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8-Chloro-8-cyano-1,2-homoheptafulvene and Its Tricarbonyliron Complexes

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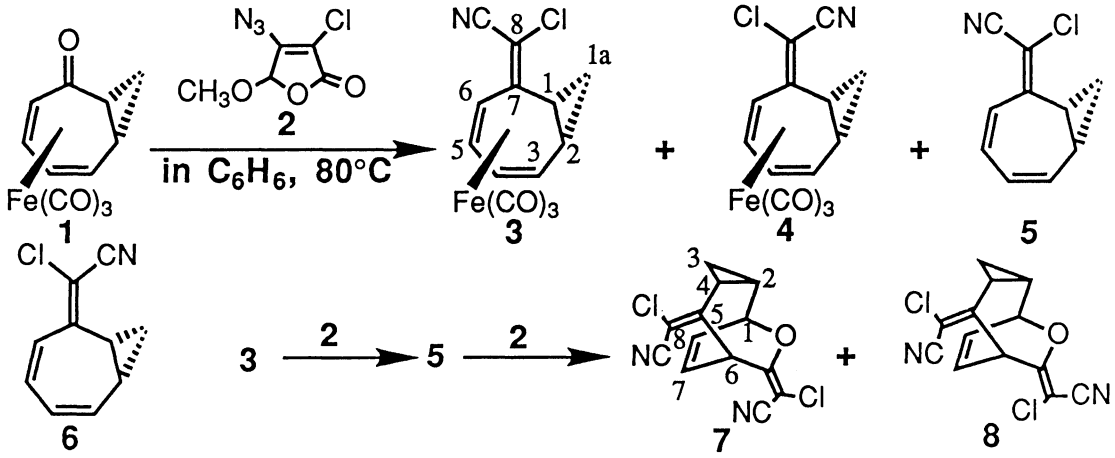
8-Chloro-8-cyano-1,2-homoheptafulvene and its tricarbonyliron complexes have been prepared. Their structures and optical activities were investigated.

Although 1,2-homoheptafulvene[1] and 3,4-homoheptafulvene[2] have already been prepared, their tricarbonyliron complexes and optical activity have not been investigated. Here we report the preparation, structural determination and optical activity of 8-chloro-8-cyano-1,2-homoheptafulvene and its exo- and endo-tricarbonyliron complexes. For the preparation we chose the reaction of homotropones with chlorocyanoketene, which is easily formed by thermolysis of 3-azido-2-chloro-4-methoxybutenolide (**2**) in benzene at 80 °C, and cycloadded to carbonyl group stereospecifically to give chlorocyanosubstituted alkenes via β-lactones.[3]

When 2,3-homotropone[4] was treated with the butenolide **2** in benzene at 80 °C for 5 h, thin layer chromatography revealed an unidentified polymeric product was obtained along with a trace amount of 1,2-homoheptafulvalene. However, a similar reaction of exo-2,3-homotropone-$Fe(CO)_3$ (**1**)[5,6] with 2 molar equivalents of **2** afforded a mixture of complexes **3** (mp 120-122 °C), **4** (mp 80-81 °C), and a decomplex product **5** (pale yellow oil) in 30%, 14%, and 8.6% yield, respectively. The complexes **3** and **4** were geometrical isomers of exo-8-chloro-8-cyano-1,2-homoheptafulvene-$Fe(CO)_3$ due to different orientation of substituents at C-8. On the basis of NMR, however, these structures could not be determined. The structure of **4** was determined by single crystal X-ray diffraction. The result is shown in Fig. 1,[7] which indicates that cyclopropane moiety and the cyano group are in the same side. Furthermore, the structural feature of 1,3-diene part coordinated to iron was the same as those of

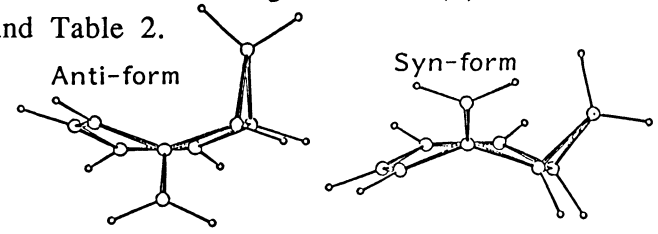
tropone-Fe(CO)3 and its derivatives.[8]

The complex **3** was found to completely decompose on heating in benzene in the presence of **2** at 80 °C for 2 h to give decomplexed product **5**, which reacted with chlorocyanoketene in the manner of [2+4]π cycloaddition to give a 1:1 mixture of **7** [mp 165-169 °C (decomp)] and **8** [mp 187-189 °C (decomp)]. Ito et al. have found that the reaction of 8,8-diphenyl-1,2-homoheptafulvene with diphenylketene afforded ketonic [2+4]π cycloadduct formed by reaction of C=C bond of ketene moiety as 2π component. IR of the products **7** and **8** did not show C=O absorption, but showed C=C absorptions at 1630 and 1632 cm^{-1}, respectively. The structures of **7** and **8** were determined as shown in the scheme by spectroscopic analyses, formed by the reaction of C=O moiety of ketene with diene of **5**. On the other hand, **4** was more stable on heating in the presence of **2**, and decomplexed product (**6**) was not formed after 2 h.



In a similar reaction with chlorocyanoketene, optically active (-)-**1** {[α]D -778° (c 0.655, $CHCl_3$)}[9] afforded (-)-**3** {[α]D -1484° (c 0.24, $CHCl_3$)}, (-)-**4** {[α]D -1318° (c 0.0402, $CHCl_3$)}, and (-)-**5** {[α]D -1894° (c 0.0325, $CHCl_3$)}. The absolute configurations of these active compounds were determined as depicted in the scheme on the basis of chemical correlation of the known absolute configuration of (+)-**1**.[9] The CD spectra and data are shown in Fig. 2 and Table 2.

Optimized conformational structures, anti-form and syn-form of 1,2-homoheptafulvene are calculated by the MNDO method as shown in the Scheme. By comparison with the CD spectrum data of (-)-**5** and those of homoheptafulvene calculated by the CNDO/S method shown in Table 2, particularly the comparison of sign of rotational strength of the longest wave length, conformation of homoheptafulvene can be estimated to be an anti-form.



Conformation of 1,2-Homoheptafulvene

Endo-2,3-homotropone-Fe(CO)3 (**9**)[6] similarly reacted with chlorocyanoketene to give a mixture of complexes **10** (mp 68-70 °C) and **11** (mp 97-98 °C) in 17 and 13%

yields, respectively. The structures of **10** and **11** were determined by comparison of NMR with those of **3** and **4**. Compared with **1**, the selectivity of products is found to decrease.

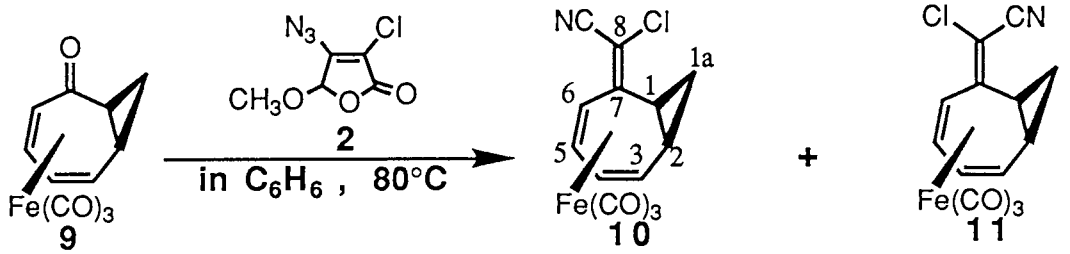


Table 1. Spectral data of homoheptafulvenes and related compounds

	IR (KBr) ν/cm^{-1}	UV λ/nm (log ε)	^{1}H NMR(CDCl3) ppm (J/Hz)
3	2216, 2060, 1996, 1982, 1552.	218sh(4.29) 293 (4.29) 320sh(3.97)	5.2-5.6(m, H-4.5), 3.96(d, J=7.5 H-6), 3.72(m, H-3), 2.0(m, H-1,2), 1.37(td, J=8.7, 4.2, H-1a,exo), 0.61(td, J=5.7, 4.2, H-1a,endo)
4	2212, 2060, 1986, 1544	218sh(4.31) 293 (4.05) 315sh(3.99)	5.3-5.6(m, H-4,5), 3.82(dd, J=7.8, 0.9, H-6), 3.72(m, H-3), 2.0(m, H-1,2), 1.27(dt, J=8.4,4.5,. H-1a,exo), 0.67(td, J=5.4, 4.5, H-1a,endo)
5	2216, 1644, 1584, 1540.	252 (3.87) 335 (4.03)	5.9-6.4(m, H-3,4,6), 5.67(dd, J=11.7, 7.2, H-5), 2.87(ddd, J=7.7, 7.7, 7.7, H-1), 1.7-2(m, 2H), 1.57(m,1H)
7	2220, 1630, 1241, 1010		6.22(m, H-7,8), 5.89(dm, J=5.2, H-6), 4.27(td, J=5.8, 2.7, H-1), 1.4-2.1(m, 2H), 1.30(ddd, J= 9.4, 8.2, 5.4, H-3exo), 0.84(ddd, J=5.4, 5.4, 5.4, H-3endo)
8	2220, 1632, 1606 1242, 1014		6.1-6.4(m, H-7,8), 5.73(dt, J=5.4,1.2, H-6), 4.26 (td, J=6.0, 1.8, H-1), 1.5-1.9(m, 2H), 1.23(ddd, J=9, 7, 5.4, H-3exo), 0.82(ddd, J=5.4, 5.4, 5.4, H-3endo)
10	2212, 2060, 2012, 1988, 1976, 1550	282 (4.14) 325 (4.02)	5.57(dd, J=7.0, 5.4, H-4), 5.32(ddd, J=7.2, 5.4, 1.6, H-5), 3.94(d, J=7.2, H-6), 3.47(m, H-3), 1.07-1.45(m, 3H), 0.47(m, H-1a,endo)
11	2208, 2060, 1992, 1546.	282 (4.08) 337 (3.95)	5.64(dd, J=6.6, 5.4, H-4), 5.31(ddd, J=7.2, 5.4, 1.6, H-5), 3.84(d, J=7.2, H-6), 3.42(m, H-3), 1.02-1.67(m, 3H), 0.58(m, H-1a,endo)

Table 2. Rotational Strength by CNDO/S Method

Anti-form			**Syn-form**			**5**	
νcalcd 10^3cm^{-1}	f[a])	Rcalcd[b]) 10^{-40}cgs	νcalcd 10^3cm^{-1}	f	Rcalcd 10^{-40}cgs.	νobsd 10^3cm^{-1}	Δεobsd M^{-1}cm^{-1}
36.5	0.10	-33.3	38.6	0.10	+14.0	29.9	-35.4
43.5	0.08	+77.0	43.0	0.02	+32.7	39.4	+60.8
46.5	0.04	+19.6	45.4	0.04	+22.2	43.5[c])	+18.0
47.4	0.02	-16.1	48.2	0.02	- 6.2	45.9	-16.9
49.0	0.05	-22.7	49.8	0.09	-16.3		

a) Oscillator strength. b) Rotational strength. c) Shoulder.

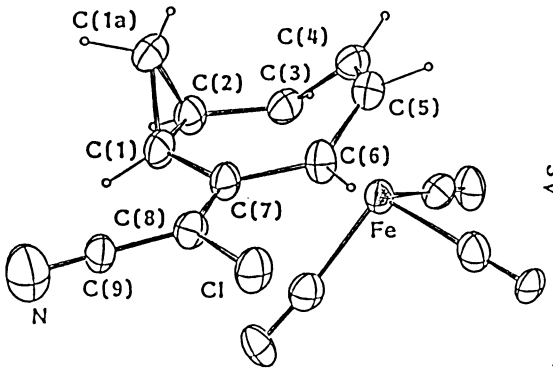


Fig. 1. ORTEP drawing of the molecular structure of complex **4**.

Selected bond lengths (l/Å)

C(1)-C(2)	1.502(13)	C(7)-C(8)	1.350(12)
C(1)-C(1a)	1.502(14)	C(8)-C(9)	1.412(12)
C(1)-C(7)	1.487(13)	C(8)-Cl	1.747(9)
C(2)-C(1a)	1.493(14)	C(9)-N	1.160(13)
C(2)-C(3)	1.484(13)	Fe-C(3)	2.123(7)
C(3)-C(4)	1.449(14)	Fe-C(4)	2.060(9)
C(4)-C(5)	1.390(14)	Fe-C(5)	2.064(9)
C(5)-C(6)	1.490(14)	Fe-C(6)	2.150(10)
C(6)-C(7)	1.461(13)		

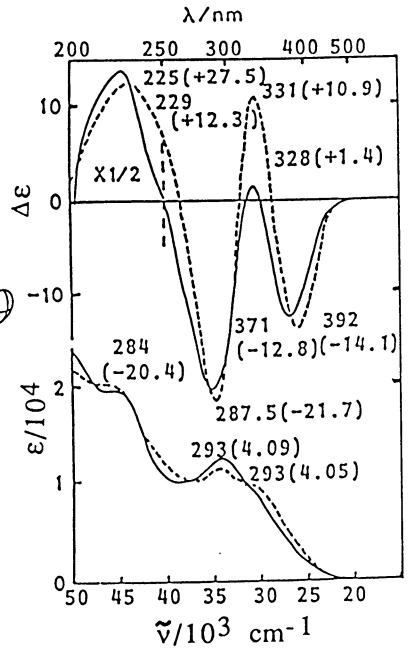


Fig. 2. Absorption(bottom) and CD (top) spectra of (-)-**3** (------) and (-)-**4** (------) in CH_3OH.

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7) Crystal data for **4** : $C_{13}H_8O_3NClFe$, M=317.51, monoclinic, a=12.980(2)Å, b=10.505(1)Å, c=10.129(1)Å, β=109.84(1)°, space group $P2_1/a$, Z=4, ρcalc = 1.68 g/cm^3. The crystal size was ca. 0.20 X 0.30 X 0.30 mm^3. Intensity measurements were carried out for 2θ<52° on Rigaku AFC-5 four-circle diffractometer with Cu-Kα (λ= 1.548Å) radiation. The structure was solved by heavy atom method and refined to R=0.076 for 1850 reflections with $|F_0|>3\sigma(F_0)$.

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