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THE SYNTHESES OF HEXACARBONYL(TROPONE)DIIRON AND SEVERAL TRICARBONYLIRON COMPLEXES OF HEPTAFULVALENE

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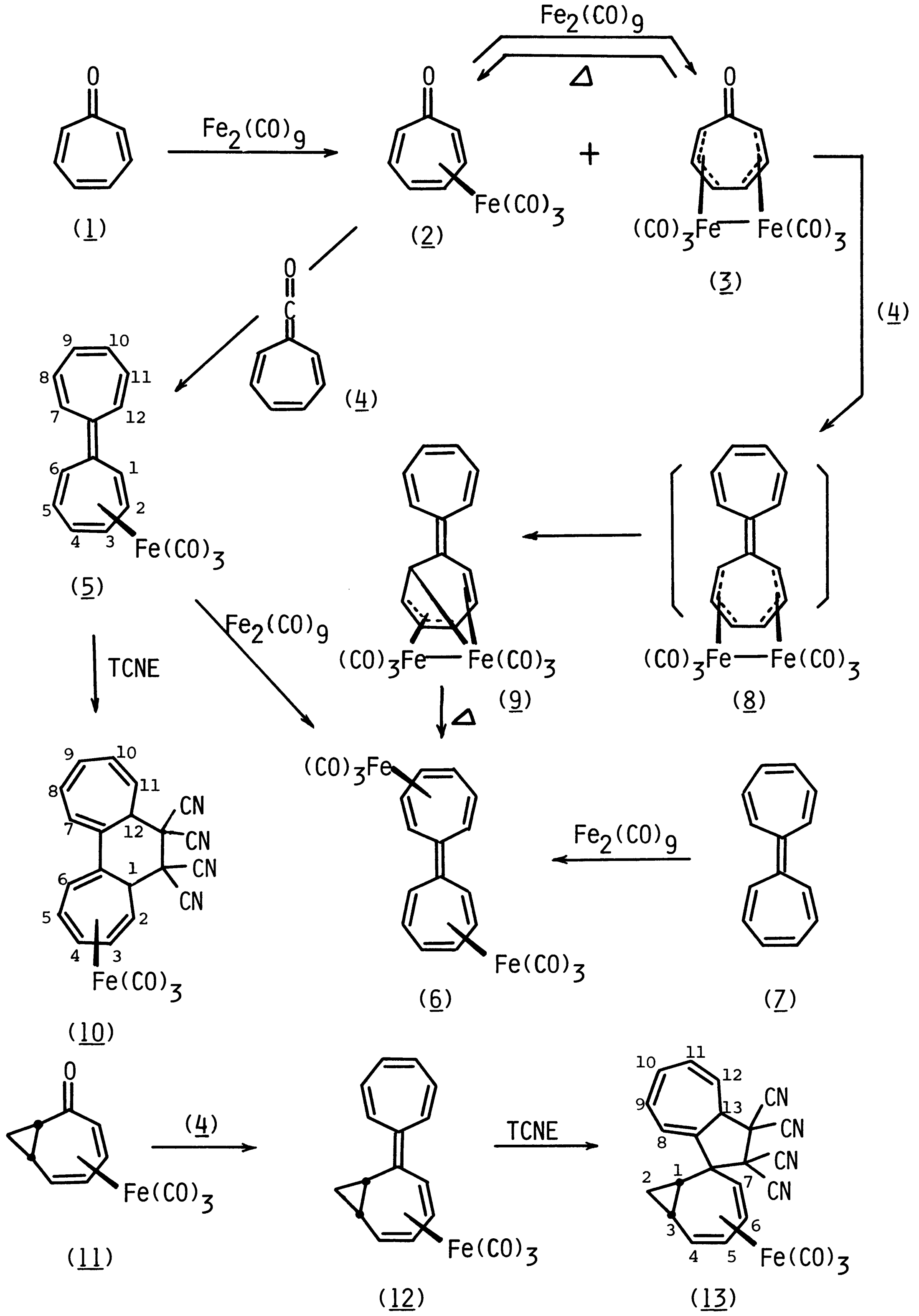
A new hexacarbonyl(tropone)diiron complex was isolated and characterized. Several carbonyliron complexes of heptafulvalene were also synthesized.

In the course of the studies of synthesis and reactivity of tricarbonyl-(tropone)iron, we isolated and characterized a new complex, hexacarbonyl(tropone)-diiron, and synthesized carbonyliron complexes of heptafulvalene. The results will be reported in this paper.

Tricarbonyl(tropone)iron (2) has been obtained from the reaction of acetylene with $Fe_2(CO)_9$,(1) by refluxing a benzene solution of tropone (1) and $Fe_3(CO)_{12}$(2) or by refluxing a ether solution of tropone and $Fe_2(CO)_9$.(3) We found that another product is contained in the reaction mixture of tropone (1) with excess $Fe_2(CO)_9$ in refluxing benzene by thin layer chromatography on silica gel, and we isolated a new complex (3) (ca. 15%) as reddish crystals, mp 118-120°C, in addition to 2 (ca. 55%) which is an orange solid.

A molecular ion peak (m/e 386) corresponding to $C_7H_6OFe_2(CO)_6$ was observed in MS of the new complex (3) by field disorption technique. Abundant fragment ions by electron impact mode were also observed at m/e 274 (1), 246 (1), 218 (5), 106 (58), 78 (100). Other spectral data are as follows; IR (KBr) 2060, 2050, 2025, 2010, 1995, 1980, 1960, 1955, 1599 cm^{-1}; UV λ_{max}^{EtOH} 224 nm (log ε 4.26), 341 (3.94), 432 (3.49); ^1H-NMR ($CDCl_3$) δ 3.30 (d, J=7.5 Hz, H-2,7), 4.54 (m, H-3,6), 4.78 (m, H-4, 5); ^{13}C-NMR ($CDCl_3$) 63.5, 73.9, 189.8, 209.4 ppm.

These spectral data suggested the structure of hexacarbonyl(2,3,4-trihapto: 5,6,7-trihaptotropone)diiron for the complex (3). A similar structure has been assigned for hexacarbonyl(cycloheptatriene)diiron.(4) The complex (3) was also


O
(1)
$Fe_2(CO)_9$
(2)
$Fe(CO)_3$
+
$Fe_2(CO)_9$
Δ
(3)
$(CO)_3Fe$
$Fe(CO)_3$
(4)
O
C
(4)
(5)
9
10
8
11
7
12
6
1
5
2
4
3
$Fe(CO)_3$
$Fe_2(CO)_9$
TCNE
$(CO)_3Fe$
$Fe(CO)_3$
(9)
Δ
(8)
$(CO)_3Fe$
$Fe(CO)_3$
(10)
CN
CN
CN
CN
(6)
$Fe_2(CO)_9$
(7)
(11)
(4)
(12)
TCNE
(13)
10
11
12
9
13
8
2
1
7
3
4
5
6

obtained from the reaction of 2 with $Fe_2(CO)_9$ in refluxing ether in 25-30% yield, and 3 easily decomposed by refluxing in benzene to give 2.

Since metal complexes of heptafulvalene have been unknown, we have synthesized carbonyliron complexes of heptafulvalene to study their physical and chemical properties.

The reaction of tricarbonyl(tropone)iron (2) with 8-oxoheptafulvene (4), generated *in situ* by the reaction of cycloheptatrienyl-7-carbonyl chloride and triethylamine,$^{5)}$ at room temperature in benzene afforded tricarbonyl(heptafulvalene)iron (5) in 72.7% yield as a reddish brown oil; MS m/e 320 (M^+, 6), 292 (26), 264 (17), 236 (91); IR (neat) 2035, 1960 cm^{-1}; UV λ_{max}^{EtOH} 341 (4.05), 419 (4.07); ^{1}H-NMR ($CDCl_3$, 200 MHz) 3.16 (d,d,d,d, J=7.5, 7.5, 1.5, 1.1, H-4), 4.05 (d,d,d, J=8.0, 1.5, 1.1, H-1), 5.43 (d,d,d, J=8.0, 5.0, 1.5, H-2), 5.54 (d,d,d, J=7.5, 5.0, 1.1, H-3), 5.69 (d,d, J=11.0, 7.5, H-5), 5.82 (d,d,d, J=11.0, 1.5, 1.1, H-6), 5.97 (d,d,d, J=12.0, 3.5, 3.5, H-8 or 11), 6.12-6.23 (m, H-7, 9, 10. 11 or 8, 12); ^{13}C-NMR ($CDCl_3$) 57.1, 60.2, 86.1, 91.4, 119, 126.6, 127.7, 129.4, 129.7, 131.8, 132.2, 133.1, 210.7. The signals of protons of the ring complexed with iron appeared at higher field than those of uncomplexed one. The complex (5) was air sensitive and gradually polymerized on standing at room temperature.

The reaction involves a [2 + 2]cycloaddition followed by decarboxylation. This mode of the reaction is similar to that of the reaction of 2 with diphenylketene or diphenyleneketene,$^{6)}$ and is in contrast to that of the reaction of tropone itself with 4 or diphenyleneketene to give a [8 + 2]cycloadduct as main product.$^{7)}$

The reaction of 5 with $Fe_2(CO)_9$ in refluxing benzene afforded hexacarbonyl(heptafulvalene)diiron (6) as air stable reddish solid, mp 185°C (dec), in 16.6% yield; MS m/e 460 (M^+, 5), 432 (32), 404 (22), 376 (12), 348 (20), 320 (24), 292 (100); IR (KBr) 2025, 1980, 1950 cm^{-1}; UV λ_{max}^{EtOH} 325 (4.19), 458 (4.29); ^{1}H-NMR ($CDCl_3$) 3.60 (m, 2H), 4.03 (m, 2H), 5.1-5.9 (m, 8H). The same complex was directly obtained by the reaction of heptafulvalene (7) with $Fe_2(CO)_9$ in poor yield.

The structure of 6 is tentatively assigned as shown in the scheme, in which two tricarbonyliron groups are located in the same side but in different rings; the NMR spectrum of 6 shows a symmetrical pattern and 6 is also obtained from the reaction of 3 with 4 as is described below.

The reaction of 3 with 4 in benzene at room temperature unexpectedly yielded the aforementioned complex (6) in 52.5% yield, presumably via the intermediate (8).

In order to isolate the complex (8), the reaction of 3 with 4 was carried out for shorter time at lower temperature, and an unstable dark brown solid was obtained in ca. 50% yield; IR (KBr) 2030, 1970, 1945, 1935 cm^{-1}; UV λ_{max}^{EtOH} 327 (4.07), 393 (3.98), 480 (3.85); ^{1}H-NMR ($CDCl_3$) 3.84 (d, J=7.0, 1H), 4.03 (m, 2H), 4.93 (m, 1H), 5.38 (m, 1H), 5.68 (m, 1H), 5.96 (m, 4H), 6.16 (m, 2H). The product was easily converted to the complex (6) by heating in benzene at 60°C for 1 h, and its NMR spectrum indicated that the product is not symmetrical. From these data the structure (9) is tentatively assigned for the product.

The reaction of 5 with TCNE afforded a [14 + 2]cycloadduct (10) in 70.5% yield as yellow crystals, mp 182-183°C (dec); MS m/e 448 (M^+,2), 420 (7), 392 (4), 364 (15); IR (KBr) 2240 (C≡N), 2060, 1996, 1940 cm^{-1}; UV λ_{max}^{EtOH} 352 (4.08); ^{1}H-NMR ($CDCl_3$) 2.16 (d, J=7.0, H-12), 2.99 (m, H-5), 3.30 (m, H-2), 3.63 (d, J=4.0, H-1), 5.46-5.72 (m, H-3, 4, 11), 6.20 (d, J=8.0, H-6), 6.25-6.5 (m, H-7, 10), 6.79 (m, H-8, 9). Attempted removal of $Fe(CO)_3$ group by the reaction with trimethylamine oxide unexpectedly afforded 7 in 62.5% yield.

The reaction of tricarbonyl(2,3-homotropone)iron (11)$^{8)}$ with 4 gave tricarbonyl(1,2-homoheptafulvalene)iron (12) in 78% yield as moderately stable brown oil; MS m/e 334 (M^+,11), 306 (35), 278 (3), 250 (100); IR (CCl_4) 2040, 1987, 1975 cm^{-1}; ^{1}H-NMR (CCl_4) 0.23 (m, 1H), 1.07 (m, 1H), 1.56 (m, 2H), 3.32 (m, 1H), 3.52 (m, 1H), 5.11 (m, 2H), 5.3-6.4 (m, 6H). The complex (12) reacted with TCNE to give a [8 + 2] cycloadduct (13) in 60% yield, mp 144-146°C (dec); MS m/e 462 (M^+, 1), 434 (3), 406 (30), 378 (27), 250 (100); IR (KBr) 2050, 1990, 1985 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 0.65 (m, 1H), 1.25 (m, 1H), 1.35 (m, 1H), 1.86 (m, H-3), 2.59 (d, J=7.0, H-7), 3.24 (m, H-13), 3.87 (t, J=6.0, H-4), 5.18 (d,d, J=6.0, 5.0, H-5), 5.42 (d,d, J=7.0, 5.0, H-6), 5.69 (d,d, J=9.0, 4.0, H-12), 6.45 (m, H-8, 11), 6.79 (m, H-9, 10).

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