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CHEMISTRY OF ORGANOSILICON COMPOUNDS

118. NOVEL RING CONTRACTION REACTION OF
(η^4 -1,2-DISILACYCLOHEXADIENE) IRON TRICARBONYLS

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Summary

1,1,2,2-Dimethyl-3,6-diphenyl-1,2-disilacyclohexadiene reacts with iron pentacarbonyl or diiron nonacarbonyl to give the corresponding (diene)iron tricarbonyl complex which undergoes novel ring contraction reaction to (η^4 -1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene)iron tricarbonyl on thermolysis at 160°C. Similar results were observed with 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexadiene.

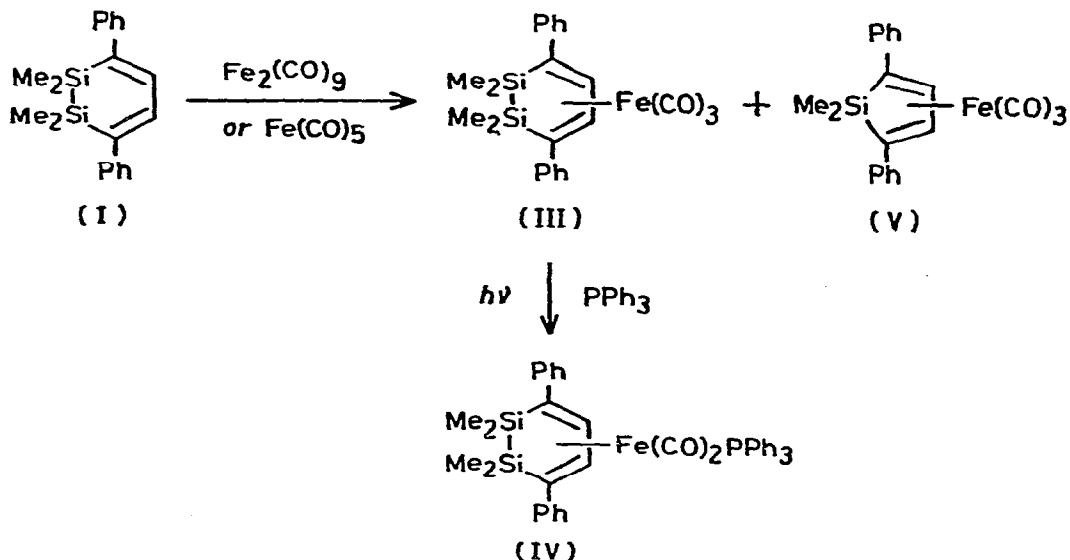
Introduction

A number of transition-metal complexes of silicon-containing unsaturated compounds has been prepared, but none of disilacyclohexadiene have been reported. We recently prepared 1,1,2,2-tetramethyl-3,6-diphenyl-1,2-disilacyclohexadiene (I) [1] and 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexadiene (II) [2], and it was of interest to investigate the preparation of transition-metal complexes of these disilacyclohexadienes. Previous investigations in this laboratory had shown the Si-Si bond to be highly reactive toward transition-metal complexes [3-6].

We report here the preparation and an unprecedented ring-contraction reaction of such complexes.

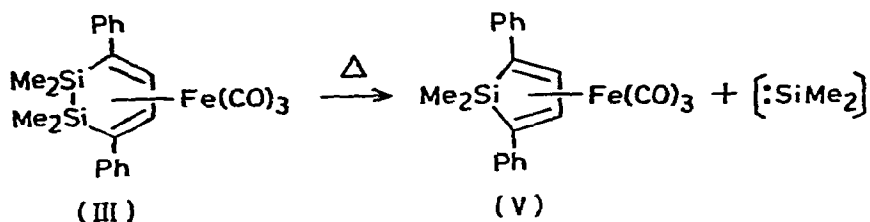
Results and Discussion

The reaction of (I) with diiron nonacarbonyl in benzene at reflux proceeded smoothly to give the expected complex (III) in 89% yield. The structure of (III) was determined by spectroscopic data and elemental analysis. (III) was also converted to (IV) by reaction with triphenylphosphine under irradiation. The reaction of (I) with iron pentacarbonyl in xylene at 130°C for 16h gave (III) in quantitative yield, but at 160°C for 19h (η^4 -1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene)iron tricarbonyl (V) [7] was obtained in 60% yield. The yield of (III) was diminished to 20%.



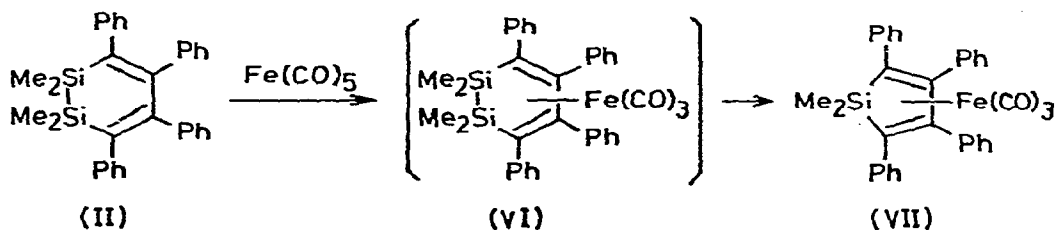
Disilacyclohexadiene (I) is thermally stable as evidenced by the fact that no change was observed after it had been heated at 250°C under vacuum for 3 days. Therefore, the formation of a large amount of (V) at higher temperature suggests that (V) is formed by thermolysis of (III). This was confirmed experimental-

ly. (V) was obtained in 77% yield at 72% conversion when (III) was heated at 160°C for 37.5h.



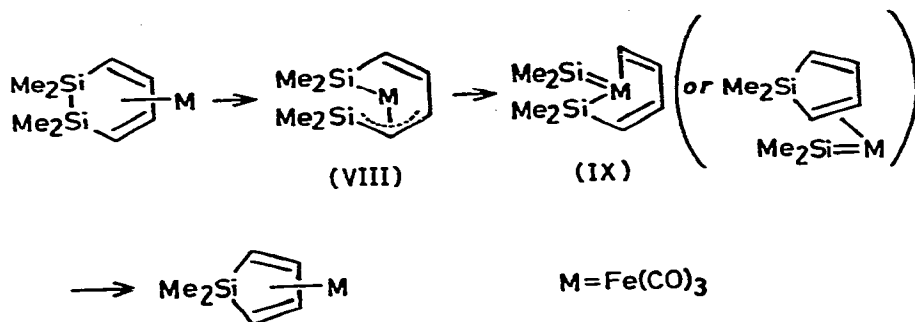
The reaction scheme indicates the formation of the dimethylsilylene. The thermolysis of (III) in the presence of diethylmethylsilane or diphenylacetylene was carried out in the hope of trapping the silylene [8]. However, 1,1-diethyl-1,2,2-trimethyl-disilane or 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene, the respective expected compounds were not obtained.

The reaction of (II) with iron pentacarbonyl did not occur at temperatures lower than 160°C. At temperatures higher than 160°C, the reaction proceeded smoothly, but the expected (n^4 -disilacyclohexadiene)iron complex (VI) was not obtained. Instead, (n^4 -1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (VII) [7] was obtained in quantitative yield based on unrecovered (II). Therefore, the expected complex (VI) apparently is thermally labile.

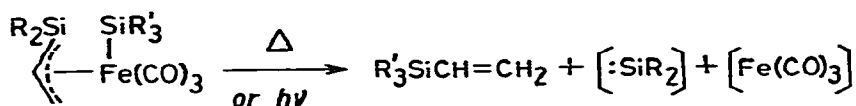
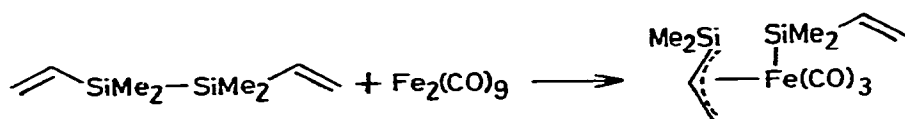


The precursor (II) is thermally stable, so that ring contraction preceding complexation can be excluded.

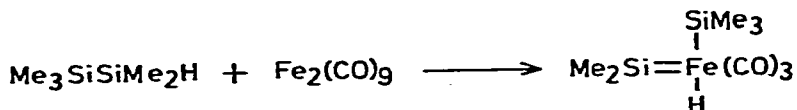
The reaction mechanism is not necessarily unequivocal but our present knowledge of the reaction modes of the Si-Si bond leads us to suggest the following mechanism.



Recently, it has been reported from this laboratory that 1,2-divinyl-1,1,2,2-tetramethyldisilane, an open chain analog of (I) and (II), undergoes reaction with diiron nonacarbonyl to give an (η^3 -1-silapropenyl)iron complex [5]. Subsequent investigations have demonstrated that such η^3 -1-silapropenyl complexes undergo silylene extrusion reactions on being heated or irradiated [9].



Other supporting evidence comes from the formation of a silylene complex in the reaction of pentamethyldisilane and diiron nonacarbonyl [10].



Although the postulated intermediates such as (VIII) and (IX) have not been isolated, this evidence provides support for this scheme. In the case of (II), another mechanism involving direct

interaction between the Si-Si bond and an iron species without formation of complex (VI) would be possible, but even in that case, complexes (VIII) and (IX) could be the key intermediates.

Experimental

Preparation of (I) and (II) has been described previously [1,2 resp.].

Reaction of (I) with diiron nonacarbonyl

A benzene (7 ml) suspension of diiron nonacarbonyl (323 mg, 0.89 mmol) and (I) (162 mg, 0.50 mmol) was heated at reflux for 2h. NMR examination revealed that 40% of the starting (I) remained unchanged (60% conversion). Preparative silica gel TLC yielded (III) (123 mg, 88% yield), m.p. 154-6°C; M^+ m/e 460; 1H -NMR $\delta(CCl_4)$ -0.15 (6H, s, SiMe), 0.33 (6H, s, SiMe), 5.90 (2H, s, -HC=CH-) ppm; IR(KBr) 2040, 1980, 1240, 1250, 1260 cm^{-1} . (Found: C, 59.97; H, 5.29. $C_{23}H_{24}O_3Si_2Fe$ calcd.: C, 60.00; H, 5.25%.)

Reaction of (I) with iron pentacarbonyl

In a 50 ml autoclave were placed (I) (493 mg, 1.54 mmol), iron pentacarbonyl (4 ml, ca 30 mmol) and dry xylene (5 ml). The mixture was heated at 130°C for 16h and volatile materials were distilled from the mixture.

The residue was dissolved in benzene and insoluble matter was removed by filtration. Almost pure (III) (703 mg, 1.53 mmol, 99% yield) was obtained by evaporation of the filtrate. An analytical sample was prepared by recrystallization from ethanol.

When the reaction of (I) (1.02 g, 3.18 mmol) with iron pentacarbonyl (5 ml) in xylene (5 ml) was carried out at 160°C for 19h, 1.06 g of a mixture of (III) and (V) was obtained. NMR examination revealed that the ratio of (III) to (V) was 1 : 3. By repeated recrystallization from ethanol and then from hexane, an analytical

sample of (V) was obtained, m.p. 115°C. (lit. [7b] 114°C); mixed m.p. with an authentic sample 115°C; M^+ m/e 402; $^1\text{H-NMR}$ $\delta(\text{CS}_2)$ -0.01 (s, 3H, exo-SiMe), 1.04 (s, 3H, endo-SiMe), 5.94 (s, 2H, -HC=CH-) ppm. (Found: C, 62.92; H, 4.72. $\text{C}_{21}\text{H}_{18}\text{O}_3\text{SiFe}$ calcd: C, 62.70; H, 4.51%.) The ratio of (III) to (V) was determined by relative areas of integrated Si-Me signals of (III) and (V).

Reaction of (III) with triphenylphosphine

A mixture of (III) (93.0 mg, 0.202 mmol), triphenylphosphine (60.0 mg, 0.229 mmol) and benzene (5 ml) was placed in a Pyrex glass tube (1cm \times 18cm) and irradiated with a 450W high pressure mercury arc lamp under nitrogen for 2h. Preparative silica gel TLC of the mixture gave unchanged (III) (16.5 mg, 17.7%) and (1,1,2,2-tetramethyl-3,6-diphenyl-1,2-disilacyclohexadiene)(triphenylphosphine)iron dicarbonyl (IV) (115 mg, 94% yield), m.p. 155°C; $^1\text{H-NMR}$ $\delta(\text{CS}_2)$ -0.38 (6H, s, SiMe), 0.43 (6H, s, SiMe), 5.36 (2H, d, -CH=CH-, $J_{\text{H-P}}=2.6\text{Hz}$) ppm; IR(KBr) 1980, 1920, 1250, 1240 cm^{-1} . (Found: C, 69.14; H, 5.64. $\text{C}_{40}\text{H}_{39}\text{O}_2\text{Si}_2\text{PFe}$ calcd.: C, 69.15; H, 5.66%.)

Thermolysis of (III)

In an ampoule (0.5cm \times 5cm) was placed (III) (55.0 mg) and benzene (0.5 ml). The ampoule was sealed after evacuation and heated at 160°C for 37.5h. Insoluble material was filtered and volatile materials were removed under reduced pressure to leave a solid (42.0 mg). NMR examination revealed that the solid contained only (III) and (V) with 1 : 2 molar ratio. The yield of (V) was calculated to be 77% at 72% conversion.

Reaction of (II) with iron pentacarbonyl

In an autoclave (50 ml) was placed (II) (41.6 mg, 0.088 mmol), iron pentacarbonyl (2 ml, ca 14 mmol) and toluene (6 ml). The mixture was heated at 170°C for 21h. Evaporation of volatile materials from the mixture at reduced pressure left a solid which was

resolved by preparative silica gel TLC. Unchanged (II) (6.5 mg, 15.6%) and (1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)-iron tricarbonyl (VII) (40.6 mg, 98.6% yield) were separated.

Acknowledgment

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