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# Optically Active Organometallic Complexes of Heptafulvalene and 1,2-Homoheptafulvalene

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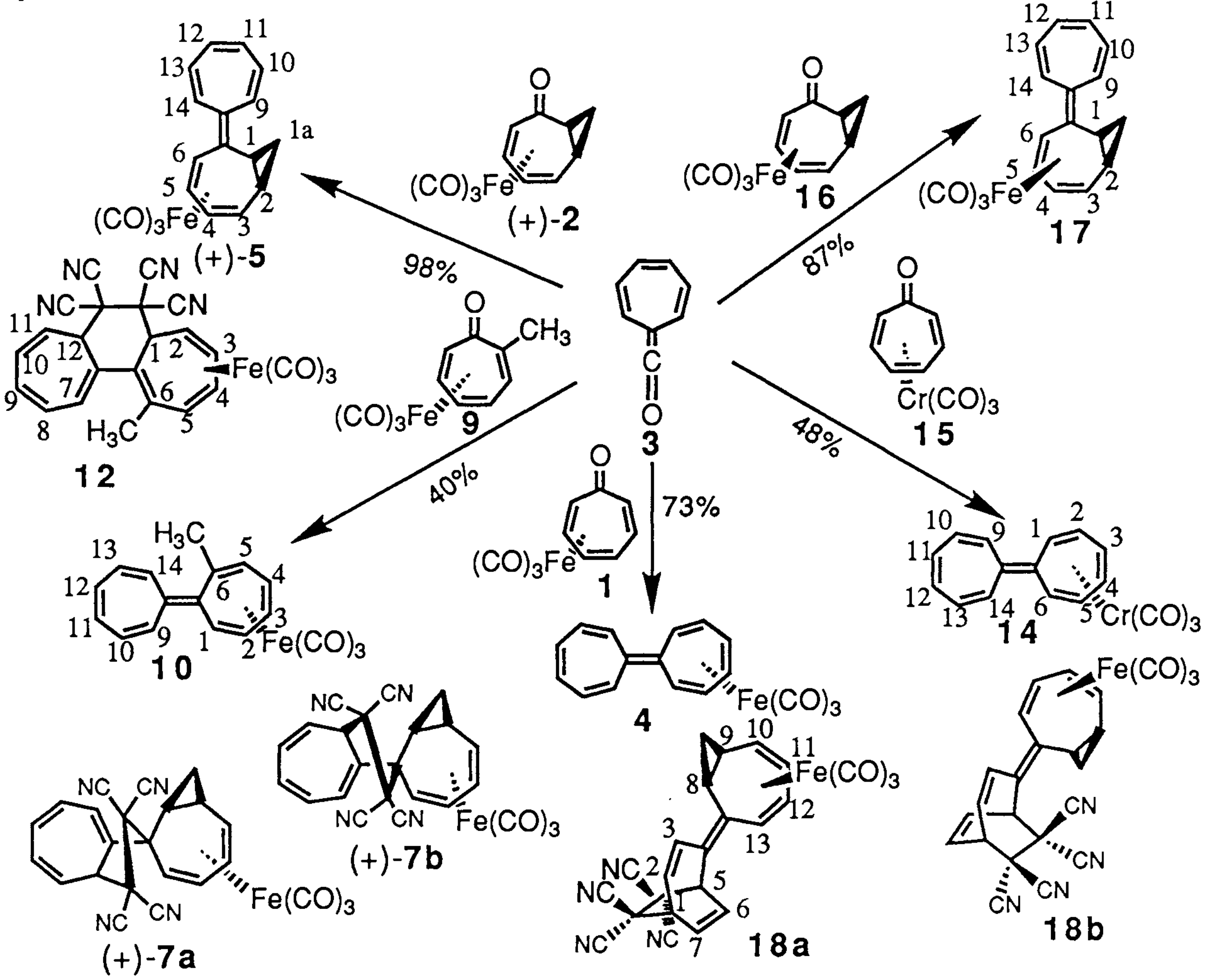
Racemic and/or optically active 7-methyltropone-Fe(CO)3, tropone-Cr(CO)3, and endo- and exo-homotropone-Fe(CO)3 reacted with 8-oxoheptafulvene to afford the corresponding racemic and/or optically active heptafulvalene metal complexes, respectively. Endo- and exo-homoheptafulvalene-Fe(CO)3 reacted with TCNE to give [2+4]π and [2+8]π cycloadducts, respectively.

In our previous paper,1) we reported that tropone-Fe(CO)3 (**1**) and exo-homotropone-Fe(CO)3 (**2**) readily reacted with 8-oxoheptafulvene (**3**)2) to give the corresponding heptafulvalene-Fe(CO)3, **4** and **5**, and that the heptafulvalene complexes also reacted with TCNE to give [2+14]π and [2+8]π cycloadducts, **6** and **7**, respectively. Using **3**, we explored the generality of the synthesis of these new heptafulvalene complexes and their reactivities with TCNE. Further, optically active metal complexes of heptafulvalene and homoheptafulvalene were prepared to study their chirality. These results are reported in this paper.

Optically active **1** and its derivatives in solution come to equilibrium with enantiomer3) or diastereomer4) by haptotropic rearrangement. The equilibrium state depends on the substituents and site of substitution. In 2-methyltropone-Fe(CO)3 (**8**) and 7-methyltropone-Fe(CO)3 (**9**), their equilibriun almost lies to **9**.5) Therefore, **9** reacted with **3** at 80 °C to give 6-methylheptafulvalene-Fe(CO)3 (**10**) in 40% yield, as an unstable brown oil. Since resonances of H-4 and H-1 appear at 2.98 and 3.97 ppm, respectively, the structure of this complex is **10**. Another possible equilibriated structure 1-methylheptafulvalene-Fe(CO)3 (**11**) can be ruled out on the basis of $^1$H NMR. Reaction of complex **10** with TCNE gave [2+14]π cycloadduct (**12**) as a pale yellow solid, mp 163-165 °C(decomp) in 58% yield. On the basis of NMR as a shown in Table 1, the structure of this adduct could be considered to be **12**, formed by the attack of TCNE at C-1 and C-9 of **10**.



Optically active (+)-**9**$^{6)}$ reacted with **3** to give (+)-**10** {[α]D +2896° (c 0.00275, $CH_3OH$)}. As shown in Fig. 1, the CD spectrum of (+)-**10** characteristically shows a strong plus band at 403 nm. Furthermore, (+)-**10** reacted with TCNE to give (-)-**12** adduct {[α]D -121°(c 0.115, $CHCl_3$)}; the CD spectrum is shown in Fig. 2.

It is known that heptafulvalene-$Cr_2(CO)_6$ is prepared by complexation of heptafulvalene (**13**) with $(CH_3CN)_3Cr(CO)_3$ and it reacts with butadiene under UV irradiation to give [4+6]π cycloadduct.$^{7)}$ So far, however, there has been no report on heptafulvalene-$Cr(CO)_3$ (**14**). Reaction of tropone-$Cr(CO)_3$ (**15**) with **3** gave **14** as a brown solid, mp 161-163 °C (decomp), in 48% yield. As shown in Table 1, its absorption spectrum shows maximum at 367 nm which is similar to **13** itself, comparing with 361 nm in **13**$^{8)}$ and 341 and 419 nm in **4**.$^{1)}$ Because chromium coordinates to triene, heptafulvalene moiety of **14** is similar to **13**. On the other hand, iron coordinates to diene. Therefore, heptafulvalene moiety is more distorted in **4** than in **14**. Complex **14** reacted with TCNE , but no clear product could be obtained.

By the Franck-Neumann procedure[9] optically active (+)-**1**[6] reacted with diazomethane to give the optically active [2+3]π cycloadduct, {$[\alpha]_D$ +326°(c 0.214, $CH_3Cl$)}. This adduct could be converted by thermolysis to optically active (+)-**2** {$[\alpha]_D$ +708°(c 0.164, $CH_3Cl$); optical purity is 91%.}. According to previously reported procedure,[1] using (+)-**2** gave (+)-**5** {$[\alpha]_D$ +1313°(c 0.0627, $CH_2Cl_2$)}. Its CD spectrum in Figure 1 characteristically shows a strong plus band at 409nm. Absolute configuration of (+)-**5** has been determined as depicted in the scheme on the basis of chemical correlation of known absolute configuration of (+)-**2**.[10] The optically active (+)-**5** reacted with TCNE to give an optically active [2+8]π cycloadduct (+)-**7a** or **7b**, $[\alpha]_D$ +428°. These optical purities are not clear. However, by the large $[\alpha]_D$ value it could be estimated that their optical purity is unchanged during chemical conversion from exo-homotropone-$Fe(CO)_3$ and these reactions proceed stereospecifically.

Endo-1,2-homotropone-$Fe(CO)_3$ (**16**)[11] reacted with **3** to give endo-homoheptafulvalene-$Fe(CO)_3$ (**17**) as a reddish brown solid, mp 80-85 °C, in 86% yield. The complex **17** reacted with TCNE in $CH_2Cl_2$ to give a [2+4]π cycloadduct **18** as yellow crystals, mp 124-126 °C(decomp), in 79% yield. Two possible structures, **18a** and **18b**, can be considered for the adduct because methylene protones of bridged structure appear at 3.7 ppm ( dd, J=7.6, 7.2, H-10), and 4.84 ppm (d, J=7.2, H-13) in $^1H$-NMR spectrum and the peak of the longest wave length in the absorption spectrum appears at 362 nm. It becomes clear that **17** reacted with TCNE in a different mannar from **5**. It is interesting that adduct **18** was stable, although it has endo-homoheptafulvene moiety. These results have stimulated our interest in pursuing a more simple preparation of homoheptafulvene-$Fe(CO)_3$.

Table 1. Spectral data of new complexes

| | IR ν/$cm^{-1}$ | UVλ/nm(logε) | $^1H$-NMR ($CDCl_3$) ppm( J/Hz ) |
|---|---|---|---|
| **10** | 2052, 1992, 1974 | 260sh(4.13)<br>342 (4.05)<br>390 (4.40) | 1.75(d, J=1.2, Me), 2.98(td, J=7.5, 1.2, H-4), 3.97(d, J=7.8, H-1), 5.3-5.7(m,H-2,3,5), 5.9-6.2(m, 4H), 6.26(m, 2H) |
| **12** | 2068, 2008, 1996 | 334 (4.04) | 1.69(d, J=1.8, Me), 2.07(dd, J=6.9, 1.2, H-12), 2.97(dd, J=7.2, 1.8, H-1), 3.27(ddd, J=6.6, 5.4, 2.1, H-2), 3.68(dd, J=5.4, 1.8, H-5), 5.47(dd, J=8.7, 6.9, H-11), 5.6(m, H-4), 5.7(m, H-3),. 6.19(m, H-7), 6.47(m, H-10), 6.84(m, H-8,9) |
| **14** | 1970, 1910, 1895, 1875 | 225sh(4.54)<br>280sh(4.06)<br>367 (4.27)<br>400sh(3.97) | 4.00(d, J=8.7, 2H), 4.81(m, 2H), 5.54-5.9(m, 8H) |
| **17** | 2048, 1982, 1964 | 210sh(4.48)<br>230sh(4.33)<br>312 (3.96)<br>384 (4.12) | 0.22(m,1H), 0.94(m,1H), 1.26(m, 1H), 3.38(m, H-4), 3.91(d, J=8.1, H-1), 4.98(ddd,J=8.1, 5.1, 2, H-2), 5.59(dd, J=5.1, H-3), 5.8(m, H-10 or 13), 6.68(m, 4H), 6.36(d, J=10.8, H-9 or 14) |
| **18** | 2256(CN), 2056,1992, 1976 | 225sh(4.35)<br>308 (4.07)<br>362 (4.16) | 0.4(m, 1H), 1.3(m, 3H), 3.43(tm, J=7.2, H-10), 3.7(dd, J=7.6, 7.2, H-1), 4.05(d, J=7.2, H-13), 4.84(d, J=7.2, H-5), 5.26(ddd, J=7.2, 4.5, 1.2, H-12), 5.66(d, J=7.2, H-11), 5.82(dd, J=8.4, 7.2, H-2), 6.39(t, J=7.2, H-6), 6.7(m, H-3, 7) |

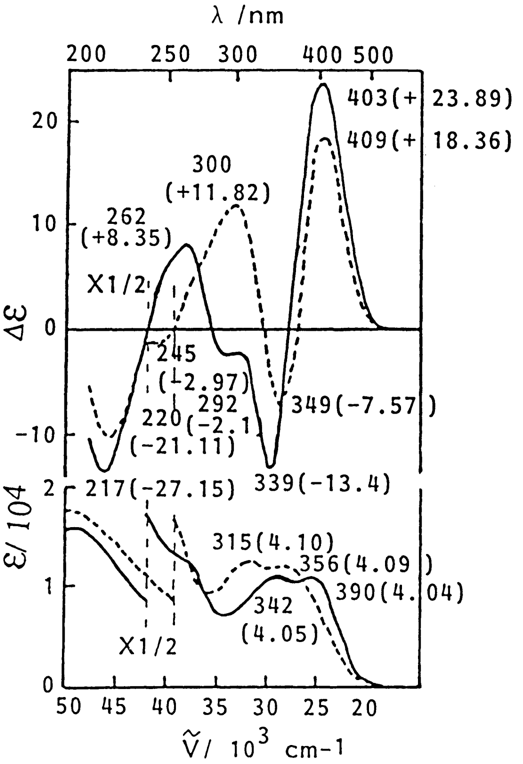


Fig. 1. Absorption(bottom) and CD (top) spectra of (+)-10 (———) and (+)-5 (----) in $CH_3OH$.

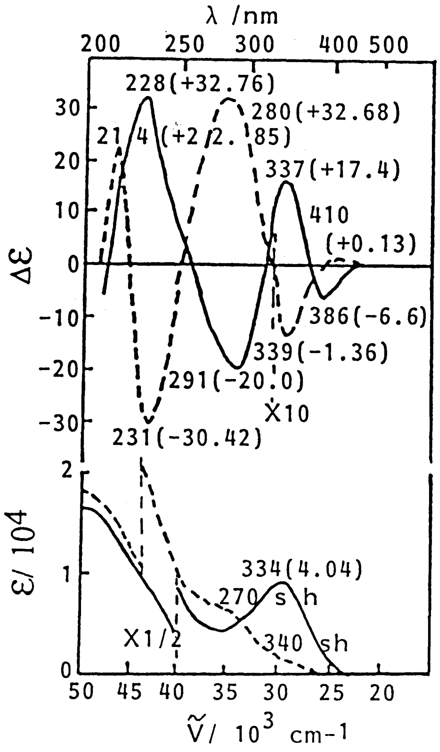


Fig. 2. Absorption(bottom) and CD (top) specta of (-)-12 (———) and (+)-7 (----) in $CH_3OH$.

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