Supplementary Material Available: Single-crystal structure report for compound 2 (9 pages). Ordering information is given on any current masthead page.

A New Mode of Transition-Metal-Catalyzed Intramolecular Dimerization of Alkynes. The First Synthesis of a Methylenecyclopropene Complex[1a]

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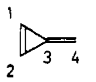
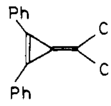
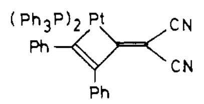
Received April 22, 1987

We report the preparation and structure of the first transition-metal-methylenecyclopropene complex by a novel intramolecular dimerization of alkynes.

Methylenecyclopropene (1) is one of the most interesting target molecules for experimental and theoretical studies in organic chemistry.[2] However, the molecule 1 is very unstable, having been synthesized and characterized only at low temperature.[3] Some derivatives, stabilized by substituents, such as 1,2-diphenyl-3-(1,1-dicyanomethylene)cyclopropene (2) are known.







Compound 1 is the simplest member of the class of cross-conjugated nonalternant hydrocarbons and being isoelectronic to cyclobutadiene, complexes of which are well known,[4] would be expected to also function as an η^4-ligand. Another reactive C_4 π system, trimethylenemethane, is also known to serve as an η^4-ligand.[5] However, transition-metal complexes of 1 or its derivatives are unknown, perhaps because of the reactivity of the strained C-C bonds toward ring opening. Thus, the reaction of 2 with (ethylene)bis(triphenylphosphine)platinum led to cyclopropene ring opening to give 3.[6] Similar reactions occur with cyclopropenes,[7] methylenecyclopropanes,[5c,8] and cyclopropanones.[9]

On the other hand, transition-metal-catalyzed intermolecular and intramolecular dimerization of alkynes to η^4-cyclobutadiene complexes is well documented.[4c,d] In particular, King et al. reported the formation of (cyclobutadiene)(cyclopentadienyl)cobalt complexes[10a] and (cyclobutadiene)iron tricarbonyl and dinuclear ferracyclopentadiene complexes[10b] from macrocyclic alkadiynes. However, the formation of the methylenecyclopropene complex has not been reported to date.

During the course of the study on macrocyclic polyacetylenic compounds,[11] we examined the reaction of

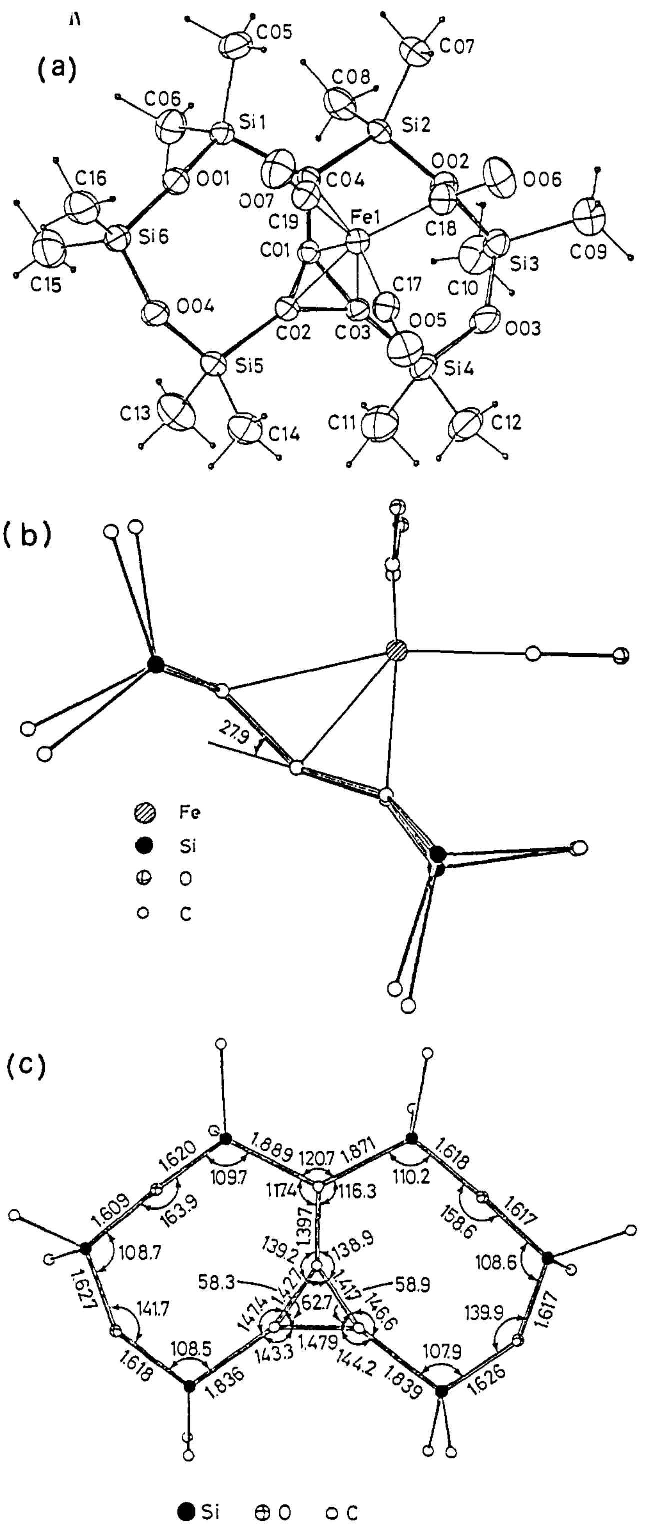


Figure 1. Structure of $C_{19}FeH_{36}O_7Si_6$ (6): (a) ORTEP diagram, (b) side view, and (c) bond lengths and angles of the ligand.

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(1) (a) Chemistry of Organosilicon Compounds. 235. (b) Present address: University of Electro-Communications, Chofu, Tokyo 192. (c) Instrumental Analysis Center for Chemistry, Faculty of Science, Tohoku University.

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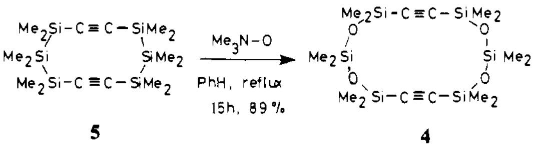
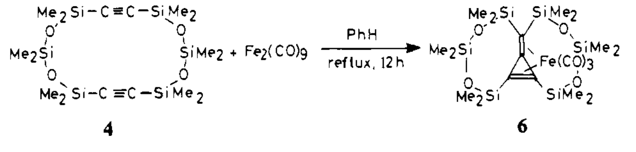
3,3,5,5,7,7,10,10,12,12,14,14-dodecamethyl-4,6,11,13-tetraoxa-3,5,7,10,12,14-hexasilacyclotetradeca-1,8-diyne (**4**) with diiron nonacarbonyl. Compound **4** was prepared from 3,3,4,4,5,5,8,8,9,9,10,10-dodecamethyl-3,4,5,8,9,10-hexasilacyclodeca-1,6-diyne (**5**) by oxidation with trimethylamine *N*-oxide.[12]



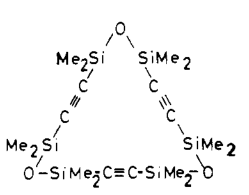
The reaction of the diyne **4** with 1.5 equiv of diiorn nonacarbonyl in refluxing benzene afforded the novel (methylenecyclopropene)iron tricarbonyl derivatives **6** in 45.5% yield, as



orange crystals, mp 122–123 °C dec,[13] isolated and purified from the reaction mixture by treatment with silica gel TLC. Its structure was established unequivocally by X-ray diffraction (Figure 1).[14]

The iron atom is bonded to four carbons of the methylenecyclopropene ligand and three carbonyl groups. It is noteworthy that both $r(C_1C_2)$ (1.479 Å) and $r(C_3C_4)$ (1.397 Å) (to a lesser extent) are elongated by comparing with the corresponding bonds of **1** (1.323 and 1.332 Å, respectively) as determined by microwave spectra.[3c] In contrast, the analogous bond distances in $r(C_1C_3)$ (1.427 Å) and $r(C_2C_3)$ (1.417 Å) are shorter than **1** (1.441 Å).[3c] Unusually wide bond angles were observed for ∠SiOSi (163.9° and 158.6°) in comparison with the normal values of disiloxanes (130 ± 10°).[15] The C_3–C_4 double bond of 6 is bent to iron by 27.9° from the planar cyclopropene ring.[16]

Apparently, the capability of silicon to undergo 1,2-shifts in disilylalkynes is responsible for the formation of the unusual product reported here. We have previously reported transition-metal-catalyzed intramolecular trimerization of macrocyclic triacetylene **7** to fulvene complexes and benzene derivatives,[11d] and, recently, we have isolated a vinylidene complex **8**, the structure of which was determined by X-ray diffraction, in the reaction of **7** and η^5-cyclopentadienyl(tricarbonyl)manganese.[17] Thermal and photochemical reactions of **8** afforded the corresponding benzene and fulvene derivatives.[17] A similar vinylidene complex must be an intermediate in the present reaction, although we have not isolated it yet.[18]



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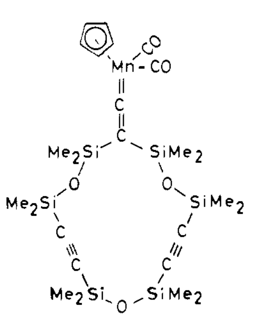

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Acknowledgment. We thank Toshiba Silicone Co., Ltd. for gifts of chlorosilanes. The work was supported in part by the Ministry of Education, Science, and Culture (Grant-in-Aid for Special Project Research, no. 61125004).

Supplementary Material Available: Tables of final atomic coordinates, anisotropic temperature factors, and bond lengths and angles (5 pages); tables of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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[13] **6**: ^{1}H NMR (CD_2Cl_2) δ 0.39 (s, 6 H), 0.28 (s, 12 H), 0.25 (s, 6 H), 0.07 (s, 6 H), 0.06 (s, 6 H); ^{13}C NMR (CD_2Cl_2) δ 212.3, 100.3, 96.9, 43.1, 4.6, 3.1, 2.7, 1.4, 1.1, 0.26; ^{29}Si NMR (CD_2Cl_2) δ –0.4, –3.3, –18.7; IR (CCl_4) 2039, 1970 cm^{-1}; UV (hexane) λ_{max} (log ϵ) 216 (4.59), 255 (4.15), 400 nm (2.72); MS, m/z (rel intensity) 585 (M^+ – 15, 0.2), 73 (100). Anal. Calcd for $C_{19}FeH_{36}O_7Si_6$: C, 37.98; H, 6.04. Found: C, 38.21; H, 6.11.

[14] Crystal data: $C_{19}FeH_{36}O_7Si_6$, Fw 600.85, space group *Pbca*, a = 20.465 (2) Å, b = 20.854 (2) Å, c = 14.631 (2) Å, V = 6244.2 (6) Å^3, Z = 8, d_{calcd} = 1.28 g cm^{-3}, crystal dimension 0.20 × 0.20 × 0.30 mm. intensities were measured on a Rigaku diffractometer with use of Mo Kα radiation within $2\theta = 55°$, and independent 7625 reflections within $|F_o| \geq 3\sigma|F_o|$ were used in the structure refinement. The final R factor was 0.055.

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[16] We have observed similar bending for a $Mo(CO)_3$ complex of fulvene derived from **7**.[11d]

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Electrophilic Azide Transfer to Chiral Enolates. A General Approach to the Asymmetric Synthesis of α-Amino Acids

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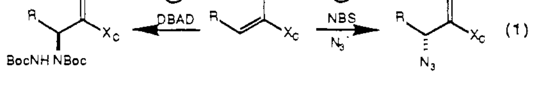
Received July 13, 1987

In connection with our interest in developing convenient, general methods for the asymmetric synthesis of α-amino acids,[1] we recently reported[2] the stereoselective "amination" of chiral imide enolates with di-*tert*-butyl azodicarboxylate (DBAD) (eq 1A).[3]



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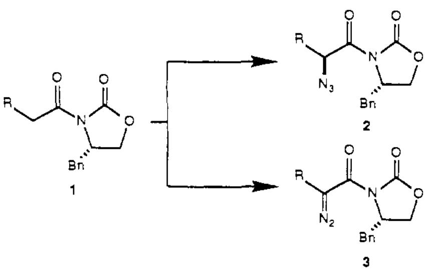

(2)

(3)

In an ensuing report[4] we outlined a complementary approach

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