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Reactivity of (2,4-cycloheptadiene-1,6-dione)$Fe(CO)_3$: synthesis of hinokitiol and (7,8-diphenylheptatriafulvalene-1,6-quinone)$Fe(CO)_3$

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Abstract

The reactivities of tricarbonyl(2,4-cycloheptadiene-1,6-dione)iron toward several kinds of nucleophiles and electrophiles were investigated. As a result, it was found that tricarbonyl(2,4-cycloheptadiene-1,6-dione)iron has several reaction sites and undergoes several types of reactions. A new synthetic route to hinokitiol and tricarbonyl-(7,8-diphenylheptariafulvalene-1,6-quinone)iron from (2,4-cycloheptadiene-1,6-dione)iron was explored.

Keywords: Hinokitiol; Nucleophile; Iron; Cycloheptadiene; Fulvalene

1. Introduction

3-Hydroxytropone exists in enol form and is known as a precursor of cross-conjugated compounds [1]. The tricarbonyl iron complex of 3-hydroxytropone has been prepared by direct complexation of 3-hydroxytropone with $Fe_2(CO)_9$. The tautomerism of 3-hydroxytropone is fixed into keto form, (2,4-cycloheptadiene-1,6-dione)$Fe(CO)_3$, by the complexation [2]. The only reaction of this complex with (cyclohexadienonium)$Fe(CO)_3BF_4^-$ was reported. As we have found a new route from (tropone)$Fe(CO)_3$ to (2,4-cycloheptadiene-1,6-dione)$Fe(CO)_3$ [3], we are interested in the reactivity and synthetic utility of (2,4-cycloheptadiene-1,6-dione)$Fe(CO)_3$ (**1**). For the purpose of preparation of $Fe(CO)_3$ complexes of other tropone derivatives and cross-conjugated compounds, the reactivity of compound **1** was studied.

2. Results and discussion

2.1. Reactivity toward nucleophiles

The enol ether of cyclobutane-1,3-dione reacts easily with primary or secondary amines to give enaminones [4]. 3-Hydroxytropone could be converted into 3-aminotropone derivatives by way of 3-chlorotropone [5]. Compound **1** is a 1,3-dione derivative. It was reacted with secondary amines (dimethylamine and morpholine) to give ligand exchange products (**2a** and **2b**) instead of the enaminone complex (**3**), which was obtained by attack of the central metal. Recently, it was reported that diene-$Fe(CO)_3$ reacted with NR_3 or PR_3 in the presence of $(CH_3)_3NO$ to give diene-$Fe(CO)_2NR_3$ or diene-$Fe(CO)_2PR_3$, respectively [6]. Comparing complex **2** with **1**, the characteristically-strong ν(CO) IR absorption shifted to lower a wavenumber and the λ_{max} of **2a** and **2b** shifted to a longer wavelength in UV spectra, as shown in Table 1.

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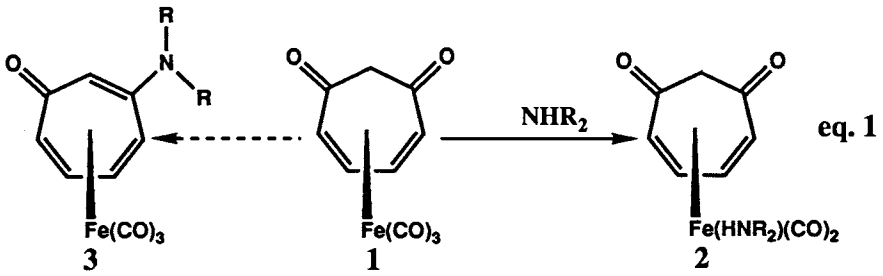
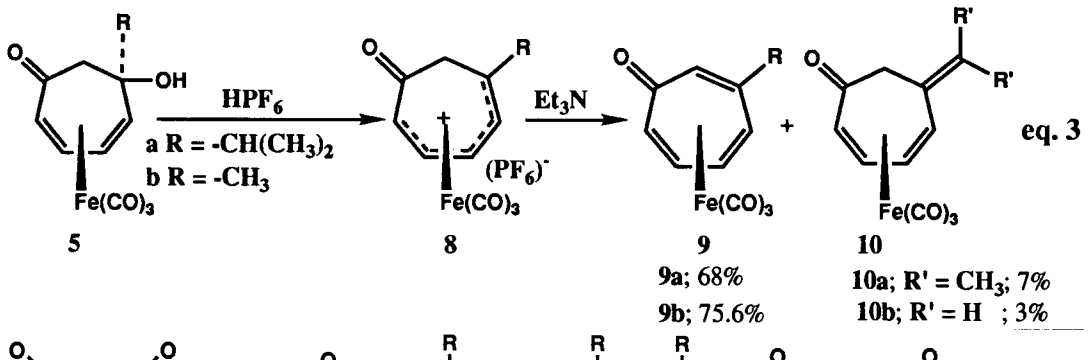


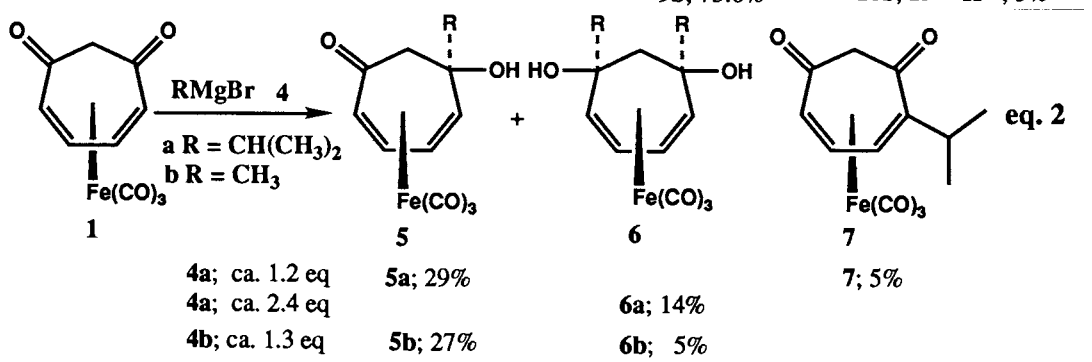
a R=CH_3 (42%)

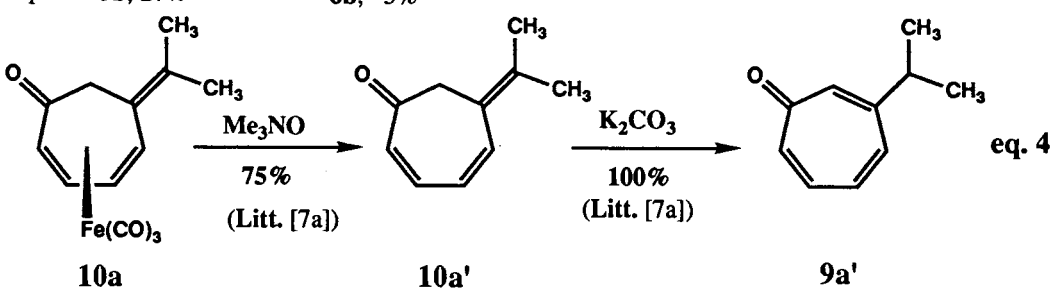
b R_2= (-CH_2CH_2)$_2$O (20%)

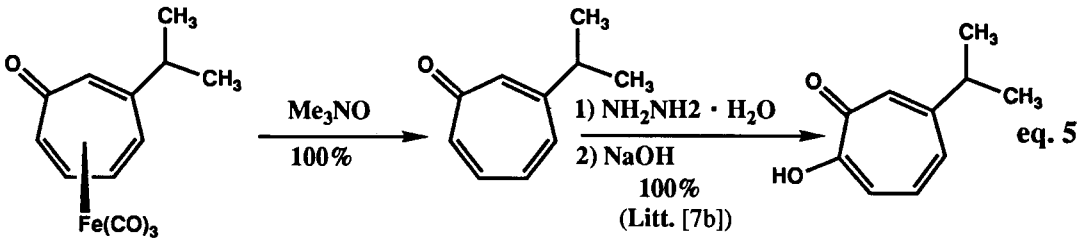
In the reaction of **1** with almost one equivalent of the strong nucleophile isopropyl magnesium bromide (**4a**), the nucleophile attacks at carbonyl group of the seven-membered ring to give a 1:1 adduct **5a** (29%) with an *exo* configuration of the isopropyl group towards $Fe(CO)_3$ along with a small amount of substitution reaction product **7** (5%). The formation mechanism of the complex **7** is not clear. When an excess amount of Grignard reagent was used, an 1:2 adduct **6a** (14%) was obtained exclusively. However, a large amount of the starting material **1** (60%) was recovered also.

In order to obtain as much of the 1:1 adduct **5a** as possible, the reaction was carried out repeatedly by using the retrieved starting material **1**, which was recovered easily after a short reaction time. The adduct **5a** was treated with hexafluorophosphoric acid in ether to give cation **8a**. This cation **8a** was treated with triethylamine to give (6-isopropyltropone)$Fe(CO)_3$ (**9a**) and the *exo*-methylene product (**10a**) in 68 and 7% yields, respectively. The iron-free 3-isopropyltropone (**9a′**) could be obtained quantitatively by the reaction of **9a** with trimethylamine *N*-oxide. The synthetic route from **10a** by way of **9a′** to hinokitiol, as shown in Eqs. (4) and (5), has been reported by Neumann et al. ([7]a) and Noyori et al. ([7]b).

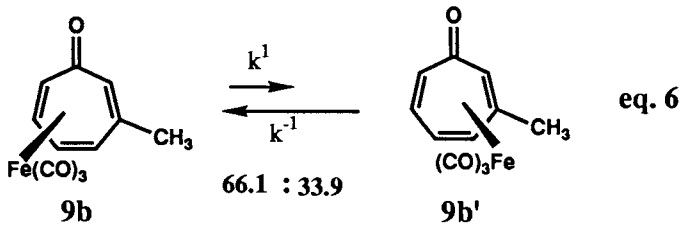






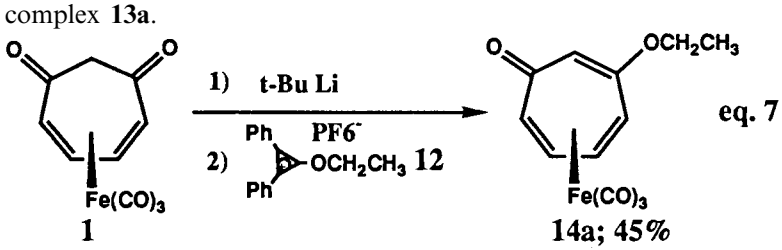


Similaly, methyl magnesium bromide reacted with **1** to give **5b** and **6b** in 27 and 5% yields, respectively. The complex **5b** could be converted to (6-methyltropone)$Fe(CO)_3$ (**9b**). There is an equilibrium between **9b** and (3-methyltropone)$Fe(CO)_3$ (**9b′**) (ratio of **9b**:**9b′** = 66.1:33.9) at 50°C. It is interesting that the equilibrium between (7-methyltropone)$Fe(CO)_3$ and (2-methyltropone)$Fe(CO)_3$ lies predominantly in the favor of (7-methyltropone)$Fe(CO)_3$. This suggests that haptotropicity in substituted (tropone)$Fe(CO)_3$ depends on the substitution site. Thermodynamic parameters of this haptotropy were measured using 90 MHz ^{1}H-NMR (see Table 2). Interestingly, the methyl group increased clearly the activation energy of haptotropy in (tropone)$Fe(CO)_3$ [8].

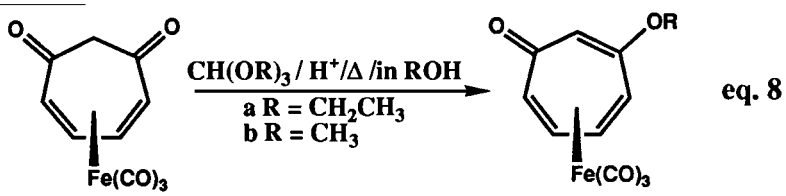


2.2. Reactivity toward electrophiles

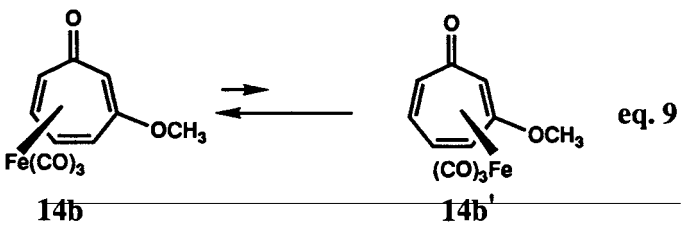
When the anion of complex **1** was reacted with diphenylethoxycyclopropenium hexafluorophosphate (**12**) to produce (7,8-diphenylheptariafulvalene-1,6-quinone)$Fe(CO)_3$ (**13a**), (6-ethoxytropone)$Fe(CO)_3$ (**14a**) was obtained in a 45% yield instead of the cross-conjugated complex **13a**.



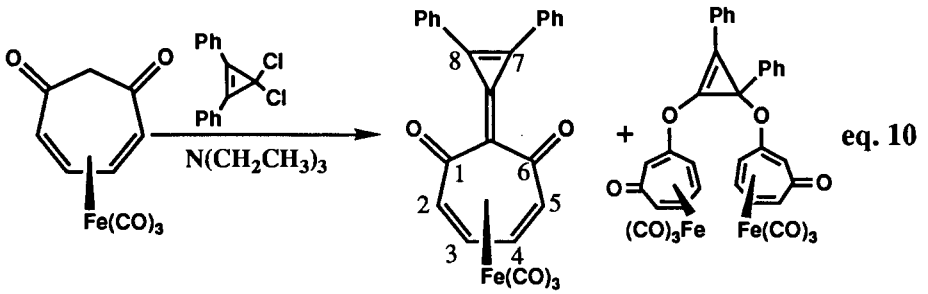
Complex **14a** was obtained in a 57% yield by the reaction of **1** with triethyl orthoformate in the presence of a catalytic amount of conc. H_2SO_4. (6-Methoxytropone)$Fe(CO)_3$ (**14b**) was obtained also by a similar reaction.



Although the methoxy group exhibits an electron-donating character by employing a positive mesomeric effect, in contrast to the methyl group which exhibits an analogous electron-donating character by using a positive inductive effect, (3-methoxytropone)$Fe(CO)_3$ could not be found spectroscopically when these 6-methoxy complexes were heated in chloroform or benzene. The equilibrium between (6-methoxytropone)$Fe(CO)_3$ and (3-methoxytropone) $Fe(CO)_3$ lies on the side of the (6-methoxytropone) $Fe(CO)_3$. It is interesting that the position of equilibrium in substituted (tropone)$Fe(CO)_3$ could not be determined using steric and electronic factors only.



3,3-Dichloro-1,2-diphenyl-cyclopropene was treated with complex **1** in the presence of triethylamine to give complex **13a** (7% yield) and the 1:2 addition product **15** (21% yield). Takahashi et al. reported that iron-free dibenzo- (**13b**) and diamino- (**13c**)derivatives were prepared by the reaction of corresponding tropone and dichlorocyclopropene in the presence of triethylamine but the iron-free compound **13a′** was not produced [1] (Fig. 1). On the basis of spectroscopic data of **13b** and **13c** [1], the properties of complex **13a** would be similar to the dibenzoderivative **13b**, which was stabilized by the contribution of an ionic triafulvene form with electron-withdrawing groups at C-4.

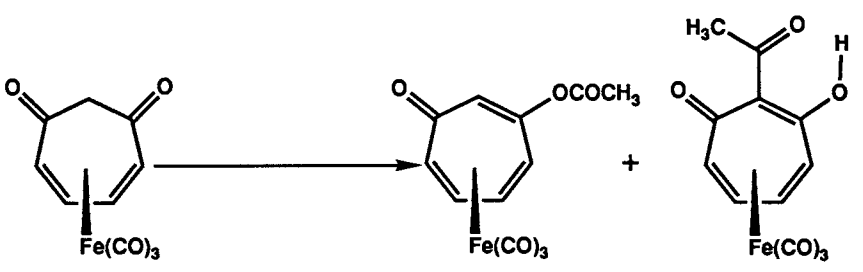


eq. 10

1 **13a** 7% **15** 21%

Reacting complex **1** with acetic anhydride in the presence of pyridine at 80°C produced (6-acetoxytropone)$Fe(CO)_3$ **16** (7%) as a minor product and its isomer **17** (48%) as a main product, which has a characteristic proton signal at 18 ppm as a singlet (O–H) due to hydrogen bonding in ^{1}H-NMR. To the best of our knowledge, this is due to the O*H* chemical shift.

The structure of this complex is considered as being similar to the C-acylation products **17a** and/or **17b** in Eq. (12). On the contrary, reaction of complex **1** with acetylchloride in the presence of triethylamine at 80°C resulted in complex **16** (91%) as a main product and **17** (4%) as a minor product. The ratio of products **16** and **17** could be controlled by acylating conditions.

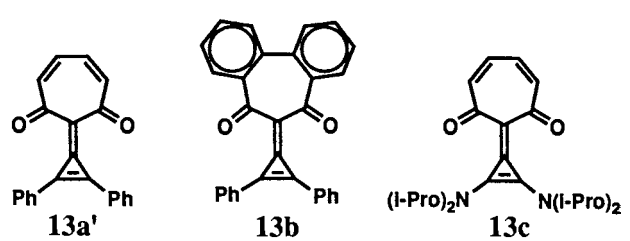


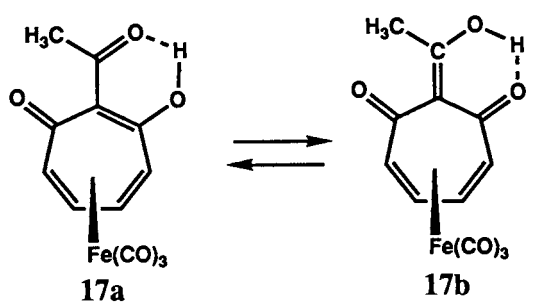
eq. 11

1 **16** **17**

$(CH_3CO)_2O$, Py 7% 48%

or $CH_3COCl/(C_2H_5)_3N$ 91% 4%





eq. 12

Fig. 1. Structural representations of compounds **13a′**, **13b** and **13c**.

Table 1
Comparison of the spectroscopic data of **2a** and **2b** with **1**

Complex	^{1}H-NMR ($CDCl_3$) (ppm)	IR (KBr) (cm^{-1})	UV (C_2H_5OH) (log ε)
1	5.88, 3.77, 3.05	2086, 2010, 1982, 1669, 1639	224 (4.36), 293 (3.70)
2a	4.95, 3.92, 3.17, 2.92	2010, 1935, 1649, 1618	229 (4.32), 349 (3.59), 440sh (2.82)
2b	4.96, 3.93, 3.11	2010, 1997, 1942, 1652, 1626	231 (4.29), 350 (3.64) 440sh (2.87)

Table 2
Thermodynamic parameters for haptotropicity in **9b** and **9b′**

T (K)	k^1	k^{-1}					
318	1.437×10^{-5}	2.880×10^{-5}					
323	3.095×10^{-5}	6.033×10^{-5}					
328	5.844×10^{-5}	1.109×10^{-4}					
Compound	$\Delta G^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	k (s^{-1})	Ratio(%)	T (K)	E_a
9b	25.6	28.4	8.6	3.1×10^{-5}	66.1	323	29.0
9b′	25.2	27.4	6.8	6.0×10^{-5}	33.9	323	28.0

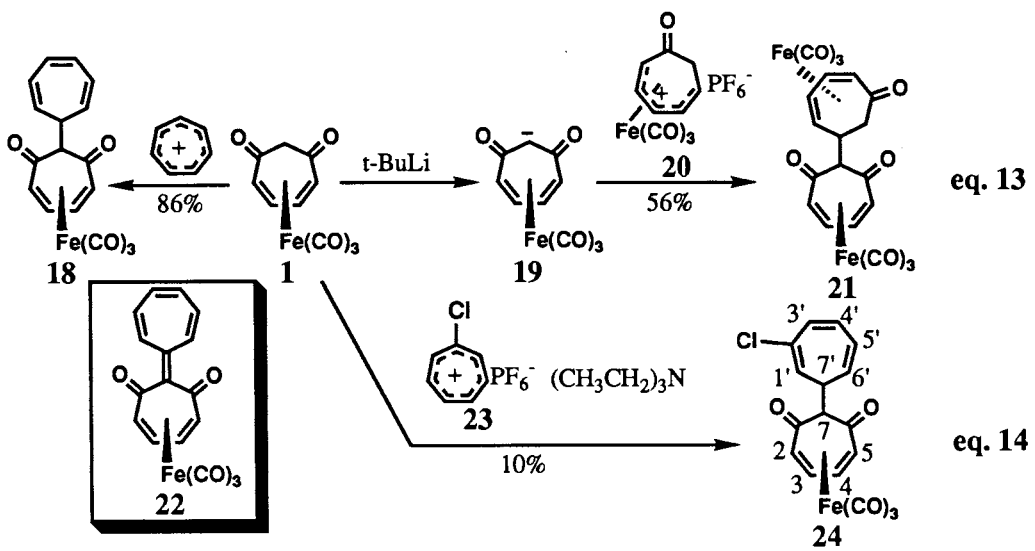
$\Delta G^{\neq}$, $\Delta H^{\neq}$, E_a in kcal mol^{-1}; $\Delta S^{\neq}$ in cal mol^{-1} K^{-1}.

Lewis et al. [2] reported that (1,3-cyclohxadienium)$Fe(CO)_3$tetrafluoroborate reacts with (2,4-cycloheptadiene-1,6-dione)$Fe(CO)_3$ to produce the 1:1 addition product in good yield. Under the same conditions, cycloheptatrienium tetrafluoroborate reacted also with **1** to give the 1:1 adduct (**18**) in an 86% yield. However, since (cycloheptadienonium)$Fe(CO)_3$hexafluorophosphate (**20**) does not react under similar conditions, complex **1** was converted to its anion (**19**) using *t*-BuLi and then treated with the cation (**20**) to give the 1:1 adduct (**21**) in a 56% yield. Finally, in order to produce (heptafulvalene-1,6-quinone)$Fe(CO)_3$ (**22**), chlorocycloheptatrienium hexafluorophosphate (**23**) was reacted with complex **1** in the presence of triethylamine. However, the expected product (**22**) could not be obtained and resulted in a complex mixture. From this mixture, only 7-(2-chlorocycloheptatrienyl)[2,4-cycloheptadiene-1,6-dione]$Fe(CO)_3$ (**24**) was isolated in a 10% yield.

Complexes **18**, **21** and **24** are considered as keto forms of the heptafulvalenes **25**, **26** and **27**, respectively (Fig. 2). Similar mono keto system has already been prepared by Nitta et al. [9]. These heptafulvalenes cannot be prepared thus far. Further experiments to prepare the enol ethers or esters of these heptafulvalenes are now in progress.

3. Conclusion

These results demonstrate that compound **1** undergoes several types of reactions and is a useful building block in the synthesis of several complexes composed of a seven-membered ring.



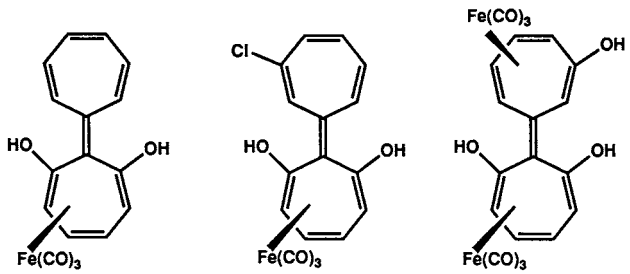


Fig. 2. Structure of compounds **25**–**27**.

4. Experimental

Melting points were determined using a Yanaco micromelting point apparatus and are uncorrected. IR spectra were recorded using a Hitachi 270-30 spectrometer. ^{1}H-NMR spectra were recorded on a Hitachi R-90H spectrometer at 90 MHz or a Bruker AM-600 spectrometer at 600 MHz for solutions in $CDCl_3$ using TMS as an internal standard. Electronic spectra were measured with a Hitachi U-3410 spectrophotometer for solutions in ethanol. Mass spectra were measured with a Jeol JMS-HX110. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University. Column chromatography was performed through silica gel (Kieselgel 60).

*4.1. 2,4-Cycloheptadiene-1,6-dione(dimethylamine) $Fe(CO)_2$ (**2a**)*

Dimethylamine (1 ml) was added to a solution of **1** (131 mg /0.5 mmol) in acetonitrile (10 ml) under ice cooling. It was then stirred at room temperature (r.t.) for 6 h. The reaction mixture was separated by column chromatography on silica gel using ethylacetate and a trace amount of methanol as eluant to give 118 mg (42%) of **2a** as brownish solid.

2a: m.p. 139.5 − 141°C (decomposed, (d)). ^{1}H-NMR ($CDCl_3$): $\delta = 4.95$ (m, H-3,4), 3.92 (m, H-2,5), 2.91 (d, $J = 9.1$, H-7), 2.91 (d, $J = 9.1$, H-7), 2.76 (s, CH_3), 2.69 (s, CH_3). IR (KBr) ν_{max}: 3215 (m), 2990 (w), 2960 (w), 2940 (w), 2870 (w), 2080 (w), 2000 (vs), 1935 (vs), 1647 (s), 1615 (s), 1460 (m), 1384 (m), 1300 (m), 1245 (w), 1232 (w), 1155 (w), 1130 (w), 1122 (m), 1075 (w), 1065 (w), 1030 (w), 1015 (w), 975 (w), 950 (m), 930 (w), 905 (w), 850 (w) cm^{-1}. UV (CH_3CH_2OH) λ_{max}: 229 nm ($\log \varepsilon$ 4.32), 349 (3.59), 440sh (2.82). HRMS Found: m/z 279.0178. Calc. for $C_{11}H_{13}O_4NFe$: M 279.072. MS m/z (rel. int.): 279 (M^+, 6), 251 (14), 223 (100), 208 (2), 178 (31), 150 (8), 122 (9), 94 (5). Anal. Calc. for $C_{11}H_{13}O_4NFe$: C, 47.34; H, 4.70; N, 5.02%. Found: C, 47.58; H, 4.74; N, 4.77%.

*4.2. 2,4-Cycloheptadiene-1,6-dione(morpholine)$Fe(CO)_2$ (**2b**)*

According to the above condition, 32 mg (20%) of morpholino product **2b** was obtained. **2b**: m.p. 143 − 145°C (d). ^{1}H-NMR ($CDCl_3$): $\delta = 4.96$ (m, H-3,4), 3.93 (H-2,5), 3.74 (m, H−N=), 3.11 (s, H-7, 2H), 4.1–2.8 (m, 8H). IR (KBr) ν_{max}: 3215 (m), 2970 (w), 2945, (w) 2865 (w), 2000 (vs), 1995 (vs), 1940 (vs), 1645 (vs), 1620 (vs), 1466 (w), 1452 (w), 1434 (m), 1428 (w), 1400 (w) 1390 (s), 1354 (w), 1312 (w), 1300 (s), 1260 (m), 1214, (w) 1200 (w), 1170 (m), 1141 (m), 1120 (s), 1090 (m), 1070 (m), 1034 (w) 986 (w), 950 (m), 921 (w), 890 (s), 854 (m), 850 (m), 830 (w), 804 (w), 650 (w) cm^{-1}. UV (CH_3CH_2OH) λ_{max}: 231 nm ($\log \varepsilon$ 4.29), 350 (3.64), 440sh (2.87). HRMS Found: 321.0297. Calc. for $C_{13}H_{15}O_5NFe$: M 321.108. MS m/z (rel. int.): 321 (M^+, 3), 265 (100), 263 (11), 207 (14), 182 (2), 178 (13), 150 (5). Anal. Calc. for $C_{13}H_{15}O_5NFe$: C, 48.62; H, 4.71; N, 4.36%. Found: C, 48.20; H, 4.81; N, 4.34%.

*4.3. Reaction of (2,4-cycloheptadiene-1,6-dione) $Fe(CO)_3$ (**1**) with isopropyl magnesium bromide*

A solution of isopropyl magnesium bromide (5 ml of 0.68 M) in THF was added dropwise at − 50°C to a solution of **1** (750 mg /2.86 mmol) in dry CH_2Cl_2 (35 ml) under an argon atmosphere. The solution turned dark orange and the mixture was then stirred for 30 min at − 50°C. Ammonium chloride (3 g) and water (20 ml) were added to the solution and the aqueous layer was neutralized with 2 N HCl. The reaction mixture was then extracted with dichloromethane, the organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was chromatographed with a silica gel column eluted with dichloromethane and ethylacetate to give 240 mg (29%) of **5a**, 43 mg (5%) of **7** and 230 mg (34%) of recovered **1**.

5a: m.p. 140 − 141°C (d). ^{1}H-NMR ($CDCl_3$): $\delta =$ 5.84 (ddd, $J = 6.4$, 5.4, 1), 5.60 (ddd, $J = 7.8$, 5.4, 0.9), 3.12 (d, $J = 6.4$), 3.03 (d, $J = 7.8$), 2.45 (s, OH), 2.17 (d, $J = 12.5$), 1.82 (dt, $J = 12.7$, 2), 1.75 (m, 1H), 1.01 (d, $J = 7.4$, CH_3), 0.93 (d, $J = 7$, CH_3). IR (KBr) ν_{max}: 3290 (m, OH), 2979 (w), 2960 (w), 2930 (w), 2870 (w), 2070 (s), 2060 (s), 2000 (s), 1980 (s), 1640 (s), 1465 (w), 1440 (w), 1415 (m), 1390 (m), 1370 (w), 1360 (m), 1325 (m), 1300 (m), 1280 (m), 1225 (m), 1190 (m), 1170 (w), 1155 (w), 1130 (m), 1110 (w), 1060 (m), 990 (m), 965 (w), 930 (w), 910 (m), 870 (w), 830 (w), 690 (w) cm^{-1}. UV (CH_3CH_2OH) λ_{max}: 207 nm ($\log \varepsilon$ 4.36), 290sh (3.54), 310sh (3.41). HRMS Found: 306.0196. Calc. for $C_{13}H_{14}O_5Fe$: M 306.0191; MS m/z (rel. int.): 306 (M^+, 0.7), 278 (56), 250 (49), 222 (100), 207 (7), 204 (39), 189 (5), 179 (95), 162 (27), 150 (2). Anal. Calc. for $C_{13}H_{14}O_5Fe$: C, 51.0; H, 4.6%. Found: C, 50.47; H, 4.62%.

7: m.p. 171 – 172°C (d). ^{1}H-NMR ($CDCl_3$): $\delta = 5.82$ (d, $J = 6.3$, H-3), 5.70 (t, $J = 6.3$, H-4), 3.60 (d, $J = 6.3$, H-5), 2.96 (s, H-7, 2H), 1.84 (m, –CH=), 1.53 (d, $J = 6.2$, 3H), 1.31 (d $J = 6.2$, 3H). IR (KBr) ν_{max}: 3050 (w), 2970 (w), 2930 (w), 2870 (w), 2090 (s), 2080 (s), 2040 (s), 2020 (s), 2010 (s), 2000 (s), 1670 (s), 1640 (s), 1460 (w), 1415 (w), 1390 (m), 1365 (w), 1305 (m), 1270 (w), 1250 (w), 1240 (w), 1215 (w), 1185 (w), 1160 (w), 1095 (w), 980 (w), 950 (w), 870 (w), 740 (w) cm^{-1}. UV (CH_3CH_2OH) λ_{max}: 229 nm (log ε 4.27), 302 (3.63), 360sh (3.30). HRMS Found: 304.0043. Calc. for $C_{13}H_{12}O_5Fe$: M 304.0078. MS m/z (rel. int.): 304 (M^+, 6), 276 (36), 248 (53), 220 (100), 204 (5), 192 (13), 176 (5), 160 (1), 150 (12). Anal. Calc. for $C_{13}H_{12}O_5Fe$: C, 51.35; H, 3.98%. Found: C, 50.52; H, 3.88%.

4.4. Reaction of **1** with excess isopropyl magnesium bromide

A solution of isopropyl magnesium bromide (2 ml of 0.68 M) in THF was added dropwise at r.t. to a solution of **1** (150 mg, 0.57 mmol) in dry CH_2Cl_2 (10 ml) under an argon atmosphere. The solution changed color to dark orange and the mixture was stirred for 30 min at r.t. Ammonium chloride (1 g) and water (10 ml) were added to the solution and the aqueous layer was acidified by 2 N HCl. Then, the reaction mixture was extracted with dichloromethane, the organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was chromatographed with a silica gel column eluted with dichloromethane and ethylacetate to give 29 mg (14%) of **6a** and 90 mg (60%) of recovered **1**.

6a: m.p. 133.5 – 134.5°C (d). ^{1}H-NMR ($CDCl_3$): $\delta =$ 5.35 (m, 2H), 2.27 (s, 2H), 2.81 (m, 2H), 1.55 (m, 2H), 0.924 (d, $J = 6.6$, 6H), 0.904 (d, $J = 6.8$, 6H). IR (KBr) ν_{max}: 3260 (m), 3040 (w), 2960 (m), 2930 (m), 2870 (m), 2060 (s), 2050 (s), 2000 (s), 1980 (s), 1950 (s), 1940 (s), 1930 (s), 1470 (m), 1430 (m), 1420 (m), 1410 (w), 1385 (m), 1370 (m), 1330 (m), 1310 (w), 1270 (w), 1230 (m), 1205 (w), 1175 (w), 1150 (m), 1080 (m), 1060 (m), 1030 (w), 995 (w), 980 (w), 960 (w), 900 (m), 865 (m), 795 (m), 690 (w) cm^{-1}. MS m/z (rel. int.): 322 ($M^+ - H_2O$, 8), 294 (32), 266 (15), 248 (100), 223 (3). Anal. Calc. for $C_{16}H_{22}O_5Fe$: C, 54.87; H, 6.33%. Found: C, 54.93; H, 6.55%.

4.5. Reaction of **1** with methyl magnesium bromide

A solution of methyl magnesium bromide (0.3 ml of 2.52 M) in THF was added dropwise to a solution of **1** (150 mg, 0.57 mmol) in dry CH_2Cl_2 (10 ml) under an argon atmosphere at – 50°C. The mixture was stirred for 3.5 h at – 50 to – 20°C. Ammonium chloride (1 g) and water (10 ml) were added to the solution and the aqueous layer was neutralized by 2 N HCl. Then, the reaction mixture was extracted with dichloromethane, the organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was chromatographed with a silica gel column eluted with dichloromethane and ethylacetate to give 43 mg (27%) of **5b**, and 9 mg (5%) of **6b** and 100 mg (67%) of recovered **1**.

5b: m.p. 139 – 140°C (d). ^{1}H-NMR ($CDCl_3$): $\delta = 5.88$ (dd, $J = 6.3$, 5.4Hz, H-3), 5.51 (dd, $J = 7.8$, 5.4 Hz, H-4), 3.22 (d, $J = 7.8$ Hz, H-5), 3.13 (d, $J = 6.3$ Hz, H-2), 2.89 (s, OH), 2.25 (d, $J = 12.9$ Hz, H-7), 2.02 (dt, $J = 12.9$, 1.8 Hz, H-7), 1.48 (s, Me). IR (KBr) ν_{max}: 3280 (m, OH), 2960 (w), 2910 (w), 2050 (s), 2040 (s), 1995 (s), 1980 (s), 1640 (s), 1360 (m), 1350 (m), 1300 (m), 1275 (m), 1240 (m), 1195 (m), 1120 (m), 1040 (m), 990 (m), 895 (m) cm^{-1}. UV (CH_3CH_2OH) λ_{max}: 207 nm (log ε 4.35), 290sh (3.35), 320sh (3.33). HRMS Found: 277.9877. Calc. for $C_{11}H_{10}O_5Fe$: M 277.9878. Anal. Calc. for $C_{11}H_{10}O_5Fe$: C, 47.51; H, 3.63%. Found: C, 46.62; H, 3.79%.

6b: m.p. 128 – 129°C (d). ^{1}H-NMR ($CDCl_3$): $\delta = 5.29$ (m, H-2,3), 3.40 (s, 2OH), 3.00 (m, H-1,4), 1.51 (dt, $J = 14.2$, 1.8 Hz, H-6), 1.30 (s, 2Me), 1.27 (d, $J = 14.2$ Hz, H-6). IR (KBr) ν_{max}: 3240 (s, OH), 3020 (m), 2970 (s), 2920 (m), 2050 (s), 1990 (s), 1960 (s), 1440 (m), 1430 (m), 1400 (m), 1390 (m), 1370 (m), 1350 (m), 1315 (m), 1280 (m), 1270 (m), 1255 (m), 1240 (m), 1200 (w), 1160 (s), 1130 (m), 1090 (w), 1060 (w), 1050 (w), 1040 (w), 1035 (w), 990 (w), 970 (m), 950 (m), 920 (m), 905 (m), 890 (s), 870 (w), 800 (m), 770 (w), 680 (w) cm^{-1}. UV (CH_3CHOH) λ_{max}: 375 nm sh (log ε 3.51). HRMS Found: 266.0241. Calc. for $C_{11}H_{14}O_4Fe$: M – CO 266.02417. MS m/z (rel. int.): 266 (M^+ – CO, 24), 238 (58), 220 (2), 210 (28), 192 (100), 174 (14). Anal. Calc. for $C_{12}H_{14}O_5Fe$: C, 49.00; H, 4.80%. Found: C, 49.40; H, 4.98%.

4.6. Preparation of (6-isopropyltropone)Fe(CO)$_3$ (**9a**) and its isomer **10a**

A solution of HBF_4/Et_2O (1 ml) was added to a solution of 100 mg of **5a** in 2 ml of dichloromethane. After reaction mixture was stirred for 10 min, diethyl ether (15 ml) was added. The reaction mixture was cooled with ice bath and a solid (cation **8a**) was collected by filtration. The solid (**8a**) was dispersed in dichloromethane (10 ml). Two drops of triethylamine was added, the solution was stirred vigorously and the colored dichloromethane solution was collected by decantation. This procedure was repeated until all of the solid (**8a**) disappeared. After the solvent was removed by evaporation, the residue was separated by column chromatography on silica gel to give 63.6 mg (68%) of **9a** and 6.4 mg (7%) of **10a**.

9a: m.p. 70 – 71°C. ^{1}H-NMR ($CDCl_3$): $\delta = 6.30$ (m, H-3,4), 5.00 (bs, H-7), 3.15 (dt, $J = 6$, 2.4Hz, H-5), 2.67 (ddd, $J = 5.9$, 2.7, 1.8Hz, H-2), 2.29 (septet, $J = 6.6$Hz, –CH=), 1.05 (d, $J = 6.6$ Hz, 2Me). IR (KBr) ν_{max}: 3050 (w), 3005 (w), 2965 (w), 2930 (w), 2875 (w), 2055 (s),

2045 (s), 2000 (s), 1990 (s), 1632 (m), 1600 (m), 1460 (w), 1400 (w), 1395 (w), 1381 (w), 1361 (w), 1346 (w), 1308 (w), 1279 (w), 1180 (w), 1150 (w), 1120 (w), 1047 (w), 1012 (w), 960 (w), 914 (w), 893 (w), 866 (w), 840 (w), 713 (w), 674 (w) cm^{-1}. UV (CH_3CH_2OH) λ_{max}: 226 nm (log ε 4.33), 270sh (3.90), 310sh (3.60), 4.29 (2.39). HRMS Found: 288.0075. Calc. for $C_{13}H_{12}O_4Fe$: *M* 288.00852. MS *m*/*z* (rel. int.): 288 (M^+, 0.3), 260 (36), 232 (45), 204 (100), 189 (0.7), 174 (6), 158 (3), 148 (6), 133 (2), 105 (13), 102 (3). Anal. Calc. for $C_{13}H_{12}O_4Fe$: C, 54.20; H, 4.20%. Found: C, 54.23; H, 4.13%. **10a**: m.p. 90 – 91°C (lit. [7] m.p. 85°C)

4.7. Preparation of 3-isopropyltropone (*9a′*)

A solution of 9a (47 mg /0.16 mmol) in benzene (10 ml) was added to a solution of trimethylamine *N*-oxide (177 mg, 2.35 mmol) in dry benzene (30 ml) under an argon atmosphere. After refluxing and stirring for 30 min, the solution turned dark orange. After the solvent was removed under reduced pressure, the residue was chromatographed on a silica gel column using ethylacetate as eluant to give 24 mg (100%) of 3-isopropyltropone as a pale yellow oil [7].

4.8. Preparation of (6-methyltropone)Fe(CO)$_3$ (*9b*) and its isomer *10b*

A solution of HPF_6/Et_2O (1 ml) was added dropwise to a solution of 152 mg of **5b** in 15 ml of diethyl ether with stirring. The solid (cation **8b**, 229 mg) was collected by filtration. Triethylamine (1 ml) was added to a dispersed dichloromethane (150 ml) solution of **8b**. It was stirred vigorously and passed through a column chromatograph on silica gel using dichloromethane and ethylacetate as solvents to give 111 mg (76%) of **9b** and 4 mg (3%) of **10b**.

9b: m.p. 99 – 100°C. ^{1}H-NMR ($CDCl_3$): $\delta = 6.28$ (m, H-3 and 4), 4.99 (broad s, H-7), 3.15 (m, H-2 or 5), 2.60 (m, H-5 or 2), 1.87 (d, $J = 1.2$ Hz, CH_3). IR (KBr) ν_{max}: 3042 (w), 2988 (w), 2842 (w), 2058 (s), 1997 (s), 1977 (s), 1636 (m), 1605 (m), 1468 (m), 1423 (m), 1399 (m), 1376 (m), 1358 (m), 1332 (m), 1284 (m), 1183 (w), 1155 (m), 1097 (w), 1054 (w), 1035 (w), 1021 (w), 990 (w), 958 (w), 945 (w), 897 (m), 882 (m), 855 (m), 794 (w), 719 (w), 633 (s), 620 (m), 612 (s), 594 (s) 561 (s), 524 (w), 498 (m) cm^{-1}. HRMS Found: 259.9774. Calc. for $C_{11}H_8O_4Fe$: *M* 259.97722. MS *m*/*z* (rel. int.): 260 (1), 232 (57), 204 (68), 176 (100), 134 (3), 120 (6). Anal. Calc. for $C_{11}H_8O_4Fe$: C, 50.81; H, 3.12%. Found: C, 50.61; H, 3.32%.

10b: ^{1}H-NMR ($CDCl_3$): $\delta = 5.86$ (dd, H-3), 5.52 (dd, H-4), 3.95 (s), 4.79 (s), 4.08 (d, $J = 8.6$ Hz, H-5), 3.29 (d, $J = 6.8$ Hz, H-2), 2.69 (s, H-7).

4.9. Thermal rearrangement of *9b*

A solution of **9b** in chloroform was warmed at 60°C for several hours. The reaction mixture was separated by middle pressure column chromatography on silica gel using hexane and ethylacetate as solvents to give (3-methyltropone)Fe(CO)$_3$ (**9b′**).

9b′: m.p. 52 – 55°C. ^{1}H-NMR ($CDCl_3$): $\delta = 6.56$ (dd, $J = 10.7$, 8.0 Hz, H-6), 6.22 (dd, $J = 7.3$, 2.2 Hz, H-4), 4.99 (ddd, $J = 10.7$, 2.2, 0.9 Hz, H-7), 3.22 (t, $J =$ 2.2Hz, H-2), 2.55, (s, CH_3), 2.52 (dd, $J = 8.0$, 7.3 Hz, H-5). IR (KBr) ν_{max}: 3044 (w), 2984 (w), 2060 (s), 1990 (s), 1980 (s), 1636 (m), 1606 (m), 1490 (w), 1450 (w), 1424 (w), 1396 (w), 1386 (w), 1282 (w), 1220 (w), 1174 (w), 1132 (w), 1040 (w), 1006 (w), 810 (m), 710 (w), 602 (m), 560 (m) 502 (w) cm^{-1}. Anal. Calc. for $C_{11}H_8O_4Fe$: C, 50.81; H, 3.10%. Found: C, 50.64; H, 3.18%.

4.10. Preparation of (6-ethyloxytropone)Fe(CO)$_3$ (*14a*) from 1-ethoxy-2,3-diphenylcyclopropenium tetrafluoroborate

A solution of *t*-BuLi (1 ml of 1.5 M in pentane) was added to a solution of **1** (131 mg, 0.5 mmol) in THF (20 ml) at −50°C under an argon atmosphere. A sample of the cation **12** (260 mg, 0.7 mmol) was added to the above solution, which was then stirred for 2 h at −50°C and was allowed to stand overnight. The reaction mixture was then passed through a short column of silica gel using THF and CH_2Cl_2 as eluant. The first fraction was separated again by middle pressure column chromatography on silica gel using ethylacetate and hexane as solvents to give 65 mg (45%) of **14a**.

14a: m.p. 117 – 118°C. ^{1}H-NMR ($CDCl_3$): $\delta = 6.19$ (m, H-3,4), 4.52 (t, $J = 2.2$ Hz, H-7), 3.7 ($J = 10.8$, 7 Hz, –CH_2–), 3.17 (m, H-2 or 5), 2.73 (dt, $J = 6.3$, 2.7 Hz, H-5 or 2), 1.31 (t, $J = 7$ Hz, H–CH_3). IR (KBr) ν_{max}: 2990 (w), 2940 (w), 2060 (s), 2010 (s), 1996 (s), 1980 (s), 1946 (m), 1606 (s), 1593 (s), 1460 (m), 1441 (w), 1433 (m), 1380 (m), 1355 (w), 1328 (m), 1281 (w), 1192 (s), 1134 (m), 1109 (w), 1053 (w), 1026 (m), 999 (w), 950 (w), 920 (w), 998 (w), 877 (w), 850 (w), 813 (w), 799 (m), 708 (w), 675 (w) cm^{-1}. UV (CH_3CH_2OH) λ_{max}: 205 nm sh (log ε 4.39), 270sh (3.81), 310sh (3.60), 400sh (2.46), 470sh (1.90). HRMS Found: 289.9886. Calc. for $C_{12}H_{10}O_5Fe$: *M* 289.9878. MS *m*/*z* (rel. int.): 290 (M^+, 0.7), 262 (33), 234 (41), 206 (100), 192 (2), 178 (6), 150 (7), 134 (2), 122 (2), 121 (3), 94 (6). Anal. Calc. for $C_{12}H_{10}O_5Fe$: C, 47.86; H, 2.89%. Found: C, 47.72; H, 3.11%.

4.11. Reaction of *1* with triethyl-o-formate

A trace amount of conc. H_2SO_4 was added to a solution of **1** (524 mg, 2 mmol) and triethyl-*o*-formate (1 g) in dry ethanol (l50 ml). The solution was heated at

50°C for 1 h. Another 1 g of triethyl-*o*-formate was then added to the solution and it was heated for a further 1 h period. After it was passed through Na_2CO_3, the product was separated by column chromatography on silica gel to give 333 mg (57% yield) of ethylether **14a**.

4.12. Reaction of **1** with trimethyl-o-formate

Similaly, (6-methoxytropone)$Fe(CO)_3$ (**14b**) was obtained in 80% yield using methanol as a solvent.

14b: m.p. 105 − 107°C. ^{1}H-NMR ($CDCl_3$): $\delta = 6.19$ (m, 2H), 4.53 (bs, 1H), 3.52 (s, 3H), 3.17 (m, 1H), 2.76 (m, 1H). IR (KBr) ν_{max}: 3020 (w), 2948 (w), 2896 (w), 2824 (w), 2068 (s), 2008 (s), 1992 (s), 1616 (s), 1602 (s), 1456 (m), 1442 (m), 1424 (m), 1392 (m), 1336 (m), 1288 (w), 1256 (w), 1210 (s), 1170 (m), 1158 (m), 1138 (m), 1016 (w), 980 (w), 962 (w), 920 (w), 892 (w), 850 (w), 822 (m), 802 (w), 774 (w), 762 (w), 744 (w), 714 (w), 678 (w), 630 (m), 608 (s), 596 (m), 548 (m), 506 (m), 482 (w), 456 (w), 426 (w), 414 (w) cm^{-1}. HRMS Found: 275.9727. Calc. for $C_{11}H_8O_5Fe$: *M* 275.9721. MS *m*/*z* (rel. int.): 276 (2), 248 (52), 220 (57), 192 (100), 177 (1), 149 (7), 136 (4), 132 (1). Anal. Calc. for $C_{11}H_8O_5Fe$: C, 47.86; H, 2.89%. Found: C, 47.72; H, 3.11%.

4.13. Preparation of (7,8-diphenylheptatriafulvalene-1,6-quinone)Fe(CO)$_3$ (**13a**)

A solution of **1** (262 mg, 1 mmol), 3,3-dichloro-1,2-diphenylcyclopropene (261 mg) and triethylamine (220 mg, 2 mmol) in dichloromethane was refluxed for 7 h. After the solvent was removed, products were separated by column chromatography on silica gel resulting in 75.8 mg (21%) of **15**, 32 mg (7%) of **13a** and 97 mg of recovered material **1**.

15: m.p. 160 − 162°C (d). ^{1}H-NMR ($CDCl_3$): $\delta = 7.26$ (m, 10 H), 6.37 (m, 2H), 5.66 (m, 2H), 5.01 (t, $J = 2.4$ Hz, 1H), 4.46 (t, $J = 1.5$, 1H), 3.54 (m, 2H), 3.44 (m, 1H), 2.95 (m, 1H). IR (KBr) ν_{max}: 3050 (w), 2085 (s), 2065 (s), 2015 (s), 2000 (s), 1994 (s), 1848 (m), 1660 (m), 1621 (s), 1612 (s), 1490 (w), 1462 (w), 1442 (m), 1435 (m), 1390 (m), 1334 (w), 1294 (m), 1259 (m), 1156 (w), 1131 (m), 1100 (s), 1076 (w), 1032 (w), 1010 (w), 997 (w), 886 (w), 877 (w), 754 (m), 740 (w), 700 (m), 680 (m) cm^{-1}. UV (CH_3CH_2OH) λ_{max}: 219 nm (log ε 4.82), 295 (4.43), 297 (4.45), 310sh (4.32). Anal. Calc. for $C_{35}H_{20}O_{10}Fe_2$: C, 59.02; H, 2.83%. Found: C, 59.00; H, 3.27%.

13a: m.p. 181 − 184°C (d). ^{1}H-NMR ($CDCl_3$): $\delta =$ 3.45 (dd, $J = 6$, 2.9Hz, H-2,5), 6.01 (dd, $J = 6$, 2.9 Hz, H-3,4), 7.6 (m, Ph, 6H), 8.43 (m, Ph, 4H). IR (KBr) ν_{max}: 3070 (w), 2060 (s), 1993 (s), 1989 (s), 1827 (m), 1619 (m), 1600 (m), 1584 (s), 1578 (s), 1495 (w), 1454 (m), 1430 (s) 1380 (m), 1336 (m), 1180 (w), 1160 (w), 1130 (w), 1090 (w), 1080 (w), 1065 (w), 1028 (w), 992 (w), 965 (w), 892 (w), 832 (w), 780 (w), 765 (m), 731 (w), 698 (w), 684 (m) cm^{-1}. UV (CH_2CH_3OH) λ_{max}: 222 nm (log ε 4.61), 264 (4.41), 351 (4.47). HRMS Found: 450.0171. Calc. for $C_{25}H_{14}O_5Fe$: *M* 450.0191. MS *m*/*z* (rel. int.): 450 (M^+, 2%), 422 ($M^+ - CO$, 10%), 394 (10), 366 (100), 309 (1). Anal. Calc. for $C_{25}H_{14}O_5Fe_2H_2O$: C, 61.75; H, 3.73%. Found: C, 62.20; H, 3.36%.

4.14. Reaction of **1** with acetylchloride in the presence of triethylamine

A solution of acetylchloride (240 mg) in dry benzene (20 ml) was added dropwise to a solution of **1** (261 mg, 1 mmol) and triethylamine (615 mg) in dry benzene (50 ml) at 80°C under an argon atmosphere for a period lasting 3 h. After this, stirring and heating was continued for 30 min and the solution was passed through silica gel column using a mixture of ethylacetate and dichloromethane (1:9) as eluants. The colored fraction was collected. After the solvent was removed, the residue was separated by middle pressure column chromatography to give 275.7 mg (91%) of (6-acetyloxytropone)$Fe(CO)_3$ (**16**) and 11 mg (4%) of (7-acetyl-6-hydroxytropone)$Fe(CO)_3$ (**17**).

16: m.p. 101 − 102°C. ^{1}H-NMR ($CDC1_3$): $\delta = 6.33$ (ddd, $J = 7.3$, 4.8, 1.1 Hz, H-3), 6.30 (ddd, $J = 7.6$, 4.8 Hz, 1.4, H-4), 4.93 (t, $J = 2.2$ Hz, H-7), 3.23 (ddd, $J = 7.6$, 2.2, 1.1 Hz, H-5), 2.55 (ddd, $J = 7.3$, 2.2, 1.4 Hz, H-2), 2.17 (s, CH_3). ^{13}C-NMR ($CDCl_3$): $\delta = 197.12$ (C–Fe*C*O), 167.50 (C–*C*O (Me)), 167.47 (C-1), 110.50 (C-7), 96.05 (C-6), 92.87 (C-4), 91.95 (C-3), 60.55 (C-2), 50.93 (C-5), 20.84 (C–*C*H_3). IR (KBr) ν_{max}: 2068 (s), 2000 (s), 1989 (s), 1765 (s), 1640 (s), 1615 (s), 1442 (m), 1396 (m), 1372 (m), 1328 (m), 1206 (s), 1176 (m), 1133 (s), 1101 (s), 1043 (m), 1011 (m), 894 (m), 638 (m), 614 (m), 602 (s), 582 (m), 571 (m), 539 (m), 504 (m), 468 (m) cm^{-1}. HRMS Found: 303.9678. Calc. for $C_{12}H_8O_6Fe$: *M* 303.9671. MS *m*/*z* (rel. int.): 304 (1), 276 (43), 248 (95), 220 (100), 206 (2), 192 (17), 177 (53), 162 (5), 149 (6). Anal. Calc. for $C_{12}H_8O_6Fe$: C, 47.40; H, 2.63%. Found: C, 47.16; H, 2.85%.

17: m.p. 106 − 108°C. ^{1}H-NMR ($CDCl_3$): $\delta = 18.07$ (s, OH), 6.13 (ddd, $J = 7.6$, 5.0, 1.3 Hz, H-3), 6.04 (ddd, $J = 7.7$, 5.5, 1.4, H-4), 3.33 (dd, $J = 7.7$, 1.2, H-5), 3.05 (dd, $J = 7.6$, 1.2 Hz, H-2), 2.40 (s, CH_3). ^{13}C-NMR ($CDCl_3$): $\delta = 206.14$ (C–*C*OFe), 198.76 (C-1), 198.66 (C–*C*OCH_3), 193.26 (C-6), 107.86 (C-7), 91.42 (C-3), 91.34 (C-4), 60.13 (C-5), 53.94 (C-2), 26.58 (C–*C*H_3). IR (KBr) ν_{max}: 2084 (s), 1997 (s), 1765 (m), 1616 (s), 1540 (m), 1472 (m), 1443 (m), 1415 (m), 1372 (m), 1205 (m), 1152 (m), 1133 (m), 1101 (m), 627 (m), 614 (m), 600 (m), 553 (m), 503 (m) cm^{-1}. HRMS Found: 303.9678. Calc. for $C_{12}H_8O_6Fe$: *M* 303.96706. MS *m*/*z* (rel. int.): 304 (M^+, 3), 276 (52), 248 (100), 220 (99), 192 (65), 177 (42), 164 (5), 150 (10). Anal. Calc. for $C_{12}H_8O_6Fe$: C, 47.40; H, 2.63%; Found: C, 47.70; H, 2.89%.

4.15. Reaction of **1** with acetic anhydride

A solution of **1** (514 mg, 2 mmol) and pyridine (300

mg) in acetic anhydride (5.589 g, 5 ml) was heated at 80°C under argon atmosphere for 7 h and was then cooled to r.t. A saturated aqueous solution of sodium bicarbonate was added to the reaction mixture and the products were extracted with ethylacetate (70 ml). The organic layer was washed three times with saturated aqueous solution of sodium carbonate. Extracts were dried over magnesium sulfate, filtered and the solvent was removed to give 575.8 mg of residue. This was separated by silica gel using hexane and ethylacetate (1:1) to give 292.9 mg (48%) of **17**, 41 mg (7%) of **16** and 76.5 mg (15%) of recovered compound **1**.

*4.16. (7-Cycloheptatrienyl-2,4-cycloheptadiene-1,6-dione)Fe(CO)$_3$ (**18**)*

A solution of **1** (262 mg, 1 mmol) and tropylium tetrafluoroborate (356 mg) in 10 ml of ethanol was heated under reflux for 30 min. After the solvent was removed, the residue was separated by silica gel column chromatography using CH_2Cl_2/AcOEt to give 304 mg (86%) of (7-cycloheptatrienyl-2,4-cycloheptadiene-1,6-dione) $Fe(CO)_3$ (**18**).

18: m.p. 176 − 178°C (d). ^{1}H-NMR ($CDCl_3$): $\delta = 6.68$ (t, $J = 3$ Hz, H-3′,4′), 6.18 (dm, $J = 9$ Hz, H-2′,5′), 5.77 (dd, $J = 4.8$, 3 Hz, H-3,4), 5.03 (dd, $J = 9$, 5.4 Hz, H-1′,6′), 3.56 (m, H-2,5), 3.46 (d, $J = 12$ Hz, H-7), 1.58 (dt, $J = 12$, 5.4 Hz, H-7′). IR (KBr) ν_{max}: 3035 (w), 3010 (w), 2050 (s), 1994 (s), 1988 (s), 1965 (m), 1646 (s), 1627 (s), 1388 (m), 1290 (m), 1250 (w), 1164 (w), 1104 (w), 1032 (w) 1009 (w), 992 (w), 902 (w), 872 (w), 866 (w), 776 (m), 746 (w), 706 (m), 683 (m) cm^{-1}. HRMS Found: 352.0035. Calc. for $C_{17}H_{12}O_5Fe$: M 352.0034. MS m/z (rel. int.): 352 (M^+, 0.4), 324 (100), 296 (2), 268 (51), 242 (2), 240 (16), 222 (1), 213 (1). Anal. Calc. for $C_{17}H_{12}O_5Fe$: C, 57.98; H, 3.44%. Found: C, 57.68; H, 3.70%.

*4.17. Reaction of the anion **19** of **1** with (cycloheptadienonium)Fe(CO)$_3$ tetrafluoroborate (**20**)*

A solution of *t*-BuLi (1 ml) in THF (1 ml) was added to a solution of **1** (131 mg) in THF (25 ml) at − 50°C. (Cycloheptadienonium)$Fe(CO)_3$ hexafluorophosphate (**20**) (170 mg) was added to the above solution, dichloromethane was added to the reaction mixture and it was acidified by 3 N H_2SO_4. Products were extracted with dichloromethane, dried over $MgSO_4$ and then filtered. After the solvent was removed, the products were isolated by column chromatography on silica gel with dichloromethane and ethylacetate as eluants to give 24.1 mg of (tropone)$Fe(CO)_3$ and 142 mg (56%) of adduct **21**.

21: m.p. 179 − 180°C (d). ^{1}H-NMR ($CDCl_3$): $\delta = 6.00$ (m, H-3,4), 5.84 (m, H-3′), 5.48 (dd, $J = 7.6$, 5.7 Hz, H-4′), 3.59 (m, H-2,5), 3.15 (d, $J = 6.6$ Hz, H-7), 3.00 (d, $J = 10.8$ Hz, H-2′), 2.86 (d, $J = 9$ Hz, H-5′), 2.60 (m, H-6′), 1.65 (m, H-7′). IR (KBr) ν_{max}: 3050 (w), 2950 (w), 2085 (s), 2065 (s), 2015 (s), 2005 (s), 1996 (s), 1990 (s), 1640 (m), 1621 (m) 1434 (w), 1390 (m), 1358 (w), 1293 (m), 1274 (w), 1225 (w), 1168 (w), 1158 (w), 1124 (w), 1096 (w), 1028 (w), 990 (w), 880 (w), 856 (w) cm^{-1}. Anal. Calc. for $C_{20}H_{12}O_9Fe_2$: C, 47.28; H, 2.38%. Found: C, 47.22; H, 2.66%.

*4.18. Reaction of **1** with chlorocycloheptatrienium hexafluorophoshate*

A solution of **1** (262 mg, 1 mmol) and triethylamine (220 mg) in 20 ml of dichloromethane was added dropwise slowly to a dispersed solution of chlorocycloheptatrienium hexafluorophoshate (**23**) (270 mg, 1 mol) in dichloromethane (10 ml). After refluxing for 6 h, the solvent was removed and the reaction mixture was separated by column chromatography on silica gel using ethylacetate and hexane (1:1) to give 39.1 mg (10%) of [7-(3-chlorocycloheptatrienyl)-2,4-cycloheptadiene-1,6-dione]$Fe(CO)_3$ (**24**). Starting material **1** (87 mg) was recovered also.

24: m.p. 152 − 153°C (d). ^{1}H-NMR ($CDCl_3$): 6.60 (m, H-3′,4′), 6.14 (dm, $J = 12$ Hz, H-5′), 5.74 (m, H-3,4), 5.12 (m, H-1′,6′), 3.6 (m, H-2,5), 3.4 (dm, $J = 15$ Hz, H-7), 1.84 (dt, $J = 15$, 7 Hz, H-7′). IR (KBr) ν_{max}: 3050 (w), 2090 (vs), 2080 (vs), 2025 (vs), 2000 (vs), 1660 (s), 1634 (s), 1470 (w), 1435 (w), 1394 (m), 1290 (s), 1250 (w), 1225 (w), 1175 (w), 1110 (w), 1095 (w), 1035 (w), 990 (w), 945 (w), 930 (w), 900 (w), 885 (m), 870 (w), 830 (w), 810 (w), 800 (w), 735 (s), 700 (w) cm^{-1}. UV (CH_3CH_2OH) λ_{max}: 203 nm (log ε 4.57), 220sh (4.44), 250sh (4.17), 290sh (3.83). HRMS Found: M 385.9646. Calc. for $C_{17}H_{11}O_5ClFe$, M 385.9645. MS m/z (rel. int.): 386 (M^+, 6), 358 (100) 350 (6), 330 (16), 302 (65), 294 (36), 286 (36), 275 (3), 238 (18) 211 (28). Anal. Calc. for $C_{17}H_{11}O_5ClFe$: C, 52.82; H, 2.87%. Found: C, 52.51; H, 3.14%.

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