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Iron Carbonyl Mediated Intramolecular Dimerization of Acetylene to a Novel (Trimethylenemethane)diiron Hexacarbonyl Complex[1)]

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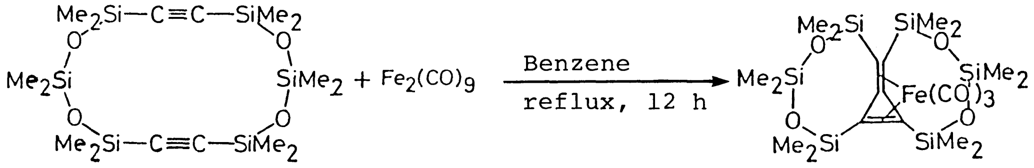
The reaction of 3,3,5,5,8,8,10,10-octamethyl-4,9-dioxa-3,5,8,10-tetrasilacyclodeca-1,6-diyne with diiron nonacarbonyl gave a (trimethylenemethane)iron tricarbonyl complex whose structure was determined by X-ray crystallographic analysis.

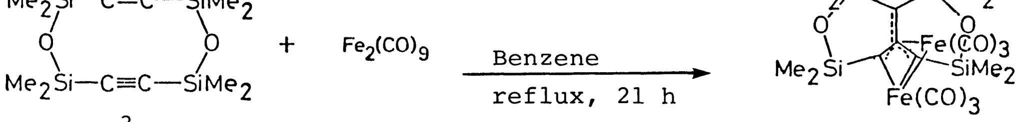
In a previous paper,[2)] we have reported the formation of a methylenecyclopropene complex (2) by the reaction of a tetraoxahexasilacyclotetradeca-1,8-diyne (1) with diiron nonacarbonyl. The structure of the novel complex was established by the X-ray diffraction method. Changing the size of the ring revealed an interesting consequence, which will be the subject of this paper.



1 2

3,3,5,5,8,8,10,10-Octamethyl-4,9-dioxa-3,5,8,10-tetrasilacyclodeca-1,6-diyne (3) was prepared from 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacyclodeca-1,5-diyne[3)] in 89% yield by oxidation with trimethylamine-N-oxide under similar reaction conditions described before.[2)]

The reaction of the diyne 3 with diiron nonacarbonyl in refluxing benzene for 21 h resulted in the formation of an iron dinuclear complex 4 in 35% yield.



3 4

The compound 4 was isolated and purified from the reaction mixture by passing through a silica gel short column followed by recrystallization from ethanol as red crystals, mp 102-104 °C; ^{1}H NMR (CD_2Cl_2) δ 0.17 (s, 6H), 0.26 (s, 6H), 0.32 (s, 6H) 0.36 (s, 6H); ^{13}C NMR (CD_2Cl_2) δ -0.1, 2.1, 2.7, 4.5, 91.5, 146.9, 168.3, 203.7, 209.1; ^{29}Si NMR (CD_2Cl_2) δ 1.4, 5.5; IR (CCl_4) 918, 988, 1258, 1939, 1995, 2035, 2065 cm^{-1}; UV λ_{max} (hexane) (log ε) 275 (4.01), 330 (3.60), 436 (3.01), 512 (2.64),

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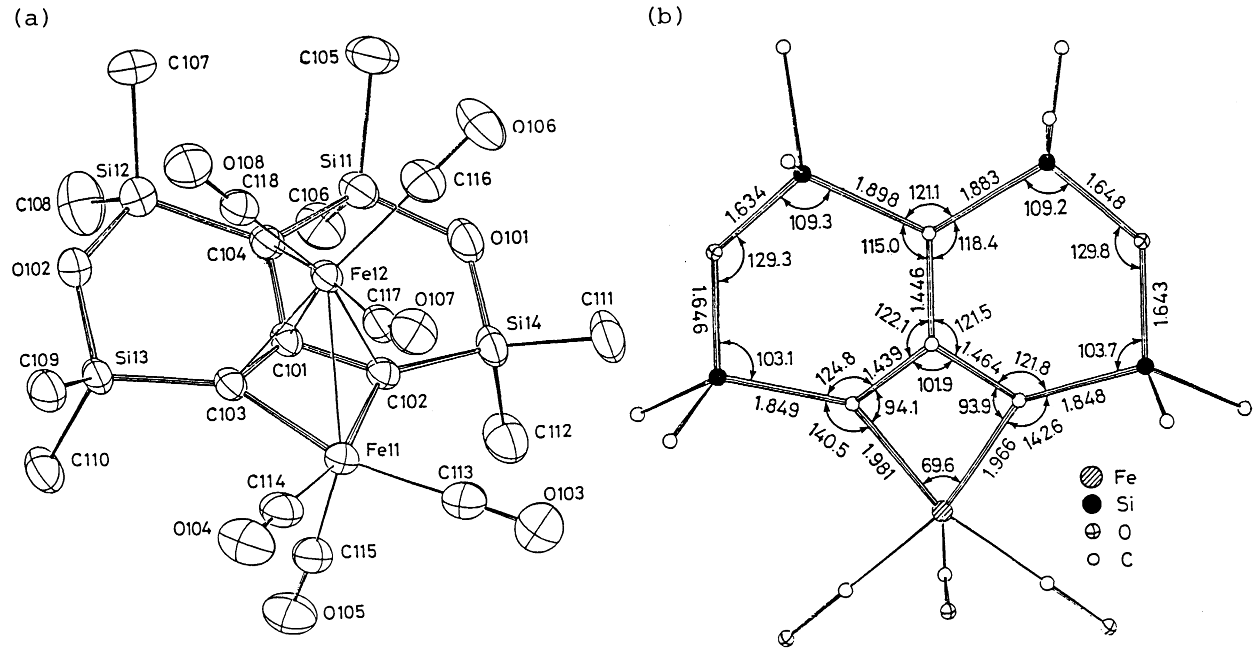

Fig. 1. (a) ORTEP diagram of **4**, (b) bond lengths and angles of the ligand.

nm; MS m/z (rel intensity) 592 (M^+, 2.1), 452 (100); Anal. Found: C, 36.52; H, 4.32%. Calcd for $C_{18}Fe_2H_{24}O_8Si_4$: C, 36.50; H, 4.08%.

The structure of **4** was established by X-ray diffraction (Fig. 1).[4] The unit cell contains 4 molecules which comprises two very similar but independent molecules. One iron atom forms a ferracycle that is almost planar. Interestingly an exomethylene group forms a trimethylenemethane structure with the ferracycle. The exomethylene double bond of **4** is bent to iron by 33.0° from the planar ferracycle. This is the first example of the formation of trimethylenemethane by dimerization of two acetylenes. The variation of the reaction mode of intramolecular dimerization of two acetylenes due to the ring size is quite remarkable. The related works are in progress.

References

1) Chemistry of Organosilicon Compounds. 246.

2) H. Sakurai, K. Hirama, Y. Nakadaira, and C. Kabuto, J. Am. Chem. Soc., 109, 6880 (1987).

3) H. Sakurai, Y. Nakadaira, A. Hosomi, A. Eriyama, and C. Kabuto, J. Am. Chem. Soc., 105, 3359 (1983).

4) Crystal data: $C_{18}Fe_2H_{24}O_8Si_4$, Fw 594.2, space group P_1, a = 15.392 (2) Å, b = 17.886 (2) Å, c = 10.658 (2) Å, α = 95.24 (1)°, β = 109.63 (1) °, γ = 97.50 (1) °, V = 2711.5 (4) $Å^3$, Z = 4 (two independent molecules), d_{calcd} = 1.45 g cm^{-3}, crystal dimension 0.25x0.25x0.30 mm^3. Intensities were measured on a Rigaku diffractometer using MoK_α radiation within 2θ = 55° and independent 9512 reflections within $|\underline{F}o| \geq 3\sigma |\underline{F}o|$ were used in the structure refinement. The final R factor was 0.067.

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