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Synthesis of Corannulene *via* an Iron-Mediated [2+2+1] Cycloaddition

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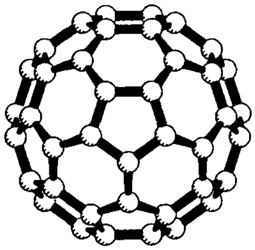
Abstract: The synthesis of corannulene **2** in seven steps and 25% overall yield from 1,8-diiodonaphthalene **3** is reported.

The discovery and subsequent investigation of the chemistry of buckminsterfullerene (C_{60}) **1**[2] has also induced great interest in bowl-shaped polycyclic unsaturated hydrocarbons over the past few years.[3] The smallest type of such a fullerene fragment is corannulene ($C_{20}H_{10}$) **2**, which was known long before the fullerenes.[4] Several novel syntheses of corannulene **2** have been reported in recent years.[5]



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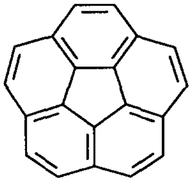

2

In connection with our studies on the iron-mediated [2+2+1] cycloaddition to annulated cyclopentadienones,[6] we investigated the application of this reaction to the synthesis of polycyclic unsaturated hydrocarbons.[7] In the present paper we describe a straightforward seven-step synthesis of corannulene **2** using an iron-mediated [2+2+1] cycloaddition of a 1,8-dialkynylnaphthalene and carbon monoxide as key-step.

The starting material 1,8-diiodonaphthalene **3** is readily prepared from 1,8-diaminonaphthalene according to a literature procedure.[8] A double Sonogashira coupling[9] of compound **3** with monotrimethylsilylacetylene afforded 1,8-bis(trimethylsilylethynyl)naphthalene **4** (Scheme 1). The iron-mediated [2+2+1] cycloaddition on

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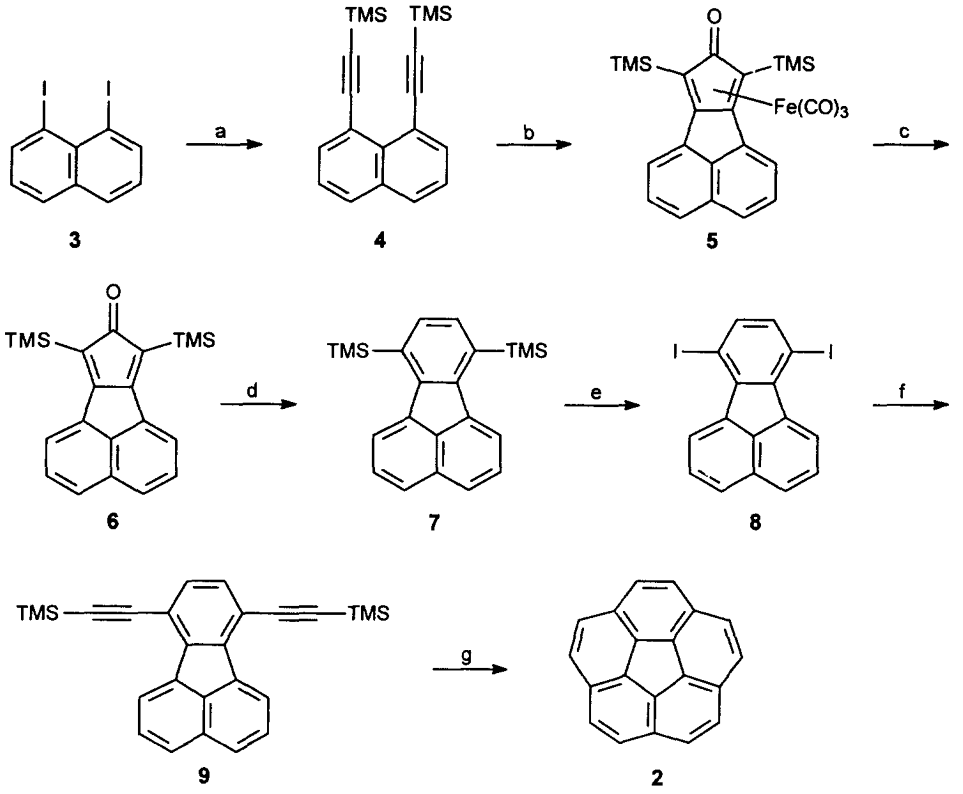
reaction of **4** with pentacarbonyliron in a sealed tube using our previously optimized reaction conditions provided the tricarbonyliron complex **5** in 90% yield. The structural assignment as the C_S symmetrical complex **5** is based on the NMR spectra[10] and was confirmed by an X-ray crystal structure determination (Figure 1).[11]



Scheme 1. Reagents and conditions: a) trimethylsilylacetylene (2.5 equiv.), $Pd(PPh_3)_2Cl_2$ (0.2 equiv.), CuI (0.2 equiv.), Et_3N, 100°C, 1 h, 91%; b) $Fe(CO)_5$ (2 equiv.), 1,2-dimethoxyethane, 140°C, 20 h, 90%; c) 1. 1 M NaOH/THF (1:2), 25°C, 2.5 h, 2. $C_5H_{11}I$ (2.4 equiv.), 25°C, 15 min, 3. H_3PO_4, 25°C, 4. air, daylight, Et_2O/THF, $Na_2S_2O_3$, Celite, 25°C, 3 h, 89%; d) norbornadiene (70 equiv.), toluene, reflux, 16 h, 98%; e) ICl (4 equiv.), CCl_4, 25°C, 20 h, 98%; f) trimethylsilylacetylene (5 equiv.), $Pd(PPh_3)_2Cl_2$ (0.2 equiv.), CuI (0.2 equiv.), diisopropylamine, 90°C, 30 min, 98%; g) flash vacuum pyrolysis, 1000°C, 1.2 mbar Ar, 36%.

For applications of the iron-mediated [2+2+1] cycloaddition to organic synthesis it is crucial to achieve a selective demetalation of the resulting tricarbonyliron complexes to the corresponding free and stable cyclopentadienones. During our studies we developed three different experimental procedures as solutions to this problem. The first uses trimethylamine *N*-oxide dihydrate with very careful control of the reaction conditions.[6b,12] The second method involves a photochemical exchange of all three carbonyl ligands with acetonitrile and subsequent demetalation of the resulting triacetonitrileiron complexes at −30°C by injection of air.[13] In the third procedure one carbonyl ligand is sequentially exchanged by a hydrido ligand with NaOH, then by an iodo ligand with iodopentane and finally the resulting dicarbonyl(η^5-hydroxycyclopentadienyl)iodoiron complexes are demetalated by contact with air in the presence of daylight.[14] In the present case demetalation of complex **5** using the third method led to a smooth transformation to the corresponding free ligand **6**.[10]

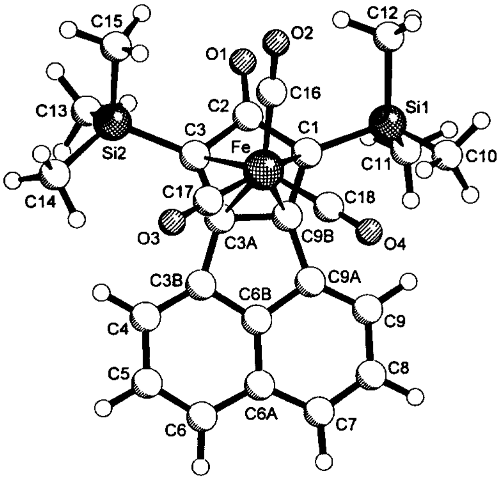


Figure 1. Molecular structure of complex **5** in the crystal. Selected bond lengths (Å): Fe-C1 2.148(3), Fe-C9B 2.092(3), Fe-C3A 2.073(3), Fe-C3 2.144(3), C1-C2 1.492(5), C2-C3 1.508(4), C3-C3A 1.436(4), C3A-C9B 1.452(4), C1-C9B 1.419(4), C1-Si1 1.879(3), C2-O1 1.228(4), C3-Si2 1.879(3).

Cyclopentadienones are highly reactive in Diels-Alder cycloadditions. They can function as dienes and dienophiles and dimerize if no bulky substituents are present in the molecule.[15] The 3,4-annulated 2,5-bis(trimethylsilyl)cyclopentadienones are stable with respect to Diels-Alder dimerization for steric reasons and show no tendency to react as dienophiles. However, they represent useful dienes for Diels-Alder cycloadditions with appropriate dienophiles.[7] The Diels-Alder reaction of the cyclopentadienone **6** with norbornadiene in toluene at reflux is followed *in situ* by the extrusion of first, carbon monoxide in a retrocheletropic reaction and secondly, cyclopentadiene in a retro-Diels-Alder reaction to provide 7,10-bis(trimethylsilyl)fluoranthene **7**. Electrophilic substitution of **7** with iodine monochloride afforded 7,10-diiodofluoranthene **8**. A further double Sonogashira coupling of compound **8** with monotrimethylsilylacetylene provided 7,10-bis(trimethylsilylethynyl)fluoranthene **9**. Finally, flash vacuum pyrolysis of **9** at 1000°C under 1.2 mbar argon afforded corannulene **2** in 36% yield.[10] During the pyrolysis a black soot was formed in the reaction zone which contained β-silicon carbide, as shown by X-ray powder diffraction.[16]

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10. Selected spectral data for the tricarbonyliron complex **5**, the cyclopentadienone **6**, and corannulene **2**. **5**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.52 (s, 18 H), 7.63 (dd, *J* = 8.2, 7.2 Hz, 2 H), 7.93 (d, *J* = 8.2 Hz, 2 H), 7.97 (d, *J* = 7.2 Hz, 2 H); ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 0.08 (6 CH_3), 69.52 (2 C), 110.33 (2 C), 123.90 (2 CH), 128.13 (2 CH), 128.44 (2 CH), 130.57 (C), 132.48 (2 C), 136.00 (C), 183.00 (C=O), 208.42 (3 CO); analysis calc. for $C_{24}H_{24}FeO_4Si_2$: C 59.01, H 4.96; found: C 59.43, H 4.83. **6**: UV ($CHCl_3$): λ = 250, 286, 354, 362, 383, 475 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.43 (s, 18 H), 7.63 (t, *J* = 7.7 Hz, 2 H), 7.85 (d, *J* = 7.7 Hz, 4 H); ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = –0.42 (6 CH_3), 122.30 (2 CH), 125.23 (2 C), 127.32 (2 CH), 128.38 (2 CH), 131.97 (C), 132.29 (2 C), 144.51 (C), 169.16 (2 C), 212.75 (C=O); analysis calc. for $C_{21}H_{24}OSi_2$: C 72.36, H 6.94; found: C 72.18, H 6.59. **2**: colorless crystals, m.p. 267-268°C; UV ($CHCl_3$): λ = 216, 228, 247, 254, 288 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81 (s, 10 H); ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 127.06 (10 CH), 130.89 (5 C), 135.85 (5 C).
11. Crystal data for **5**: $C_{24}H_{24}FeO_4Si_2$; M = 488.46 g/mol^1, crystal size 0.80 · 0.30 · 0.15 mm, orthorhombic, space group $P2_12_12_1$, λ = 0.71073 Å (Mo-Kα radiation), a = 10.3705(12) Å, b = 11.765(2) Å, c = 20.014(3) Å, V = 2441.9(6) Å^3, Z = 4, μ = 0.742 mm^{-1}, $\rho_{calc.}$ = 1.329 g/cm^3, T = 143(2) K, θ range: 3.32-27.51°; 5933 reflections collected, 5516 independent (R_{int} = 0.0201), refinement method: full-matrix least-squares on F^2 (program: SHELXL-93), final R values [$I > 2\sigma$ (I)]: R_1 = 0.0431, wR_2 = 0.0841, maximal residual electron density: 0.387 e/Å^3. Diffractometer: Stoe STADI-4. Graphical representation: SCHAKAL-97. Atomic coordinates, bond lengths and angles, and thermal parameters for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre.
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