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The synthesis of tricarbonyl(2,4-cycloheptadiene-1,6-dione)iron and tricarbonyl(2,4-cyclooctadiene-1,6-dione)iron

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Abstract

Tricarbonyl(6-hydroxy-2,4-cycloheptadien-1-one)iron derived from tricarbonyl(tropone)iron was easily oxidized to give tricarbonyl(2,4-cycloheptadiene-1,6-dione)iron. This procedure was also extended to tricarbonyl(2-substituted tropone)iron and exo(bicyclo[5.1.0]octa-3,5-dien-2-one)tricarbonyliron to yield tricarbonyl(2-substituted 2,4-cycloheptadiene-1,6-dione)iron and tricarbonyl(2,4-cyclooctadiene-1,6-dione)iron, respectively.

1. Introduction

During our investigation of tricarbonyl(tropone)iron complexes [1], we became interested in the preparation of tricarbonyl(3-hydroxytropone)iron complexes which, having a cross conjugated system, could be a similar precursor to 2-cyclopentene-1,4-dione [2], 1,3-cyclobutanedione derivatives [3], and 3-hydroxytropone [4]. The parent complex, tricarbonyl(3-hydroxytropone)iron, has been prepared by the direct complexation of 3-hydroxytropone with $Fe_3(CO)_{12}$ [5]. This direct method is, however, hardly applicable to the synthesis of its derivatives because of the poor availability of substituted 3-hydroxytropones. It has also been reported [5] though without spectral data that this complex exists in diketo form, tricarbonyl(2,4-cycloheptadiene-1,6-dione)iron (1a). Here we report a new and more generally applicable synthetic route for this and related complexes.

2. Results and discussion

Tricarbonyl(6-hydroxy-2,4-cycloheptadien-1-one)iron (5a) has been readily prepared from tropone in two steps [6]. Moreover, it was reported [7] that the tricarbonyl(2-substituted tropone)iron complexes (2b–d) were converted into dienonium cation (4b–d) by

isomerization of the dienonium cation (3b–d) in concentrated sulfuric acid. These solutions were therefore neutralized with Na_2CO_3/H_2O under the same conditions as in the synthesis of 5a to give, regioselectively, tricarbonyl(2-substituted 6-hydroxy-2,4-cycloheptadien-1-one)iron complexes (5b–d) in 75, 53 and 60% yields, respectively. Sometimes the yields of 5c and 5d were decreased due to the formation of ether complexes (6c and 6d) as side products whose structures were established on the basis of spectral data. Their molecular ion + hydrogen (MH^+) peaks in their mass spectra were observed by FAB techniques. Ether complexes 6a, 6a', 6b, and 6b' were also obtained when cations 4a and 4b were decomposed slowly by the addition of small amounts of iced water. The relationship of 6a to 6a' and of 6b to 6b' is thought to be as diastereomers of a racemic form and a meso form, respectively.

The oxidation of alcohol tricarbonyliron complex with chromium trioxide in pyridine has been reported by Pettit and others [8]. However, the yield of ketone was only 17% which was disappointing from the standpoint of synthetic chemistry. We found that the yield of the similar oxidation increased to 75% in the synthesis of tropoquinodimethane-$Fe(CO)_3$ [9] when dichloromethane was the solvent. This condition was applied to 5a–d. Complexes 5a–d were oxidized with CrO_3/pyridine in CH_2Cl_2 at room temperature to give 1a–d in 65, 58, 60 and 90% yields, respectively. Each of the

TABLE 1. The C=O stretching bands of indicated complexes

	IR (KBr) cm^{-1}
1a	2080, 2000, 1980, 1665, 1635
1b	2076, 2008, 1994, 1670, 1636
1c	2080, 2070, 2020, 2010, 2000, 1665, 1640
1d	2090, 2080, 2070, 2030, 2020, 2010, 1680, 1650
17	2070, 2050, 2000, 1990, 1985, 1655, 1640

two characteristic absorptions attributable to carbonyl stretching in IR of 1 appears between 1600 cm^{-1} and 1700 cm^{-1} (Table 1), which suggests that all of these complexes exist in the diketone forms.

Decomplexation of 1a with triphenylphosphite on reflux in bromoform afforded 7. Although the yield (39%) was not high, a new synthetic way of 3-hydroxytropone from tropone was thereby established.

This procedure was extended to the synthesis of tricarbonyl(2,4-cyclooctadiene-1,6-dione)iron (17) from exo-(bicyclo-[5.1.0]octa-3,5-dien-2-one)tricarbonyliron (8). The complex 8 was prepared in better yield along with the endo-(bicyclo[5.1.0]octa-3,5-dien-2-one)tricarbonyliron (19) by Aumann's procedure [10]. Childs has reported [11] that the complex 8 was converted into monocyclic dienonium cation (10) in concentrated sulfuric acid by ring opening of initially formed bicyclic
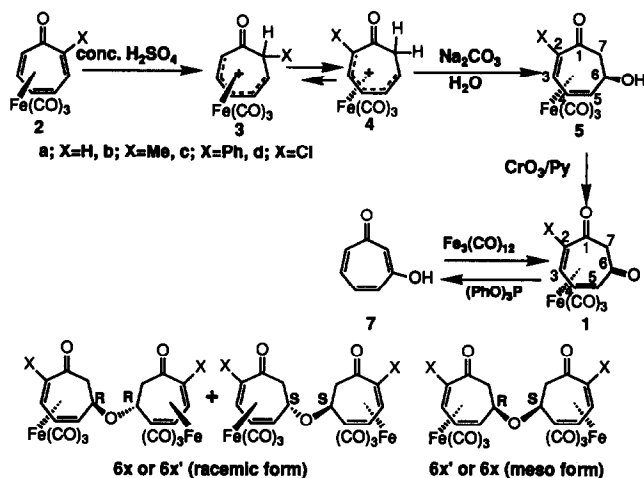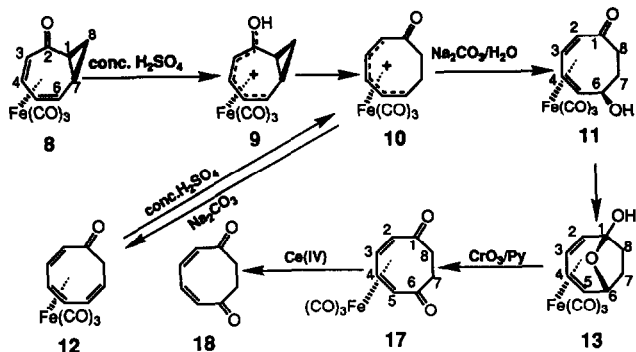

Scheme 1.

dienonium cation (9). The solution was neutralized with Na$_2$CO$_3$/H$_2$O in the same way as 5a to give tricarbonyl(2,4,6-cyclooctatrien-1-one)iron (12) [12] and the colorless and unexpected complex 13 in 19 and 66% yields, respectively. The structure of the latter complex is not 11, but 13 because there is OH absorption at 3325 cm^{-1} and carbonyl absorption could not be found between 1700 cm^{-1} and 1600 cm^{-1} in its IR

TABLE 2. ^{1}H NMR data of tricarbonyliron complexes

	^{1}H NMR (CDCl$_3$) ppm (J, Hz)
1a	5.88 (m, H-3,4), 3.70 (m, H-2,5), 3.05 (s, H-7, 2H)
1b	5.92 (d, J = 6.75, H-3), 5.74 (t, J = 6.75, H-4), 3.6 (d, J = 6.75, H-5), 3.13 (dd, J = 12.3, 1.5, H-7), 2.95 (d, J = 12.3, H-7), 1.8 (s, Me)
1c	7.5–7.3 (m, Ph), 6.51 (d, J = 6.75, H-3), 5.93 (t, J = 6.75, H-4), 3.69 (d, J = 6.75, H-5), 3.14 (s, 2H, H-7)
1d	6.36 (dd, J = 6.4, 0.7, H-3), 5.79 (t, J = 6.4, H-4), 3.60 (d, J = 7, H-5), 3.25 (dd, J = 12.5, 1.8, H-7), 2.91 (d, J = 12.5, H-7)
5a	5.81 (ddd, J = 6.6, 5.4, 1.2, H-3), 5.55 (ddd, J = 7.4, 5.4, 1.2, H-4), 4.45 (ddd, 11.4, 5.6, 1.8, H-6), 3.28 (m, 2H), 2.40 (ddt, J = 11.4, 5.6, 1.8, H-7), 2.01 (t, J = 11.4, H-7)
5b	5.82 (d, J = 6, H-3), 5.38 (dd, J = 8, 6, H-4), 4.44 (dd, J = 10.5, 6, H-6), 3.19 (d, J = 8, H-5), 2.46 (ddd, 10.5, 4.5, 2, H-7), 1.91 (t, J = 10.5, H-7), 1.8 (m, OH), 1.64 (s, Me)
5c	7.3 (m, Ph), 6.39 (d, J = 5.7, H-3), 5.53 (dd, J = 7.5, 5.7, H-4), 4.51 (dd, J = 10.8, 5.1, H-6), 3.29 (d, J = 7.5, H-5), 2.47 (dd, J = 10.8, 5.1, H-7), 2.2 (m, OH), 2.06 (t, J = 10.8, H-7)
5d	6.27 (dd, J = 5.7, 0.9, H-3), 5.45 (dd, J = 7.9, 5.7, H-4), 4.47 (ddd, J = 11, 5.5, 1.8, H-6), 3.21 (d, J = 7.9, H-5), 2.59 (ddd, J = 11, 5.5, 2, H-7), 1.89 (t, J = 11, H-7), 1.79 (m, OH)
6a	5.80 (t, J = 6.6, H-3), 5.52 (t, J = 6.4, H-4), 4.14 (dd, J = 10.3, 4, H-6), 3.26 (d, J = 6.6, H-2), 3.14 (d, J = 6.6, H-5), 2.42 (dd, J = 10.3, 4, H-7), 2.03 (t, J = 10.3, H-7)
6a'	5.80 (dd, J = 6.3, 5.4, H-3), 5.54 (dd, J = 7.4, 5.4, H-4), 4.12 (ddd, J = 11.4, 5.4, 1.7, H-6), 3.23 (m, H-2,5), 2.31 (ddm, J = 11.4, 5.4, H-7), 1.90 (t, J = 11.4, H-7)
6b	5.79 (d, J = 5.7, H-3), 5.32 (dd, J = 7.8, 5.7, H-4), 4.15 (m, H-6), 3.03 (d, J = 7.8, H-5), 2.44 (m, H-7), 1.90 (t, J = 11.4, H-7), 1.64 (s, Me)
6b'	5.79 (d, J = 5.7, H-3), 5.36 (dd, J = 7.5, 5.7, H-4), 4.12 (dd, J = 10.2, 5.7, H-6), 3.09 (d, J = 7.5, H-5), 2.34 (m, H-7), 1.81 (t, J = 10.2, H-7), 1.64 (s, Me)
6c	7.3 (m, Ph), 6.38 (d, J = 5.7, H-3), 5.53 (dd, J = 7.8, 5.7, H-4), 4.29 (dd, J = 10.9, 5.9, H-6), 3.17 (d, J = 7.8, H-5), 2.53 (ddd, J = 10.9, 5.9, 2.2, H-7), 2.11 (t, J = 10.9, H-7)
6d	6.25 (d, J = 5.9, H-3), 5.41 (m, H-4), 4.15 (m, H-6), 3.04 (m, H-5), 2.54 (m, H-7), 1.89 (m, H-7)
13	5.34 (m, H-3,4), 4.66 (t, J = 6.8, H-6), 3.01 (m, H-2,5,OH), 2.63 (m, H-8), 2.30 (m, H-7), 2.0 (m, H-7), 1.8 (m, H-8)
16	4.96 (dd, J = 6.8, 5.8, H-3), 4.4 (ddd, J = 8.4, 5.8, 0.6, H-4), 3.85 (dd, J = 8.7, 4.8, H-6), 3.32 (dd, J = 8.4, 4.8, H-5), 2.83 (m, H-2,7), 2.34 (ddd, J = 11.3, 6.6, 1.8, H-8), 1.94 (td, J = 11.3, 0.8, H-8)
17	5.87 (m, H-3,4), 3.53 (m, H-2,5), 2.27 (m, H-7,8)

Scheme 2.

spectrum. The yield of 12 increased to 80% if only a very small amount of water was used when after addition of sodium carbonate the reaction mixture was reacted with water little by little (see Experimental section).

The synthesis of complex 12 from 2,4,6-cyclooctatrien-1-one (14) has already been reported by King and Brookhart [12]. According to King's conditions, compound 14 reacted with 2 equivalents of $Fe_2(CO)_9$ to give complex 12 and the known dinuclear complex 15 along with the unknown complex 16 in 31, 16 and 12% yields, respectively. The structure of the complex 16 was proposed on the basis of spectral data and the following reaction. 16 is less polar than 12 or 15. It was observed that 16 was decomposed in chloroform to give 12 along with traces of 14 and 15. These observations suggested that the relative position of the two iron atoms in 16 is anti.
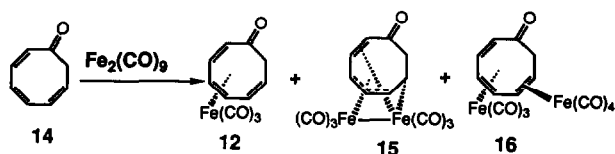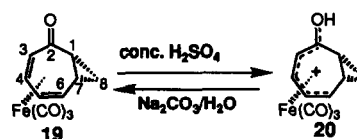

Scheme 3.

Complex 12 could also be converted into complex 13 in 58% yield by successive treatment with concentrated sulfuric acid and Na_2CO_3/H_2O by the usual way.

Complex 13 was oxidized with chromium trioxide/pyridine in dichloromethane to give tricarbonyl-(2,4-cyclooctadiene-1,6-dione)iron (17) as pale yellow crystals in 66% yield. Treatment of 17 with ceric ammonium nitrate gave free 2,4-cyclooctadiene-1,6-dione (18) [13] in 73% yield.

Similarly, endo-(bicyclo[5.1.0]octa-3,5-dien-2-one)tricarbonyliron (19) [10] was treated with concentrated sulfuric acid and Na_2CO_3/H_2O. However, complex 19 was recovered almost quantitatively. It is interesting that ring opening of the dienonium cation (20) did not occur, in contrast to the smooth transformation of 9.

Scheme 4.

Compared with 8, the bond length of C(1)–C(7) in 19 is shorter by 0.018–0.036 Å [14]. This may be the main reason for its stability towards concentrated sulfuric acid.

(2,4-Cycloheptadien-1-one)Fe(CO)$_3$ (22) is a useful intermediate for the preparation of 2a and 3a from tricarbonyl(cycloheptatriene)iron [6]. The complex 22 has been prepared in 14% yield by nucleophilic attack by hydroxide ion on (cycloheptadienyl)Fe(CO)$_3$ tetrafluoroborate followed by oxidation with chromium trioxide in pyridine [15]. The yield of (5-hydroxy-1,3-cycloheptadiene)Fe(CO)$_3$ (21) from (cycloheptadienyl)Fe(CO)$_3$ tetrafluoroborate was 86% [16]. Synthetically, the yield of oxidation of complex 21 was not good (ca. 17%). Therefore, our oxidation conditions were applied to the complex 21, to give 22 in 60% yield. Further studies on the chemical properties of complexes 1 and 17 are now in progress.
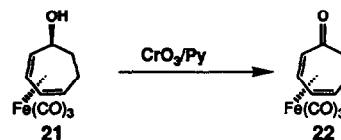
Scheme 5.

3. Conclusions

Tricarbonyl(2,4-cycloheptadiene-1,6-dione)iron and its derivatives were easily obtained from tricarbonyl(2-substituted tropone)irons in two steps. Similarly, tricarbonyl(2,4-cyclooctadiene-1,6-dione)iron was obtained from exo-(bicyclo[5.1.0]octa-3,5-dien-2-one)tricarbonyliron or tricarbonyl(2,4,6-cyclooctatrien-1-one)iron. In the complexation of 2,4,6-cyclooctatrien-1-one with $Fe_2(CO)_9$, the new diiron complex 16 was obtained.

4. Experimental section

Melting points were determined by a Yanaco micromelting point apparatus and are uncorrected. Infrared spectra were taken on a Hitachi 215 spectrometer. ^1H NMR spectra (90 MHz) were measured with a Hitachi R-90H spectrometer for solution in CDCl$_3$ with TMS as an internal standard. Electronic spectra were measured with a Hitachi 340 spectrometer for solution in ethanol. Mass spectra were measured with a Jeol JMS-HX110. Column chromatography was performed through silica gel (Kieselgel 60).

4.1. Preparation of 8 and 19

A dispersed solution of 1,2-homotropone [17] (1.66 g, 13.8 mmol) and $Fe_2(CO)_9$ (7.2 g, 19.3 mmol) in dry ether (30 ml) was refluxed for 2 h under argon. After removal of the solvent, the residue was chromatographed on silica gel with hexane and ethyl acetate as solvents to give the endo complex 19 (635 mg, 17%) and the exo complex 8 (1.43 g, 81%) [10].

4.2. General procedure for the preparation of 5a–d and 13

A solution of tricarbonyl(substituted tropone)iron (2 mmol) in 5 ml of dichloromethane was mixed with 1.5 ml of concentrated sulfuric acid at 0°C. The color of the dichloromethane solution changed from red to black and then disappeared. The sulfuric acid layer became red. After 30 min at room temperature, the sulfuric acid solution was poured onto an excess of sodium carbonate (3.5 g, 30 mmol) at 0°C, with thorough stirring. The resulting paste was diluted with dichloromethane (20 ml). Iced water (10 ml) was poured into the above dispersed solution at 0°C. After the evolution of carbon dioxide ceased, the products were extracted with dichloromethane. The extracts were combined and washed with a saturated aqueous solution of sodium carbonate, dried over magnesium sulfate and the solvent removed. Products were separated by column chromatography on silica gel, using a mixture of dichloromethane and ethyl acetate as solvents.

5a was obtained in 91% yield along with a trace of 6a and its isomer 6a′.

5a: mp 146–148°(dec.); UV λ_{max} (C_2H_5OH) nm (logϵ) 240sh(4.13), 280sh(3.69).

5b: 75% yield; mp 102–104°C(dec.); IR(KBr) 3320(OH), 2060, 2050, 2010, 1990, 1620, 1435, 1422, 1380, 1335, 1268, 1235, 1050, 1030, 1015 cm^{-1}; UV λ_{max} (C_2H_5OH) nm (log ϵ) 220sh(4.29), 255sh(4.08), 320sh(3.58); Mass(13.5 eV), m/z (rel intensity) 278 (M$^+$, 2.8), 250(31), 223(2.4), 222(81), 205(7), 204(1.7), 195(2.4), 194(100), 176(65), 122(18), 120(6.7). Found: C, 47.68; H, 3.49. Calcd. for $C_{11}H_{10}O_5Fe$: C, 47.51; H, 3.63%.

5c: 53% yield; mp 125–127°C(dec.); IR(KBr) 3350(OH), 2060, 2010, 2000, 1990, 1985, 1970, 1650, 1305, 1100, 715, 700 cm^{-1}; UV λ_{max} (C_2H_5OH) nm (log ϵ) 286sh(3.86); Mass(13.5 eV), m/z (rel intensity) 340(M$^+$, 1), 323(2), 321(3), 285(14), 284(100), 282(7), 268(6), 257(12), 256(95), 239(32), 238(44), 211(10), 185(9), 184(64), 183(12), 157(10). Found: C, 56.47; H, 3.54. Calcd. for $C_{16}H_{12}O_5Fe$: C, 56.50; H, 3.56%.

6c: 5% yield; mp 175–178°C(dec.); IR(KBr) 2060, 2050, 1990, 1980, 1640, 1490, 1445, 1435, 1390, 1320, 1300, 1285, 1275, 1200, 1130, 1105, 1050, 1030, 1015, 990, 915, 800, 770, 715, 695 cm^{-1}; Mass, m/z (rel

intensity) 663(40), 578(18), 495(23), 494(44), 460(22), 438(11), 324(18), 323(73), 309(16), 308(43), 307(100), 293(14), 292(19), 291(24), 289(83), 288(11), 154(97), 139(65), 138(8), 137(88), 136(90). Found: C, 53.62; H, 3.32. Calcd. for $C_{32}H_{22}O_9Fe_2$: C, 58.04; H, 3.35%.

5d: 60% yield; mp 115–117°C(dec.); IR(KBr) 3420(OH), 3040, 2060, 1990, 1985, 1655, 1370, 1340, 1310, 1270, 1240, 1125, 1030, 970, 920 cm^{-1}; UV λ_{max} (C_2H_5OH) nm (log ϵ) 222(4.37), 237sh(4.22), 268sh (3.99), 330sh(3.54); Mass(13.5 eV) m/z (rel intensity) 300(0.6), 298 (M$^+$, 1.4), 297(3.7), 280(0.1), 270(4.5), 254(1.3), 253(3.1), 252(10), 244(10), 242(35), 226(3.1), 225(7.1), 224(12), 217(1.4), 216(39), 215(11), 199(1), 198(5.5), 197(5.4), 196(15), 195(15), 194(60), 176(12), 144(46), 142(100). Found: C, 40.45; H, 2.51. Calcd. for $C_{10}H_7O_5ClFe$; C, 40.24; H, 2.36%.

6d: 8% yield; mp 138–140°C(dec.); IR(KBr) 2080, 2070, 2010, 2000, 1995, 1665, 1380, 1330, 1320, 1300, 1140, 1050, 1030, 998, 920 cm^{-1}; Mass m/z (rel intensity) 581(15), 579(23), 363(8), 362(18), 361(16), 308(8), 307(36), 301(28), 300(15), 299(76), 298(12), 289(23), 283(28), 282(12), 281(75), 271(9), 253(15), 244(11), 243(13), 214(18), 199(19), 154(100), 136(85). Found: C, 41.63; H, 2.60. Calcd. for $C_{20}H_{12}O_9Cl_2Fe_2$; C, 41.49; H, 2.09%.

From 8, compounds 12 and 13 were obtained in 18.8 and 65.8% yield, respectively.

13: 66% yield; mp 139–141°C(dec.); IR(KBr) 3325(OH), 2050, 1990, 1975, 1465, 1330, 1190, 1160, 1070, 1030, 810, 795 cm^{-1}; UV λ_{max} (C_2H_5OH) nm (log ϵ) 225sh(4.26), 270sh(3.53), 340sh(2.63); Mass m/z 250 (M$^+$ – CO, 48), 222(57), 194(26), 192(4), 138(20), 122(54), 121(1), 120(61), 104(11), 94(15), 93(21), 92(9), 91(3), 80(100), 79(23), 78(17). Found: C, 47.88; H, 3.79. Calcd. for $C_{11}H_{10}O_5Fe$: C, 47.51; H, 3.62%.

From 12, compound 13 was obtained in 57.8% yield.

4.3. General procedure for the preparation of 6a–b and 6a′–b′

A solution of tricarbonyl(tropone)iron (2 mmol) in 5 ml of dichloromethane and 1.5 ml of concentrated sulfuric acid was mixed at 0°C. The sulfuric acid layer was poured onto an excess of sodium carbonate (3.5 g, 30 mmol) at 0°C, with thorough stirring. Dichloromethane (20 ml) was added to the resulting paste, which was slowly decomposed by a minimum amount of iced water. The products were extracted with dichloromethane. Extracts were combined and washed with a saturated aqueous sodium carbonate, dried over magnesium sulfate, and the solvent was removed. Products were separated by column chromatography on silica gel, using a mixture of hexane and ethyl acetate as solvents.

5a: 20% yield.

6a: 25% yield; mp 180–182°C(dec.); IR(KBr) 2084, 2072, 2012, 1981, 1649, 1395, 1328, 1005, 621, 607, 579, 543 cm^{-1}; Mass m/z (rel intensity) 512(12), 511 (MH$^+$, 41), 510(4), 509(6), 460(6), 398(4), 362(4), 361(4), 343(7), 342(16), 341(4), 308(10), 307(41), 291(4), 290(6), 289(20), 273(4), 251(4), 248(10), 247(61), 245(5), 219(15), 208(4), 191(11), 179(8), 167(4), 166(5), 165(5), 163(6), 162(3), 155(30), 154(100), 153(7), 152(8), 150(3), 140(3), 139(14), 138(32), 137(58), 136(68), 135(8), 124(9), 123(7), 122(4), 121(7), 120(14), 119(5), 108(6), 107(20), 106(5), 105(6); Found: C, 44.14; H, 2.72. Calcd. for $C_{20}H_{14}O_9Fe_2$: C, 47.10, H, 2.77%.

6a′: 23% yield; mp 193–195°(dec.); IR(KBr) 2072, 2062, 1989, 1650, 1325, 1301, 1030, 1013, 614, 595, 580, 561, 551, 499 cm^{-1}; Mass m/z (rel intensity) 512(13), 511 (MH$^+$, 44) 510(4), 426(4), 398(7), 362(5), 361(5), 359(4), 344(4), 343(11), 342(23), 341(5), 340(4), 316(4), 307(8), 289(5), 251(6), 249(4), 248(16), 247(100), 245(5), 235(5), 234(4), 220(4), 219(25), 208(5), 192(4), 191(18), 180(4), 179(11), 164(3), 163(8), 162(5), 161(3), 155(8), 154(31), 149(4), 138(9), 137(16), 136(28), 120(7), 107(9).

5b: 17% yield.

6b: 28%; mp 128–130°(dec.); IR(KBr) 2066, 1998, 1974, 1648, 1375, 1337, 1047, 1022, 621, 607, 584, 566, 500 cm^{-1}; Mass m/z (rel intensity) 540(9), 539 (MH$^+$, 30), 537(4), 454(5), 426(4), 371(10), 370(27), 369(6), 368(5), 362(4), 361(4), 314(5), 307(5), 289(4), 265(6), 263(4), 262(17), 261(100), 259(8), 250(4), 249(6), 248(5), 235(4), 234(4), 233(28), 208(6), 206(6), 205(30), 194(4), 193(11), 191(3), 179(5), 178(5), 177(14), 176(6), 175(6), 163(4), 155(6), 154(24), 139(4), 138(7), 137(13), 136(25), 121(5), 120(7), 107(6), 105(3), 91(8), 90(7), 89(6).

6b′: 27%; mp 167–169°(dec.); IR(KBr) 2066, 2008, 1985, 1653, 1441, 1375, 1336, 1052, 1031, 617, 606, 586, 564, 552, 498 cm^{-1}; Mass m/z (rel intensity) 541(3), 540(14), 539 (MH$^+$, 44), 538(4), 537(7), 454(5), 426(6), 371(10), 370(27), 369(5), 368(5), 362(5), 361(4), 314(3), 308(4), 307(16), 289(8), 265(4), 263(3), 262(18), 261(100), 259(9), 250(3), 249(5), 248(4), 234(5), 233(25), 208(5), 206(5), 205(24), 194(3), 193(9), 179(4), 178(4), 177(11), 176(5), 165(3), 155(12), 154(45), 153(3), 152(4), 139(5), 138(12), 137(21), 136(30), 124(3), 121(5), 120(7), 107(8), 105(3), 91(7), 90(7), 89(7).

4.4. General procedure for the oxidation of 5a–d, 13 and 21

Chromium trioxide (360 mg, 3.6 mmol) was added to a solution of pyridine (570 mg, 7.2 mmol) in 30 ml of dichloromethane with stirring. After stirring for 1 h, a solution of the hydroxy complexes (**5a–d, 13** and **21**) (100 mg) in 20 ml of dichloromethane was added to the solution. It was stirred for 20 h. The reaction mixture was passed through silica gel with dichloromethane

and ethyl acetate as solvents. The product was eluted with dichloromethane and ethyl acetate (9:1).

1a: 65%; mp 203–205°C(dec.); IR(KBr) 3040, 2080, 2000, 1980, 1665, 1635, 1410, 1390, 1300, 1240, 1180, 1135, 1035, 1000, 955, 945, 910, 860, 845, 670 cm^{-1}; UV λ_{max} (C_2H_5OH) nm (log ϵ) 221(4.38), 294(3.71); ^{1}H NMR(CDCl$_3$) 5.88(m, H-3,4), 3.70(m, H-2,5), 3.05(s, H-7, 2H).

1b: 58%; mp 158–159°C(dec.); IR(KBr) 3050, 2076, 2008, 1994, 1670, 1636, 1438, 1386, 1332, 1272, 1242, 1134, 1080, 956, 672, 616, 600, 590, 554, 498, 452 cm^{-1}; UV λ_{max} (C_2H_5OH) nm (log ϵ) 229(4.32), 301(3.69): Mass m/z (rel intensity) 276 (M$^+$, 2) 249(2), 248(45), 221(5), 220(100), 218(5), 193(2), 192(78). Found: C, 47.66; H, 2.95. Calcd. for $C_{11}H_8O_5Fe$: C, 47.86; H, 2.98%.

1c: 60%; mp 184–186°C(dec.); IR(KBr) 2080, 2070, 2020, 2010, 2000, 1665, 1640, 1305, 1285, 1250, 695 cm^{-1}; UV λ_{max} (C_2H_5OH) nm (log ϵ) 220sh(4.39), 311(3.81); Mass m/z (rel intensity) 310 (M$^+$ – CO, 5.5), 285(2), 284(32), 282(100), 281(12), 256(11), 255(65), 253(5), 199(10), 198(1), 171(10); Found: C, 56.67; 3.02. Calcd. for $C_{16}H_{10}O_5Fe$; C, 56.83; H, 2.98%.

1d: 90%; mp 173–174°C(dec.); IR(KBr) 2090, 2080, 2070, 2030, 2020, 2010, 1680, 1650, 1375, 1300, 920 cm^{-1}; UV λ_{max} (C_2H_5OH) nm (log ϵ) 231(4.25), 300sh(3.71); Mass m/z (rel intensity) 296(3), 270(20), 269(4), 268(57), 266(1), 243(2.7), 242(59), 241(15), 240(100), 239(1), 238(8), 214(13), 212(35), 184(12). Found: C, 40.23; H, 1.89. Calcd. for $C_{10}H_5O_5ClFe$: C, 40.51; H, 1.70%.

17: 66%; mp 198–199°C(dec.); IR(KBr) 2070, 2050, 2000, 1990, 1985, 1655, 1640, 1450, 1380, 1320, 1285, 1230, 1185, 1125, 1010, 980, 885, 860 cm^{-1}; UV λ_{max} (C_2H_5OH) nm (log ϵ) 222(4.29), 320sh(3.51); Mass m/z (rel intensity) 248 (M$^+$ – CO, 29), 221(6), 220(100), 218(1), 192(88), 120(8), 108(11), 94(8). Found: C, 48.16; H, 3.05. Calcd. for $C_{11}H_8O_5Fe$: C, 47.88; H, 2.92%.

22: 60% yield.

4.5. Preparation of 3-hydroxytropone (7) from 1a

A solution of tricarbonyl(2,4-cycloheptadiene-1,6-dione)iron (**1a**) (131.8 mg, 0.5 mmol) and triphenylphosphite (777 mg, 2.5 mmol) in bromoform (5 ml) was refluxed for 6 h under argon. Chromatography on silica gel using ethyl acetate and methanol as solvents gave 3-hydroxytropone (**7**) (24 mg, 39% yield).

4.6. Preparation of tricarbonyl(2,4,6-cyclooctatrien-1-one)iron (12) from exo-(bicyclo[5.1.0]octa-3,5-dien-2-one)tricarbonyliron (8)

Complex **8** (500 mg) was dissolved in 5 ml of dichloromethane. To the solution was added 2 ml of concentrated sulfuric acid with ice cooling. It was

shaken and allowed to stand for 15 min in an ice bath then for 30 min at room temperature. The sulfuric acid layer was added onto anhydrous sodium carbonate with cooling by ice bath. To the resulting paste was added 100 ml of dichloromethane and then less than 100 mg of ice was added. After stirring for a few minutes, the dichloromethane solution was collected. This procedure was repeated until the dichloromethane solution became colorless. The extracts were combined, dried over magnesium sulfate, and filtered. The solvent was removed by rotary evaporator. Products were separated by column chromatography on silica gel using dichloromethane and ethyl acetate as solvents. Tricarbonyl(2,4,6-cyclooctatrien-1-one)iron (12) (402 mg, 80%) and tricarbonyl(1-hydroxy-9-oxo-bicyclo-[4.2.1]nona-2,3-diene)iron (13) (40 mg, 7%) were obtained.

4.7. Preparation of 12 from 14

A solution of 1.9 g of 2,4,6-cyclooctatrien-1-one (14) [17] and 12 g of $Fe_2(CO)_9$ in 100 ml of dry ether was refluxed for 7 h under argon. After the solvent was removed, the reaction mixture was separated by column chromatography on silica gel using a mixture of hexane and ethyl acetate as solvents to give complex 16 (798 mg, 12%), recovered 14 (343 mg, 18%), complex 12 (1.29 g, 31%), and complex 15 (1.009 g, 16%).

16: mp 101–103°C(dec.); IR(KBr) 2086, 2054, 2006, 1980, 1966, 1959, 1660, 1436, 1288, 1242, 1108, 632, 611, 600, 551, 513, 488 cm^{-1}; UV λ_{max} (C_2H_5OH) nm (log ϵ) 336(3.98), 390sh(3.54), 460sh(3.11); Mass m/z (rel intensity) 429(MH$^+$, 52%), 401(18), 400(20), 385(11), 373(19), 372(13), 363(10), 362(25), 361(14), 345(16), 344(73), 342(10), 329(19), 316(32), 307(32), 289(18), 265(19), 261(22), 249(10), 248(8), 235(13), 233(10), 223(14), 209(12), 208(14), 205(18), 193(10), 179(17), 177(16), 155(27), 154(100), 152(9), 151(19), 145(10), 139(13), 138(29), 137(54), 136(85), 121(8), 120(22), 107(20), 105(8).

4.8. Preparation of 2,4-cyclooctadiene-1,6-dione (18) from 17

A solution of 100 mg of tricarbonyl(2,4-cyclo-octadiene-1,6-dione)iron (17) and 550 mg of ceric ammonium nitrate in 100 ml of ethyl acetate was stirred at room temperature for 2 h. After column chromatography on silica gel, 36 mg (73%) of 2,4-cyclooctadiene-1,6-dione (18) was obtained as pale yellow liquid [13].

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