2,2-Dimethyl-1,1,1,1-tetracarbonyl-1-ferra-2-silacyclopentane: Insertion of $[Fe(CO)_4]$ into a Strained Organosilicon Ring

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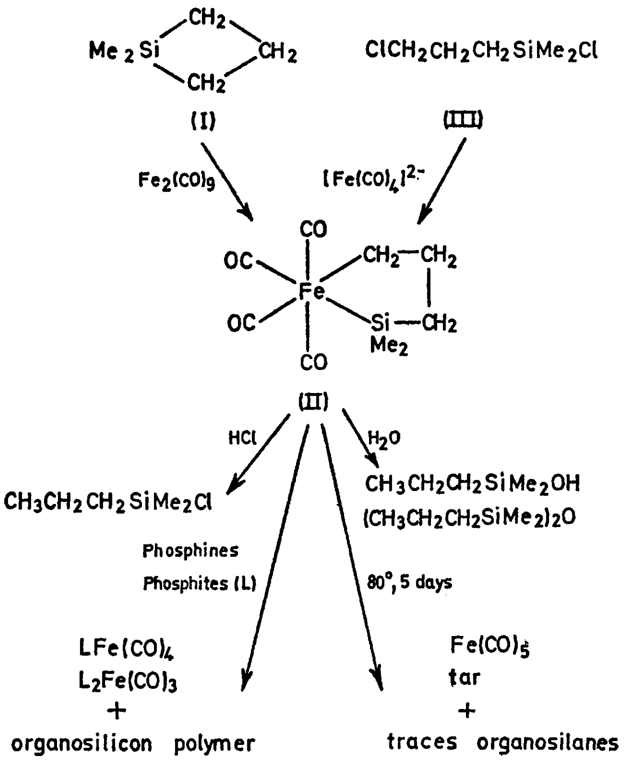
Summary The strained organosilicon heterocycle, 1,1-dimethyl-1-silacyclobutane reacts with nonacarbonyldi-iron to give a new type of binuclear chelate complex, $\overline{(CO)_4Fe-[CH_2]_3-SiMe_2}$, which is thermally stable, but chemically reactive.

Current interest in the transition metal-promoted valence isomerisation of strained polycyclic hydrocarbons[1] and in transition metal complexes derived from cyclopropanes[2] has led us to investigate the organometallic chemistry of analogous strained organosilicon heterocycles such as silacyclobutanes.[3] These compounds may be regarded as the "olefins" of organosilicon chemistry and are important as precursors of organosilicon polymers having a silicon–carbon backbone.[4]

1,1-Dimethyl-1-silacyclobutane (I) in benzene reacts smoothly with nonacarbonyldi-iron at 6—20° to give (II) and pentacarbonyliron (see Scheme). The new binuclear heterocyclic compound (II) is a volatile, white, crystalline solid, m.p. 87·5—88·5°, very soluble in non-polar solvents. As with $(\pi\text{-}C_5H_5)Fe(CO)_2SiMe_3$,[5] the crystals are readily deformed by pressure. The proposed structure is confirmed by elemental analyses, molecular weight measurement (cryoscopically in benzene), spectroscopic data, chemical reactions, and an alternative synthesis from the α,ω-dichloro-compound (III).

The mass spectrum shows a molecular ion, fragmentation occurring by stepwise loss of five units with *m/e* 28 ($4CO + C_2H_4$) or loss of silacyclobutane. In their n.m.r. spectra both (II) and the parent silacyclobutane (I) exhibit three resonances in the ratio 1 (multiplet):2 (multiplet):3 (singlet, $SiMe_2$), τ 9·09, 8·13, 9·39 (II) and 7·73, 8·85, 9·66 (I). Thus, from the Me_2Si- group shifts, the $Fe(CO)_4$ unit appears to exert considerable *deshielding* influence. The i.r. spectrum of (II) contains four strong carbonyl absorptions at 2083, 2021, 2000 (sh), and 1998 cm^{-1} (cyclohexane solution), as required for C_s symmetry. The remainder of the spectrum

(Nujol) shows the expected bands due to the organosilicon function, but the characteristic silacyclobutane ring vibrations[6] (1188, 1122, 927 cm^{-1}) are absent. A medium band at 302 cm^{-1} [absent from the i.r. spectrum of (I)] may be ν(Fe–Si);[7] there is no corresponding absorption in the spectrum of the 2,2-dimethoxy analogue of (II).



Scheme

Complex (II) has considerable thermal stability: after 2·5 days at 80°, approximately half the initial sample condensed on cooling to room temperature. The compound is decomposed only slowly (hours) by pure oxygen, but is rapidly (<1 min) destroyed by moist air. A number of reactions is outlined in the Scheme.

Neither carbon monoxide nor hydrogen reacted with (II) at 1 atm. and 20—80°, while chlorine in carbon tetrachloride at 22° caused total decomposition to $FeCl_3$, no volatile silicon products being detected.

Reactions of (II) with HX (X = Cl, OH) parallel those[8] of the parent silacyclobutane (which were run as controls) but that of (II) with deoxygenated water is very much faster. Complex changes occur upon addition of neutral ligands L, the latter being incorporated in the resulting polymer in some cases (*e.g.*, L = 4-picoline). The role of ring-insertion processes is under investigation. We have not to date observed any release of intact silacyclobutane from (II).

Preliminary experiments show that the insertion of $Fe(CO)_4$ is a general reaction for silacyclobutanes, 1,3-disilacyclobutanes, and 2,3-benzo-1-silacyclobutenes.

The present results are significant for the reasons outlined in the introductory paragraph and additionally because (a) reactions between suitable transition metal complexes and strained heterocycles could furnish a general synthesis for compounds having metal–metal bonds, (b) (II) may be the forerunner of a family of stable transition metal chelate alkyls [*cf.*, $Li_3Cr_3(C_4H_8)_3{\cdot}2{\cdot}5C_4H_8O_2$[9]], and (c) (II) represents a model for intermediates proposed[10] in the transition metal complex catalysed polymerisation of silacyclobutanes and related compounds.

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