 H, m)	5.78 (5 H, s, $\mathrm{C_5H_5}$)
(6) $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)_2\{SiMe(Pr^n)(OH)\}}]$	Pale amber	[e]	2 002(sh), 1 999vs, 1 944vs	9.30	8.0—9.2 (7 H, m)	5.75 (5 H, s, $\mathrm{C_5H_5}$)[f]
(7) $[\mathrm{Mn(CO)_5\{Si(Me)CH_2CH_2CH_2\}}]$	Yellow-orange	*ca.* 0	2 095m, 2 003(sh), 1 995s, 1 963w	9.23	7.58 (2 H, qnt), 8.56 (4 H, t) [^3J(HH) 8.0 Hz]	

[a] In cyclohexane. [b] In benzene (τ 2.73). t = triplet, qnt = quintet. [c] Singlet. [d] In benzene. [e] See Experimental section. [f] SiOH not observed.

As with $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiMe_3)]$,[8,10] complexes (1)—(3) showed considerable stability towards either dioxygen or water. Thus, solutions in dry benzene stirred under oxygen developed a slight brown flocculent precipitate over 1 h, but no decomposition was detectable against an internal standard by ^1H n.m.r. spectroscopy. Solutions in diethyl ether stirred with deoxygenated water did not change in appearance or in the n.m.r. spectra over 1 h. However, pure liquid (1) showed appreciable decomposition on exposure to moist air at 21 °C in <1 h. The complex was quite stable for at least 20 h in methanol under dinitrogen at 21 °C.

All the complexes (1)—(3) displayed characteristic silacyclobutane behaviour in being catalytically polymerised[4] by $[\{Pt(C_2H_4)Cl_2\}_2]$ in benzene solution. Under comparable conditions (0.02 mmol of complex in 0.5 cm^3 of benzene; 0.01 mmol of $[\{Pt(C_2H_4)Cl_2\}_2]$ added), the following amounts of complex remained unpolymerised after 30 min at 21 °C: 38 (1), 14 (2), and 0% (3), so that reactivity with respect to the electrophilic catalyst increased with increasing phosphine substitution (and thus presumably electron density) at iron. A similar reactivity sequence was found towards $[Fe_2(CO)_9]$, which is believed to act as an electrophile in the reaction[5] giving silaferracyclopentanes with most silacyclobutanes. The amounts of complex remaining unchanged under the usual[5] reaction conditions were: 100 (1), 30 (2), and 0% (3). However, no discrete products could be detected for complexes (2) or (3), the broad new ^1H n.m.r. signals observed being indicative of polymer formation. Like $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiMe_3)]$,[10] complex (1) exhibits fair thermal stability, 96% being recovered unchanged after heating at 100 °C for 1 h. However, the presence of 0.25 mol Pt/Fe% of $[\{Pt(C_2H_4)Cl_2\}_2]$ drastically altered the behaviour of complex (1), 65% conversion into the solid polymer $\{\text{-}Si(Me)[Fe(\eta\text{-}C_5H_5)(CO)_2]CH_2CH_2CH_2\text{-}\}_n$ (4) occurring under the same conditions. The polymer was obtained as an analytically pure powder by precipitation from benzene with n-hexane. It displayed the expected spectroscopic properties and may be considered as a model for a type of resin-bound transition-metal catalyst, formed from a monomeric complex by polymerisation of a functional ligand.

Complex (1) reacted rapidly with dichlorine in carbon tetrachloride to afford equimolar amounts of $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ and $Cl(Me)\overline{SiCH_2CH_2C}H_2$ as the major products (60%). Spectroscopic examination of the reaction solution indicated only trace amounts of other materials, oxidative decomposition presumably completing the product balance. Addition of Cl_2 in excess of the equimolar quantity caused very extensive decomposition of the reaction mixture. Thus, in terms of isolable products, attack of Cl_2 on complex (1) gave almost exclusively Fe–Si bond cleavage; the silacyclobutane ring was unaffected. This parallels the behaviour found for other silacyclobutanes (run as control reactions under similar conditions), $Cl(Me)\overline{SiCH_2CH_2C}H_2$ showing only a small change after 20 h and $Me_2\overline{SiCH_2CH_2C}H_2$ being transformed [mainly into $SiMe_2(CH_2CH_2CH_2Cl)Cl$] over several hours (67% after 5.5 h). The analogous reaction between (1) and dibromine was studied spectroscopically. A near-quantitative Fe–Si cleavage, to yield $[FeBr(\eta\text{-}C_5H_5)(CO)_2]$ and a compound with properties consistent with those expected for the unknown $Br(Me)\overline{SiCH_2CH_2C}H_2$, occurred with equimolar proportions of reactants. Excess of Br_2 caused extensive decomposition.

The reaction between complex (1) and anhydrous HCl was of considerable interest since both $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiMe_3)]$[10] and $Me_2\overline{SiCH_2CH_2C}H_2$[1,5] are readily cleaved by this reagent. Thus, intramolecular competition was anticipated. Also, although $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiMe_3)]$ is cleaved[10] in the sense $[Fe(\eta\text{-}C_5H_5)(CO)_2H] + SiR_3Cl$, the complex $[Fe(\eta\text{-}C_5H_5)(CO)_2\{SiMe_2(CH{=}CH_2)\}]$ has been shown[11] to react in the opposite sense to afford $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ and SiR_3H, while $[Fe(\eta\text{-}C_5H_5)(CO)_2\{SiPh_2(CH{=}CH_2)\}]$ did not react.[12] Complex (1) reacted rapidly with excess of hydrogen chloride under mild conditions to give (*i*) cleavage of the Fe–Si bond to yield $[Fe(\eta\text{-}C_5H_5)(CO)_2H]$ and $Cl(Me)\overline{SiCH_2CH_2C}H_2$ (20%), (*ii*) cleavage of the silacyclobutane ring to afford the new complex $[Fe(\eta\text{-}C_5H_5)(CO)_2\{SiMe(Pr^n)Cl\}]$ (5) (70%), and (*iii*) a mixture of unidentified minor products (10%). The iron hydride was the only η-cyclopentadienyliron product detected and no evidence for formation of $H(Me)\overline{SiCH_2CH_2C}H_2$ was obtained. Mixture (*iii*) probably consists largely of byproducts containing Si–O bonds formed from side reactions[10] involving carbonyl species. Although it was found that $Me_2\overline{SiCH_2CH_2C}H_2$ was quantitatively transformed into $SiMe_2(Pr^n)Cl$ under the same conditions, $Cl(Me)\overline{SiCH_2CH_2C}H_2$ [either with or without complex (1) present] was unaffected. Furthermore, the Fe–Si bond in complex (5), unlike that in (1), was resistant to attack by HCl. Presumably the inductive effect of the chloride ligand on silicon is responsible for the relative resistance of the chlorosilane products to electrophilic attack by HCl. It is noteworthy that, because of the inertness of these reaction products towards excess of HCl, there is no ambiguity concerning their mode of formation. This is in contrast to the reaction of complex (1) with methanolic K[OH] discussed below. The complex $[Fe(\eta\text{-}C_5H_5)(CO)_2\{SiMe(Pr^n)Cl\}]$ (5), in common with the related species $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiMe_2Cl)]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiMeCl_2)]$,[13] showed more than two metal-carbonyl stretches in its i.r. spectrum at room

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[10] M. A. Nasta and A. G. MacDiarmid, *J. Organometallic Chem.*, 1968, **18**, P11.

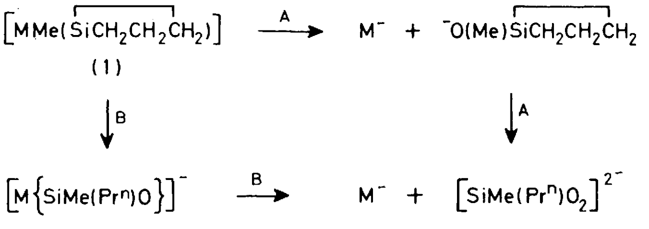
[11] W. Malisch and P. Panster, *J. Organometallic Chem.*, 1974, **64**, C5.

[12] R. J. P. Corriu and W. E. Douglas, *J. Organometallic Chem.*, 1973, **51**, C3.

[13] Ref. 2, p. 286, and also ref. 164 therein.

temperature. The three possible conformers of (5) could give rise to a maximum of six carbonyl peaks, of which two pairs were observed.

As with hydrogen chloride, the reaction between methanolic K[OH] and complex (1) might be expected to involve intramolecular competition, since both the Fe–Si bond in $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiMe_3)]$ [10] and the ring in silacyclobutanes [1] are cleaved by this reagent. It was found (by i.r. and ^1H n.m.r. spectroscopy) that dissolution of complex (1) in methanol containing an excess of K[OH] caused destruction of the neutral complex and formation of the anions $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ and $[SiMe(Pr^n)O_2]^{2-}$. However, there is, as shown below $\{M = [Fe(\eta\text{-}C_5H_5)(CO)_2]\}$, ambiguity (paths A or B) in the manner in which these ions are formed.



A series of experiments was carried out to differentiate between these alternatives. The disiloxane $CH_2CH_2CH_2Si(Me)OSi(Me)CH_2CH_2CH_2$ was chosen to represent the intermediate in path A, and the complex $[Fe(\eta\text{-}C_5H_5)(CO)_2\{SiMe(Pr^n)(OH)\}]$ (6) (see below) was selected to represent the intermediate in path B. Under conditions where complex (1) was totally cleaved within 15 min, the above disiloxane was completely transformed (into the same organosilicon product) within 10 min. Under the same conditions, complex (6) underwent no appreciable change in 15 min; after 24 h, 70% conversion into the same product had occurred. We thus conclude that the attack of methanolic K[OH] on complex (1) proceeds by path A.

It is also known [10] that, under certain specified conditions, *ca.* 50% of the $SiMe_3$ groups present in a sample of $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiMe_3)]$ are released as $SiMe_3(OMe)$ and $O(SiMe_3)_2$ by methanolic K[OH] in 1 h. Using solutions more dilute by a factor of ten, we found >75% cleavage for complex (1) in the same time. Thus, under identical conditions, cleavage of the cyclic compound appears to be faster than its acyclic analogue. This is in accord with the observations of Sommer *et al.*[14] on substitution at constrained endocyclic silicon where similar enhancements in rate were observed in, for example, displacement of H^- by $[OH]^-$. It was suggested that a five-co-ordinate intermediate, involving *d*-orbital participation by silicon, was involved, with the entering and leaving groups *cis* to one another [S_N2(Si) mechanism].

The complex $[Fe(\eta\text{-}C_5H_5)(CO)_2\{SiMe(Pr^n)(OH)\}]$ (6) is most conveniently prepared by controlled hydrolysis of $[Fe(\eta\text{-}C_5H_5)(CO)_2\{SiMe(Pr^n)Cl\}]$ (5). It may be noted that the transformations of complex (1) into (4), (5), or (6) represent reactions at silicon co-ordinated to a transition metal which leave the transition metal–silicon bond intact. Such reactions are rare,[2] although the $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiX_3)]$ system seems particularly stable.[15]

A suspension of sodium pentacarbonylmanganate(–I) in n-hexane reacted with 1-chloro-1-methyl-1-silacyclobutane to yield a yellow-orange volatile liquid containing the complex $[Mn(CO)_5\{Si(Me)CH_2CH_2CH_2\}]$ (7), together with $[Mn_2(CO)_{10}]$ and the disiloxane $CH_2CH_2CH_2Si(Me)OSi(Me)CH_2CH_2CH_2$. All the disiloxane and a large proportion of the manganese carbonyl could be removed by column chromatography and distillation. However, the properties of $[Mn_2(CO)_{10}]$ and (7) are so similar from the aspect of separation processes that appreciable quantities of (7) uncontaminated with $[Mn_2(CO)_{10}]$ were not obtained, and the data reported are those found by difference from mixtures. Characteristic silacyclobutane i.r. bands (thin film) were seen at 1 182w, 1 116m, and 925w cm^{-1}.

It has been noted by several workers [2,16] that reactions between chlorosilanes and transition-metal carbonyl anions, particularly in ether solvents, usually fail to yield products containing transition-metal–silicon bonds, compounds with O–Si bonds predominating. Rearrangements may be involved, as in $[Co(CO)_4(SiMe_3)]$,[17] which is completely transformed within 1 h into more complex products simply by dissolving in thf at room temperature. The best results are usually obtained either with hydrocarbon solvents or in the absence of solvents. Our findings regarding reactions between $Cl(Me)SiCH_2CH_2CH_2$ and a carbonyl anion of Mo, Mn, or Co are summarised as follows: (*i*) in n-hexane, $[Mn(CO)_5]^-$ gave complex (7), disiloxane $CH_2CH_2CH_2Si(Me)OSi(Me)CH_2CH_2CH_2$, and $[Mn_2(CO)_{10}]$; (*ii*) in thf, $[Mn(CO)_5]^-$ gave a minute amount of complex (7), disiloxane, and a red substance containing no organosilicon residue (i.r.), which may be related to the product described in a similar reaction involving $SiPh_3Cl$;[18] and (*iii*) in n-hexane, no transition-metal–silicon product was obtained from $[Co(CO)_4]^-$, $[Co(CO)_3(PPh_3)]^-$, or $[Mo(\eta\text{-}C_5H_5)(CO)_3]^-$.

No reaction occurred between $H(Me)SiCH_2CH_2CH_2$ and $[Mo(\eta\text{-}C_5H_5)(CO)_3H]$ in n-pentane up to reflux temperature. No ring-opening HX addition reaction occurred between $Me_2SiCH_2CH_2CH_2$ and $[Co(CO)_4H]$ between 6 and 21 °C, although, in a system related to

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[14] L. H. Sommer, O. F. Bennett, P. G. Campbell, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, 1957, **79**, 3296; and refs. cited in ref. 1 of the present paper, pp. 87—88.

[15] T. J. Marks and A. M. Seyam, *J. Organometallic Chem.*, 1971, **31**, C62; M. Höfler and J. Scheuren, *ibid.*, 1973, **55**, 177.

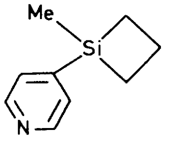
[16] B. K. Nicholson, B. H. Robinson, and J. Simpson, *J. Organometallic Chem.*, 1974, **66**, C3.

[17] W. M. Ingle, G. Preti, and A. G. MacDiarmid, *J.C.S. Chem. Comm.*, 1973, 497.

[18] M. D. Curtis, *Inorg. Chem.*, 1972, **11**, 802.

dihalogen addition, $TiCl_4$ gave $[TiCl_3\{SiMe_2(CH_2CH_2CH_2Cl)\}]$.[19]

In summary, silacyclobutyltransition-metal complexes combine the properties of their transition-metal and organosilicon constituents rather than display new corporate features. Although such complexes are unique, related compounds have recently been reported. The substituted pyridine (8) has been used as a ligand to Co^{II} and Ni^{II},[20] and η-arene complexes (9) (R = Ph, X = CH_2; R = Me, X = $SiMe_2$) have been prepared.[21] Attempts to prepare η-arene complexes from (10) and $[Cr(CO)_6]$ failed.[19] We also found only polymerisation and decomposition in attempts to prepare similar complexes from (10) or its tetracarbonyliron adduct (11) and $[W(CO)_3(CNMe)_3]$.



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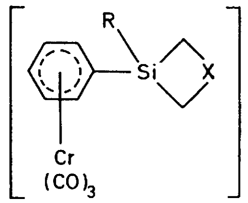

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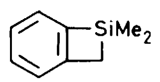

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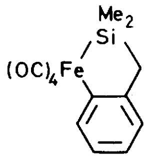

(11)

EXPERIMENTAL

Experimental procedures and instrumentation were as described previously.[5,7] Silacyclobutanes were prepared by published methods.[1]

Preparation of Complex (1).—A solution of $Na[Fe(\eta-C_5H_5)(CO)_2]$ was prepared from $[\{Fe(\eta-C_5H_5)(CO)_2\}_2]$ (10.64 g, 0.030 0 mol) and 1% sodium amalgam (Na, 2.064 g, 0.090 0 mol; Hg, 206 g) in thf (180 cm^3). To the decanted solution (120 cm^3) in an apparatus screened from the light was added dropwise over 45 min at 21 °C a solution of 1-chloro-1-methyl-1-silacyclobutane (4.820 g, 0.040 mol) in thf (40 cm^3). After stirring for 19 h, volatiles were removed *in vacuo* and the residual red-brown gum was extracted with n-hexane (50 cm^3). Volatiles were removed from the filtrate *in vacuo* to leave a red-brown oil. Extraction with more n-hexane (50 cm^3), filtration, and solvent removal, followed by molecular distillation (50 °C, 10^{-3} mmHg; * 12 °C condenser) of the resulting oil gave the amber liquid *dicarbonyl*(η*-cyclopentadienyl*)(1*-methyl-*1*-silacyclobutan-*1*-yl*)*iron*(II) (1) (5.818 g, 56%), d_4 = *ca.* 1.22 g cm^{-3} at 20 °C [Found: C, 50.2; H, 5.5; Fe, 21.0; O (by difference), 12.9; Si, 10.45%; *M* 251 (cryoscopically in benzene), 262 (mass spectrometrically). $C_{11}H_{14}FeO_2Si$ requires C, 50.4; H, 5.4; Fe, 21.3; O, 12.2; Si, 10.7%; *M* 262]; the mass spectrum included prominent ions at *m/e* 262 (M^+), 234 ($[M - CO]^+$), 186 $\{[Fe(C_5H_5)_2]^+\}$, and 206 ($[M - 2CO]^+$).

Reaction of Complex (1) *with Methyldiphenylphosphine to give Complexes* (2) *and* (3).—Methyldiphenylphosphine (0.704 g, 3.510 mmol) was added to a solution of complex (1) (0.613 g, 2.340 mmol) in n-hexane (20 cm^3) in a Pyrex tube to form a column (8 × 2 cm) of liquid. This was irradiated at a distance of 2 cm from a Hanovia 125-W medium-pressure mercury lamp, and the reaction was followed by ^1H n.m.r. spectroscopy. After 8 h, organometallic compounds in solution were: (1), 20; (2), 60; and (3), 20%. Crystallisation of the mixture gave complex (2) (0.004 g) and (3) (0.116 g). Column chromatography (Florisil) of the residue in n-hexane, eluting with benzene–hexane mixtures, gave more (2) (0.131 g) and (3) (0.015 g). Total yields: (2) (0.135 g, 13%); (3) (0.131 g, 9%). For *carbonyl*(η*-cyclopentadienyl*)(*methyldiphenylphosphine*)(1*-methyl-*1*-silacyclobutan-*1*-yl*)*iron*(II) (2) [Found: C, 63.9; H, 6.5%; *M* 434 (mass spectrometrically). $C_{23}H_{27}FeOPSi$ requires C, 63.6; H, 6.3%; *M* 434], the mass spectrum showed prominent ions at *m/e* 434 (M^+), 406 ($[M - CO]^+$), 378 ($[M - CO - C_2H_4]^+$), 364 ($[M - C_3H_6Si]^+$), 321 ($[M - CO - C_4H_9Si]^+$), and 121 ($[M - CO - C_{13}H_{13}P - C_4H_9Si]^+$). For (η*-cyclopentadienyl*)*bis*(*methyldiphenylphosphine*)(1*-methyl-*1*-silacyclobutan-*1*-yl*)*iron*(II) (3) [Found: C, 68.9; H, 6.9%; *M* 606 (mass spectrometrically). $C_{35}H_{40}FeP_2Si$ requires C, 69.3; H, 6.65%; *M* 606], the mass spectrum showed prominent ions at *m/e* 606 (M^+), 520 ($[M - C_4H_9Si - H]^+$), 506 ($[M - C_4H_9Si - CH_3]^+$), and 406 ($[M - C_{13}H_{13}P]^+$).

Photolysis of Complex (1).—Complex (1) (0.060 g, 0.229 mmol) in benzene (0.50 cm^3) in a soda-glass n.m.r. tube was irradiated with u.v. light. Over several hours the solution darkened from yellow to deep red-orange and the ^1H n.m.r. spectrum in the τ 5.4—5.9 ($\eta-C_5H_5$) and 7—10 (CH_2, CH_3) regions became very complex. After 12.5 h only a small amount of (1) remained. The solution was poured on to a Florisil chromatography column set up in hexane, and eluted with hexane–dichloromethane mixtures to give amber (1) (0.05 g, 8%), maroon $[\{Fe(\eta-C_5H_5)(CO)_2\}_2]$ (0.010 g, 25%), and a trace amount of a green material which did not appear to be $[\{Fe(\eta-C_5H_5)(CO)\}_4]$, in addition to gum-like, predominantly organic, materials.

Pyrolysis of Complex (1).—Complex (1) (0.085 g) was sealed in a Pyrex ampoule under 10 mmHg pressure of dinitrogen. The ampoule was wrapped in foil to exclude light and heated at 100 °C. After 2 h, the cooled ampoule was opened, and the complex (darkened slightly in colour) was purified by molecular distillation (recovery 0.082 g, 96.5%). Similarly, 38% of the pure complex was recovered after 24 h.

Catalytic Polymerisation of Complex (1) *to give Complex* (4).—Complex (1) (0.358 g, 1.368 mmol) and $[\{Pt(C_2H_4)Cl_2\}_2]$ (0.001 g, 0.001 7 mmol) were sealed as in the above pyrolysis. After 1 h at 100 °C the mobile amber complex was converted into a brown syrup; after 2 h it had solidified to a brown resin. The cooled tube was opened and the contents were taken up in benzene (3 cm^3). n-Hexane (10 cm^3) was added with stirring. After 18 h, decantation gave the crude polymer, the decantate containing (i.r.) complex (1) and $[\{Fe(\eta-C_5H_5)(CO)_2\}_2]$. Reprecipitation from benzene with hexane gave the pure *polymer* $\{-Si(Me)[Fe(\eta-C_5H_5)(CO)_2]CH_2CH_2CH_2-\}_n$ (4) (0.233 g, 65%) [Found:

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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C, 50.2; H, 5.55%. $(C_{11}H_{14}FeO_2Si)_n$ requires C, 50.4; H, 5.4%].

Reaction of Complex (1) *with Dichlorine*.—To the complex (0.041 g, 0.155 mmol) in carbon tetrachloride (2.0 cm^3) was added slowly a solution of dichlorine in the same solvent (0.62 cm^3 of a 0.25 mol dm^{-3} solution containing 0.155 mmol Cl_2). After 10 min, volatile material was removed *in vacuo* to give a clear colourless solution which was found (g.l.c. and ^{1}H n.m.r.) to contain $Cl(Me)\overline{SiCH_2CH_2CH_2}$ (60% yield). The red residue was extracted with benzene (0.7 cm^3), the decanted extract evaporated, and the product shaken with hexane (1 cm^3) and left at 0 °C. Decantation gave an orange solution containing (i.r.) complex (1), $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$, and a trace amount of an unidentified material (possibly $[Fe(\eta\text{-}C_5H_5)(CO)_2\{SiMe(CH_2CH_2CH_2Cl)Cl\}]$). The i.r. and ^{1}H n.m.r. spectrum of the residual red microcrystalline solid showed it to be $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ (0.019 g, 58%). A similar experiment using (1) : Cl_2 = 1 : 2 gave a dark mixture.

Reaction of Complex (1) *with Dibromine*.—To the complex (0.010 g, 0.039 mmol) in CCl_4 (0.5 cm^3) was added an equimolar amount of dibromine (0.049 g cm^{-3}) in CCl_4. A clean transformation of (1) into $[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$ and an organosilicon compound having the expected characteristics of the unknown $Br(Me)\overline{SiCH_2CH_2CH_2}$ was observed by i.r. and ^{1}H n.m.r. methods. Addition of excess of Br_2 caused extensive decomposition.

Reaction of Complex (1) *with Hydrogen Chloride; Preparation of Complex* (5).—(*i*) A solution of complex (1) (0.247 g, 0.941 mmol) in benzene (1 cm^3) was degassed and frozen (−78 °C) *in vacuo*. Hydrogen chloride at 650 mmHg pressure was then admitted and the mixture allowed to warm to 10 °C; after stirring for 5 min the pressure had fallen to 550 mmHg. Excess of HCl was then removed by cycles of freezing (−78 °C) and thawing *in vacuo*, and the resulting (darker orange) solution was examined by ^{1}H n.m.r. spectroscopy. All the material volatile at 21 °C was then condensed *in vacuo* into a receiver at −196 °C. This material was analysed by g.l.c. and ^{1}H n.m.r., and the residue (in C_6H_6) by ^{1}H n.m.r. spectroscopy. Complex (1) had been converted into a mixture of volatile $[Fe(\eta\text{-}C_5H_5)(CO)_2H]$ [τ 21.61 (FeH); *cf.*,[22] 21.91] and $Cl(Me)\overline{SiCH_2CH_2CH_2}$ (20%), and the relatively involatile new complex $[Fe(\eta\text{-}C_5H_5)(CO)_2\{SiMe(Pr^n)Cl\}]$ (5) (70%). Very small amounts of other unidentified materials were apparent, but no $SiMe(Pr^n)Cl_2$ was detected.

(*ii*) The above experiment was repeated using complex (1) (0.493 g, 1.882 mmol) in benzene (10 cm^3). The residual red oil, after removal of material volatile at 21 °C *in vacuo*, was purified by molecular distillation (50 °C, 10^{-3} mmHg; 0 °C probe) to give the amber liquid *dicarbonyl*[*chloro*(*methyl*)-*n-propylsilyl*](*η-cyclopentadienyl*)*iron*(II) (5) (0.381 g, 68%) [Found: C, 44.2; H, 4.9; Cl, 11.8; Fe, 18.4; O (by difference) 11.3; Si, 9.4%; *M* 298 (mass spectrometrically). $C_{11}H_{15}ClFeO_2Si$ requires C, 44.2; H, 5.1; Cl, 11.9; Fe, 18.7; O, 10.7; Si, 9.4%; *M* 298]; the mass spectrum included prominent ions at *m/e* 298 (M^+), 270 ($[M - CO]^+$), 263 ($[M - Cl]^+$), 255 ($[M - CO - CH_3]^+$), 245 ($[M - 2CO]^+$), 242 ($[M - CO - Cl]^+$), 227 ($[M - 2CO - CH_3]^+$), and 186 $\{[Fe(C_5H_5)_2]^+\}$.

Hydrolysis of Complex (5) *to give* (6).—A solution of complex (5) (0.069 g, 0.232 mmol) in diethyl ether (4 cm^3) was dropped into a rapidly stirred mixture of ether (10 cm^3) and water (5 cm^3) using K[OH], with a trace amount of phenolphthalein, to keep the aqueous layer just alkaline. When the addition was complete, the ether layer was separated, combined with ether washings of the aqueous layer, and dried ($Mg[SO_4]$). Removal of ether *in vacuo* and molecular distillation of the residue gave the viscous, pale amber, liquid *dicarbonyl*(*η-cyclopentadienyl*)[*hydroxy*(*methyl*)-*n-propylsilyl*]*iron*(II) (6) (0.055 g, 85%) (Found: C, 46.9; H, 6.2. $C_{11}H_{16}FeO_3Si$ requires C, 47.2; H, 5.8%). Infrared spectrum (thin film, cm^{-1}): 3 630m, 3 350s, br (SiO–H); and SiOSi (*ca.* 1050vs, br) *absent*. On cooling, the complex gradually solidified to a glass.

Reaction of Complex (1), (6), *or Bis*(1-*methyl*-1-*silacyclobutan*-1-*yl*) *Ether with Methanolic Potassium Hydroxide Solution*.—(*i*) Complex (1) (0.013 g, 0.050 mmol) was added to 0.5 cm^3 of a solution of K[OH] in methanol (1 mol dm^{-3}) in an n.m.r. tube. After 15 min the solution had changed from yellow to orange and ^{1}H n.m.r. spectroscopy showed total conversion of (1) into new materials, the SiMe singlet of (1) being replaced by a new singlet of equal intensity 46 Hz to higher field, with corresponding changes in the methylene proton pattern. Volatile material was distilled off *in vacuo* and the residue extracted, first with benzene (0.5 cm^3) and then with thf (0.5 cm^3). Only methanol could be detected (g.l.c. and ^{1}H n.m.r.) in the distillate. The benzene solution showed only a small amount of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$. The yellow-brown thf solution showed ν(CO) at 1 876 and 1 788 cm^{-1} {*cf.*,[23] $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ at 1 858 and 1 770 cm^{-1} (KBr)} in addition to weak absorptions due to $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$.

(*ii*) Experiment (*i*) was repeated using the ether (0.009 g, 0.050 mmol) in place of complex (1). A rapid reaction occurred to give (within 10 min) the same organosilicon product as in (*i*) together with a trace amount of another material.

(*iii*) Experiment (*i*) was repeated using complex (6) in place of (1). After 15 min no significant change had occurred. After 24 h the reaction, giving the same products as were found in (*i*), was 70% complete.

(*iv*) (*Cf.*,[10] with a molar ratio of Fe : K[OH] : MeOH = 1.0 : 1.6 : 15.9). To a solution of K[OH] (0.007 g, 0.124 mmol) in MeOH (0.395 g, 12.3 mmol) was added complex (1) (0.020 g, 0.077 mmol) (molar ratio 1.0 : 1.6 : 159). After 1 h the reaction, as in (*i*), was >75% complete. {Besides the previously observed product, several others with SiMe within a range of τ 0.2 were produced in this reaction using more dilute base, representing incomplete conversion into the dianion $[SiMe(Pr^n)O_2]^{2-}$.}

Preparation of Complex (7).—To sodium pentacarbonylmanganate(−I) {from $[Mn_2(CO)_{10}]$ (1.00 g, 2.56 mmol), Na (0.175 g, 7.60 mmol), and Hg (18 g) in thf (25 cm^3)} suspended in hexane (15 cm^3) was slowly added, with stirring, $Cl(Me)\overline{SiCH_2CH_2CH_2}$ (0.99 g, 8.20 mmol). After 20 min the pale green-grey mixture had become dull yellow. The filtered concentrated solution was chromatographed on Florisil. Elution with hexane gave $\overline{CH_2CH_2CH_2Si}(Me)O\overline{SiMeCH_2CH_2CH_2}$ (g.l.c.) followed by overlapping orange bands due to complex (7) and $[Mn_2(CO)_{10}]$. The first portion of the orange eluate [rich in (7)] was taken

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

[23] R. B. King, K. H. Pannell, C. A. Eggers, and L. W. Houk, *Inorg. Chem.*, 1968, **7**, 2353.

and the solvent evaporated. Molecular distillation gave a small amount of the yellow-orange liquid *pentacarbonyl-*(1-*methyl*-1-*silacyclobutan*-1-*yl*)*manganese*(I) (7), containing a trace of decacarbonyldimanganese [Found: C, 38.55; H, 3.65%; *M* 280 (mass spectrometrically). $C_4H_9MnO_5Si$ requires C, 38.6; H, 3.2%; *M* 280]. The mass spectrum contained peaks at 280 (M^+, 100), 252 ($[M - CO]^+$, 83), 224 ($[M - 2CO]^+$, 55), 196 ($[M - 3CO]^+$, 65), 168 ($[M - 4CO]^+$, 37), 140 ($[M - 5CO]^+$, 65), 85 {$[M - Mn(CO)_5]^+$, 60}, and 57 {$[M - Mn(CO)_5 - C_2H_4]^+$, 35%}.

Attempts to separate further pure (7) by chromatography on alumina, sublimation, or differential oxidative decomposition were unsuccessful. Addition of Br_2 to the mixture in CCl_4 precipitated $[MnBr(CO)_5]$; hexane extraction of the dried mixture showed new ν(CO) bands at 2 110m, 2 060, and 2 022s cm^{-1}, possibly due to $[Mn(CO)_5\{SiMe(CH_2CH_2CH_2Br)Br\}]$.

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