Pergamon

*Tetrahedron: Asymmetry* Vol. 6, No. 1, pp. 35-38, 1995
Elsevier Science Ltd
Printed in Great Britain
0957-4166/95 \$9.50+0.00

0957-4166(94)00345-9

# Optically Active Hexacarbonyl(2-methyltropone)diiron; Reaction Mechanism of Tricarbonyl(7-methyltropone)-iron with $Fe_2(CO)_9$

**Noboru Morita,* Mitsuhiro Kurita, Shunji Ito, Toyonobu Asao, and Hideo Sotokawa**

Department of Chemistry, Faculty of Science, Tohoku University, Kawauchi Aoba-ku, Sendai 980-77, Japan

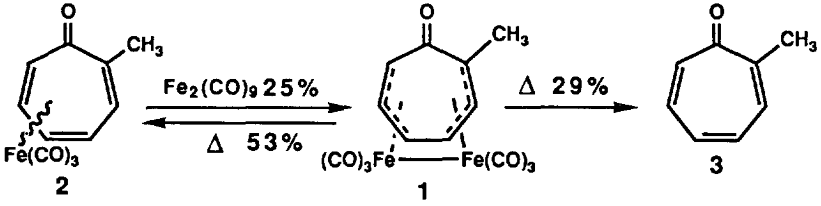
**Akio Tajiri**

Department of Chemistry, College of General Education, Hirosaki University, Hirosaki 036, Japan

**Abstract:** An optically active di-π-allyl hexacarbonyldiiron complex was prepared for the first time starting from racemic 7-methyltropone$Fe(CO)_3$. The reaction mechanism of (substituted tropone)$Fe(CO)_3$ with $Fe_2(CO)_9$ was discussed.

The reaction of $Fe_2(CO)_9$ with polyenes sometimes gives diiron hexacarbonyl complexes along with mono iron tricarbonyl complexes. The yield of the diiron complex increases with the amount of $Fe_2(CO)_9$ used.[1] Although interesting results were reported for the reaction of cyclooctatrienes with $Fe_2(CO)_9$, the mechanism of this reaction was ambiguous.[2] Tropone$Fe_2(CO)_6$ seems to play a role as an important intermediate in the preparation of tropone$Fe(CO)_3$ from acetylene with $Fe_2(CO)_9$ under a carbon monoxide atmosphere.[3] Tropone$Fe_2(CO)_6$ can be also prepared by the reaction of tropone$Fe(CO)_3$ with $Fe_2(CO)_9$.[4] Although optically active tricarbonyl complexes of tropone and its derivatives have been reported,[5] there is no report of their optically active diiron hexacarbonyl counterparts. We thus addressed ourselves to the problem of preparing optically active hexacarbonyl(substituted tropone)diiron. The structure of hexacarbonyl(tropone)diiron is a symmetric di-π-allyl complex and is therefore achiral.[6] However, 2-methyltropone$Fe_2(CO)_6$ is expected to be a planar chiral complex. Its resolution by HPLC using a chiral column has so far failed. Here we report the preparation of optically active 2-methyltropone$Fe_2(CO)_6$ from optically active 7-methyltropone$Fe(CO)_3$ and the mechanism of its formation.

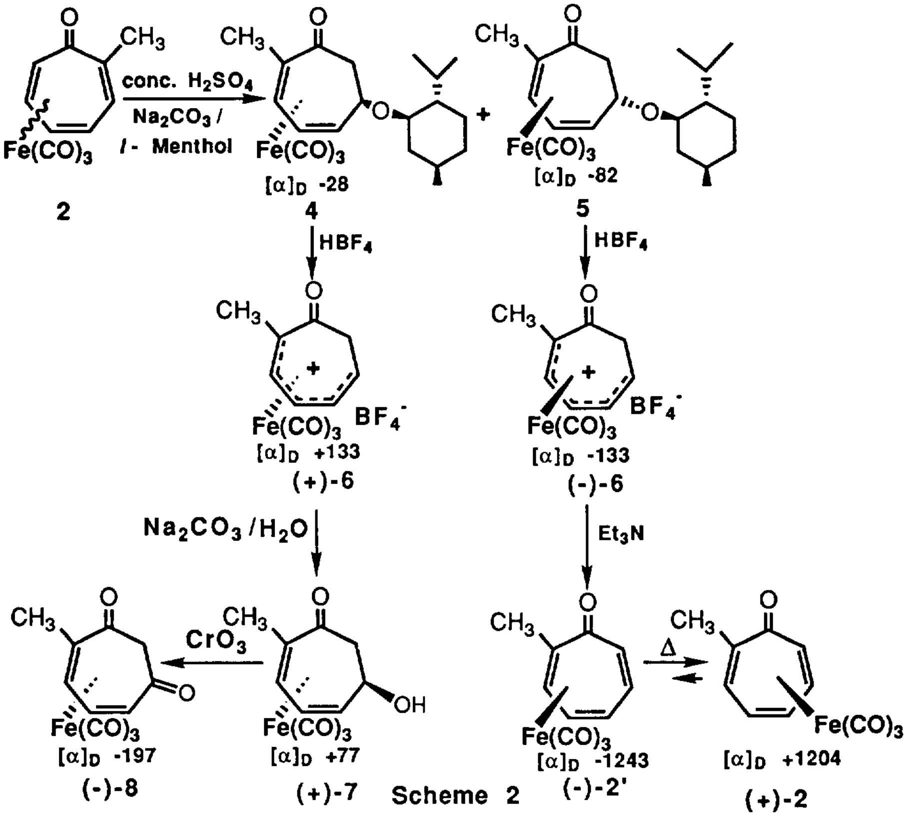
7-Methyltropone$Fe(CO)_3$ (2) reacted with 1.6 equivalents of $Fe_2(CO)_9$ in ether solution at reflux to give racemic 2-methyltropone$Fe_2(CO)_6$ (1) in 25% yield, which decomposed in refluxing benzene to give 2 and 2-methyltropone (3) in 53 and 29% yields, respectively.



**Scheme 1**

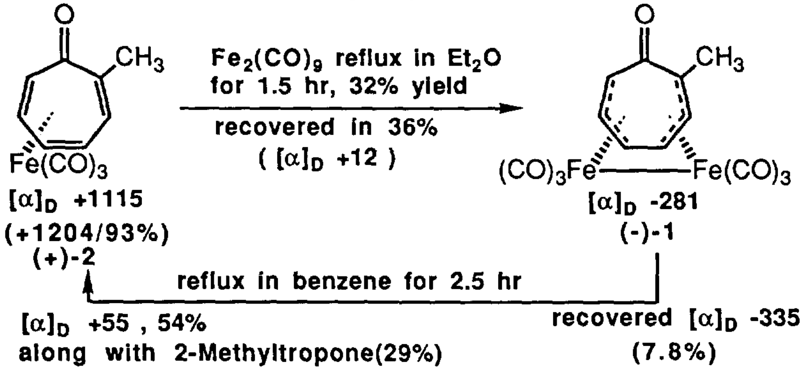
Our first working hypothesis was as follows. Nonacarbonyldiiron thermally decomposes by losing carbon monooxides sequentially to give unsaturated diiron species $Fe_2(CO)_{9-n}$ (n=1, 2, 3 or 4). Since the uncoordinated double bond in **2** is subject to steric hindrance, the unsaturated diiron species attacks from the side opposite to the irontricarbonyl group. Optically active **1** could be expected to be obtained if optically active **2** is used.

Optical resolution of **2** was carried out as follows similar to parent complex.[5d] Racemic **2** was treated with conc. $H_2SO_4$ and neutralized with $Na_2CO_3$ in the presence of *l* -menthol to give diastereomeric ethers **4** ( mp 126 - 7°C(d), $^1H$ NMR($CDCl_3$) 5.78(d, J=5.6 Hz, 1H), 5.36(dd, J=7.7, 5.6 Hz, 1H), 4.07(m, 1H), 3.08(m, 2H), 2.42(m, 1H), 1.63(s, $CH_3$, 3H), 0.92(d, J=6.6 Hz, $CH_3$), 0.84(d, J=7.0 Hz, $CH_3$), 0.67(d, J=7.0 Hz, $CH_3$), 0.7-2.15 ppm (m, 10H); IR(KBr) 2062, 1993, 1981, 1954, 1651 $cm^{-1}$; $[\alpha]_D$ -28, CD($CH_3OH$) $\lambda$ nm ($\Delta\varepsilon$) 257(+7.61), 313(-9.32), 370(+2.76)) and **5** (mp 89 - 91°C, $^1H$ NMR($CDCl_3$) 5.79(d, J=5.7 Hz, 1H), 5.35(dd, J=7.7, 5.7 Hz, 1H), 4.06(m, 1H), 3.22(m, 2H), 1.64(s, $CH_3$), 0.93(d, J=7.0 Hz, $CH_3$), 0.89(d, J=6.8 Hz, $CH_3$), 0.812(d, J=7.0 Hz, $CH_3$), 0.6-2.5 ppm (m, 11H); IR(KBr) 2068, 2004, 1977, 1951, 1660 $cm^{-1}$; $[\alpha]_D$ -82; CD($CH_3OH$) $\lambda$ nm($\Delta\varepsilon$) 257(-7.95), 311(+9.27), 367(-3.02) ), which were separable by column chromatography on silica gel. Although both complexes are levo rotatory, their CD spectra showed bands as one would expect for enantiomers. They reacted with $HBF_4$ in the solution of diethyl ether to give cation (+)-**6** ( $[\alpha]_D$ +133; CD ($CH_3CN$) $\lambda$ nm($\Delta\varepsilon$) 215(-3.23), 228(+4.23), 242(-0.43), 263(+2.73), 316(+0.43), 341(-0.63), 385(+0.63)) and (-)-**6** ($[\alpha]_D$ -133), respectively. Cation (-)-**6** was treated with triethylamine in dichloromethane to give (-)-**2'** ($[\alpha]_D$ -1243; mp 81-83°C; IR(KBr) 2068, 1999, 1978, 1633, 1603 $cm^{-1}$; $^1H$ NMR($CDCl_3$) 6.48(dd, J=11, 7.8 Hz, H-6), 6.27 (m, H-3,4), 5.10(d, J=11 Hz, H-7), 2.66(t, J=7.8 Hz, H-5), 1.55 ppm (s, $CH_3$)), which was thermally isomerized to (+)-**2** ($[\alpha]_D$ +1204). According to

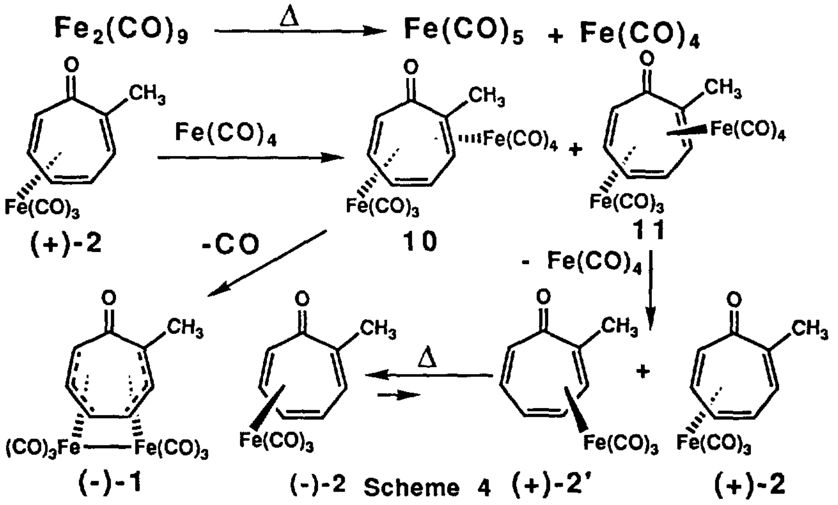


Scheme 2

calculations using the extended Hückel method, there is a difference in the NHOMO of **2'** and **2**. This is one of the reasons for the thermal stability of **2**. Their CD spectra are shown in Fig 1. The absolute configuration of the complex (+)-**2** could be assigned as 2S configuration by comparison with CD spectrum of (+)-troponeFe(CO)$_3$.[5a] Optically active (+)-**6** was neutralized by $Na_2CO_3$/water to give optically active alcohol (+)-(**7**) ($[\alpha]_D$ +77; CD ($CH_3OH$) $\lambda$ nm($\Delta\varepsilon$) 220(+7.25), 257(+7.59), 308(-10.88), 367(+3.45)), which was oxidized with $CrO_3$/pyridine in dichloromethane to give optically active 2-methyl-2,3-cycloheptadiene-1,6-dione (-)-(**8**) ($[\alpha]_D$ -197; CD in Fig. 2).[7] This is the first example of an optically active substituted (2,3-cycloheptadiene-1,6-dione)Fe(CO)$_3$ complex. Next, the complexation of **2** was carried out by using optically active (+)-**2** ($[\alpha]_D$ +1115 (93% ee)). As a result, optically active (-)-**1** ($[\alpha]_D$ -281) was obtained[1]. The specific rotation of the recovered **2** was +12. These results suggest that racemization proceeds under the reaction conditions. To examine the relative structure of (+)-**2** and (-)-**1**, (-)-**1** was thermally decomposed in refluxing benzene. The specific rotation of the (+)-**2** so obtained was +55. Although racemization of **2** proceeded under these conditions, positive optical rotation still remained. Contrary to the working hypothesis, both iron atoms were coordinated at the same side of 2-methyltropone in both (+)-**2** and (-)-**1**. This result indicates that the iron reagent attacks from the same side to which the iron tricarbonyl is attached when **2** reacted with $Fe_2(CO)_9$. On the other hand, specific rotation of recovered (-)-**1** is -335 (Its CD spectrum of (-)-**1** is shown in Fig. 2, although its optical purity is uncertain.), which means (-)-**1** does not racemise under these conditions.



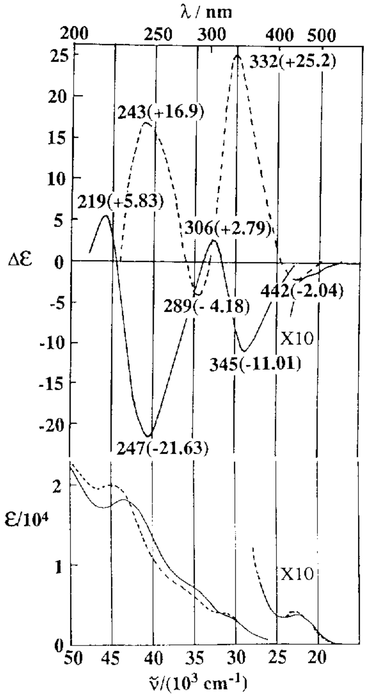
Scheme 3



Scheme 4

Enantiomeric excess could be increased by recrystalization. On the basis of these results, the reaction mechanism can be considered as shown in scheme 4. Nonacarbonyldiiron decomposes to $Fe(CO)_5$ and $Fe(CO)_4$. Unsaturated $Fe(CO)_4$ attacks to uncoordinated double bond from both side of tropone ring in **2** to give labile intermediates **10** and **11**. Complex **10** easily loses carbon monoxide to give stable **1**. On the other hand, complex **11** decomposes to (+)-**2** and isomer (+)-**2'**, which isomerizes to enantiomer (-)-**2**, although vinilogous complex of cyclooctatrienone like **11** could be isolated.[7] It is racemization mechanism of the starting material (+)-**2**. The CD spectrum of (-)-**1** in Fig. 2 characteristically showed small bands.

This procedure will become the general method for chiral hexacarbonyl(tropone)diiron from racemic tricarbonyl(tropone)iron and the generality of this procedure is under investigation.



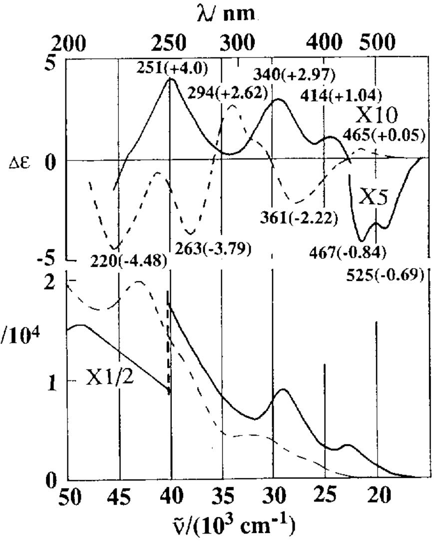


Fig. 1 Absorption (bottom) and CD (top) spectra of (-)-**2'** (———) and (+)-**2** (------) in iso-propanol

Fig. 2 Absorption (bottom) and CD (top) spectra of (-)-**1** (———) and (-)-**8** (------) in methanol

## References

1. Morita, N.; Asao, T.; Tajiri, A.; Sotokawa, H.; Hatano, M. *Chem. Lett.* **1985**, 1879.
2. Salzer, A.; von Philipsborn, W. *J. Organomet. Chem.* **1978**, *161*, 39.
3. Hogarth, G.; Kayser, F.; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G. ; Turner, M. L. *J. Chem. Soc., Chem. Commun.* **1988**, 358.
4. Morita, N.; Asao, T. *Chem. Lett.* **1982**, 1575.
5. **a)** Tajiri, A.; Morita, N.; Asao, T. ; Hatano, M. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 329; **b)** Morita, N.; Asao, T.; Tajiri, A.; Sotokawa, H.; Hatano, M. *Tetrahedron Lett.* **1986**, *27*, 3873; **c)** Sotokawa, H.; Tajiri, A.; Morita, N.; Hatano, M.; Asao, T. *Tetrahedron Lett.* **1987**, *28*, 5873; **d)** Morita, N.; Asao, T.; Sotokawa, H; Hatano, M.; Tajiri, A. *J. Organomet. Chem.* **1988**, *339*, C1.
6. Morita, N.; Kabuto, C.; Asao, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1677.
7. Morita, N.; Ito, S.; Asao, T. *J. Organomet. Chem.* **1993**, *460*, 67.

(*Received in Japan* 5 *September* 1994; *accepted* 14 *October* 1994)