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Fluxional behavior of methyl-substituted tricarbonyl(tropone)iron complexes and their different reactivity

Ambroz Almássy [a,*], Zuzana Benková [b], Branislav Horváth [c], Andrej Boháč [a]

[a] Department of Organic Chemistry, Comenius University, Faculty of Natural Sciences, Mlynská dolina, 842 15 Bratislava, Slovakia
[b] Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia
[c] Chemical Institute, Comenius University, Faculty of Natural Sciences, Mlynská dolina, 842 15 Bratislava, Slovakia

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ABSTRACT

The compositions of regioisomeric mixtures of tricarbonyliron complexes of 2-methyltropone (**1a,b**), 3-methyltropone (**2a,b**) and 2,6-dimethyltropone (**3a,b**) are studied and compared with the results of *ab initio* computations. The structures, frontier orbitals, and population analysis are evaluated by means of density functional theory. The thermodynamic and kinetic parameters of regioisomerizations are determined using dynamic ^{1}H NMR technique. The influence of methyl-substituent(s) on the equilibrium ratio of regioisomers resulting from the haptotropic rearrangement is discussed. Significant differences in the reactivity of *C*-protonized methyl- and dimethyl-substituted tricarbonyl(tropone)iron complexes **4–6** in nucleophilic additions and corresponding *O*-trimethylsilylated complexes **7–9** in [3+2] cycloadditions are explained in terms of electronic and steric effects of the methyl group(s). Various hydroazulenone cycloadducts of tricarbonyl(η^4-2,6-dimethyltropone)iron **3a,b** have been prepared by stereoselective [3+2] cycloaddition with Fp-reagents **12–14** and characterized. Formerly proposed mechanism of [3+2] cycloaddition was approved.

1. Introduction

Tricarbonyliron complexes of cyclohepta-2,4,6-trienones (tropones) serve as useful intermediates in stereoselective synthesis. Tropone composes a stable 18e complex by η^4-coordination to the tricarbonyliron moiety with one of the outer π-bonds remaining outside the iron coordination sphere. The structure possesses a stereogenic plane and exists in two enantiomeric forms. The coordinated diene moiety is protected by the $Fe(CO)_3$ group while the uncoordinated enone part is accessible to the 1,4-additions of functionalized zinc-copper reagents [1], organolithium reagents [2], and Diels–Alder cycloadditions [3]. While the $Fe(CO)_3$ group undergoes an 1,3-haptotropic rearrangement through the coordinatively unsaturated 16e intermediate each of the tropone double bonds can be coordinated to iron [4]. The regioisomerization of unsubstituted tropone $Fe(CO)_3$ complex corresponds to a racemization and its activation energy was assigned to 107 kJ mol^{-1} [5]. The enantiomers could be separated because the racemization proceeded very slowly at 25 °C [6]. This activation energy surpassed the activation energy of isomerization of tricarbonyl(η^4-cyclohepta-1,3,5-triene)iron (93 kJ mol^{-1}) as a result of electron withdrawing effect of the carbonyl group of tropone [7]. The fluxional behavior was observed also in a variety of tricarbonyliron complexes of cycloheptatrienes [8], tropones [9], azepines [10], and oxepines [11] for which the activation parameters of regioisomerizations were determined. For the sake of clarity when a shift of $Fe(CO)_3$ group along the π-conjugated system is considered, we use numbering of the atoms in the coordinated tropone ligand obeying the nomenclature rules established for the free ligand.

The tricarbonyliron complexes of unsymmetrically substituted tropones occur as the mixtures of two thermodynamically unequal regioisomers. The composition of an equilibrated mixture of tricarbonyl(η^4-2-methyltropone)iron complex **1a,b** is substantially shifted toward the (η^4-4,5,6,7) isomer **1a** possessing the methyl-substituted carbon outside the coordination sphere of iron (Chart 1). We have determined the difference in energy between regioisomers **1a** and **1b** to 8.8 kJ mol^{-1} [12]. The same trend was reported in the case of 2-acetoxy- and 2-benzoyloxytropone tricarbonyliron complexes, while the (η^4-2,3,4,5) coordinated isomer of tricarbonyl(η^4-2-trimethylsilyloxytropone)iron complex was not observed at all [13].

The relative energies of the regioisomers **1a,b** and **3a,b** (Chart 1) and transition structures connecting these regioisomeric forms were computed by Ariafard and Lin at the DFT level [14]. They found the regioisomeric form **1a** and **3a** with the methyl-substituted carbon outside the coordination sphere of iron to be more stable by 15.1 kJ mol^{-1} and 12.1 kJ mol^{-1}, respectively, than the regioisomeric forms **1b** and **3b** with the methyl-substituted carbon within the iron coordination sphere. The activation energy of the

* Corresponding author. Tel.: +421 2 6029 6322; fax: +421 36 26029 6690.
E-mail address: almassy@fns.uniba.sk (A. Almássy).

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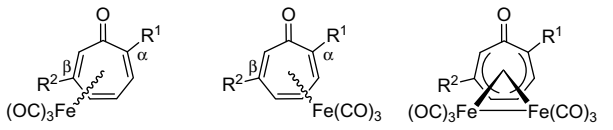
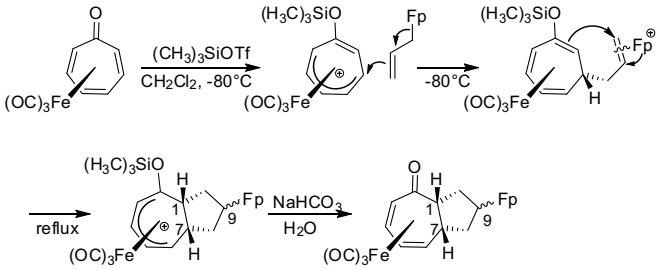


1a R^1: CH_3; R^2: H **1b** R^1: CH_3; R^2: H **1c** R^1: CH_3; R^2: H
2a R^1: H ; R^2: CH_3 **2b** R^1: H ; R^2: CH_3 **2c** R^1: H ; R^2: CH_3
3a R^1: CH_3; R^2: CH_3 **3b** R^1: CH_3; R^2: CH_3 **3c** R^1: CH_3; R^2: CH_3

Chart 1. Methyl-substituted tricarbonyl(η^4-tropone)iron complexes.



Scheme 1.

isomerization was determined to 83.3 kJ mol^{-1} and 84.2 kJ mol^{-1} for **1a** and **3a**, respectively. The differences in relative stabilities were ascribed to steric factors.

Tricarbonyl(4-methyltropone)iron complex occurs as an inseparable mixture of both regioisomers. The (η^4-2,3,4,5) isomer with the methyl substituent located at the inner carbon of the coordinated diene prevails [15]. The equilibrium ratio of regioisomers has not been published. In the equilibrated mixture of (4-bromotropone)tricarbonyliron complex thermodynamically more stable form is (η^4-4,5,6,7) isomer in which the peripheral carbon of the coordinated diene fragment is substituted [16].

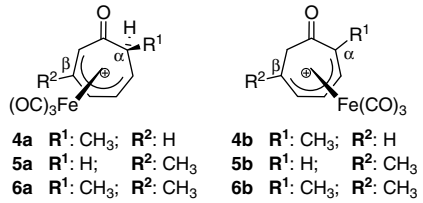
While the equilibrium distribution of tricarbonyl(3-methyltropone)iron complexes **2a** and **2b** (Chart 1) is 34:66 at 323 K in $CDCl_3$ [17], the tricarbonyliron complexes of 3-methoxytropone [15] and 3-bromotropone [16] occur exclusively in the (η^4-4,5,6,7) form due to a large energetic difference between the two possible regioisomers. Density functional computations were employed to explain the differences in the equilibrium compositions of regioisomers of the tricarbonyliron complexes of 3-bromotropone and 4-bromotropone [18]. As the energy barrier due to the isomerisation did not depend on the position of Br atom in tropone, the absence of (η^4-2,3,4,5) coordination in the 3-bromotropone complex was attributed to the low thermodynamic stability of this regioisomer.

The fluxional behavior of the cationic tricarbonyl(η^5-tropylium)iron (tropylium : $C_7H_7^+$) complexes manifests itself by the sequential 1,2-haptotropic shifts of the $Fe(CO)_3$ moiety along the π-conjugated system of the ligand [19]. Formation of four thermodynamically unequal regioisomers is possible upon the insertion of a substituent into the structure of tropylium ligand. The most abundant isomer of η^5-methyltropylium complex in $CDCl_3$ is the one with a substituent located at the uncoordinated carbon (50%). The isomer substituted at C2 of iron-coordinated pentadienylium system occurs in 43% [20].

The fluxional behavior of various protonized 2-substituted tricarbonyl(η^4-tropone)iron complexes was discussed by Eisenstadt and Winstein [21]. In strongly acidic media the neutral complex **1** undergoes the protonization of uncoordinated α-carbon. The ligand of cationic complex **4a** (Chart 2) occurs preferentially in keto-form. The regioisomerization to the more stable isomer **4b** proceeds readily through the 1,2-haptotropic rearrangement of $Fe(CO)_3$ group followed by the 1,3-hydrogen shift (Scheme 2). The equilibrium was established at ambient temperature after 15–20 min. The nucleophilic addition of methanol to complex **1** in concentrated H_2SO_4 was preceded by selective protonization of carbon C7. This indicates that at equilibrium the protonized form of complex **1** (complex **4**) is dominated almost exclusively by regioisomer **4b**. However, when the nucleophile was added before the equilibration of protonized complexes was established the product of addition to the regioisomer **4a** was also detected. Therefore, the approach of methanol to C3 is not prevented by the methyl group at C2. The enantiomers of tricarbonyl(η^4-tropone)iron and tricarbonyl(η^4-2-methyltropone)iron **1** were separated after the addition of (−)-menthol [6,12,22].

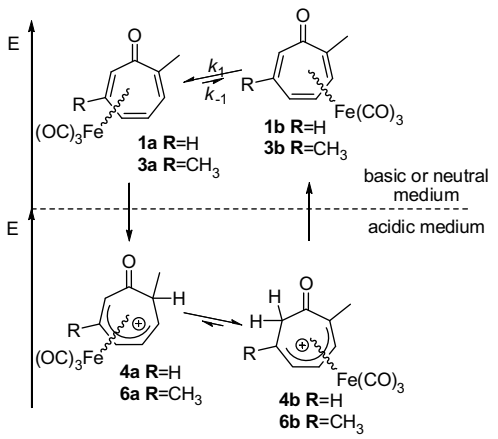
Bulky tricarbonyliron fragment hindering one site of tropone ring and protecting the coordinated diene system represents stereochemically stable chiral unit relevant to stereoselective synthesis. This type of complexes was employed in Diels–Alder cycloadditions [3] and stereoselective synthesis of polyhydroxylated cycloheptane derivatives [23]. In our work we focused on the [3+2] cycloaddition reactions leading to hydroazulenone structures.

The [3+2] cycloaddition of tricarbonyl(η^5-tropylium)iron complexes with (η^1-allyl)Fp-reagents (Fp: η^5-$CpFe(CO)_2$) as a convenient method for stereoselective synthesis of hydroazulene skeletons was suggested by Rosenblum et al. (Scheme 1) [24a]. Various hydroazulenone derivatives related to the naturally occurring guaianolides and guaiazulenes can be synthesized by this reaction *via O*-trimethylsilylated cations prepared *in situ* from tricarbonyl(η^4-tropone)iron complexes on treatment with trimethylsilyltriflate ($(CH_3)_3SiOTf$) (Scheme 1). The outer position of pentadienylium chain adjacent to the enol ether double bond reacts with the electron rich terminal carbon of (η^1-allyl)Fp-reagent. Intramolecular five-membered ring annulation requires an elevated temperature and proceeds through the addition of an electron deficient terminal carbon of Fp complexed η^2-allyl chain to the enol ether double bond. Desired neutral two-nuclear hydroazulenone complex was obtained, after mild basic hydrolysis of Si–O

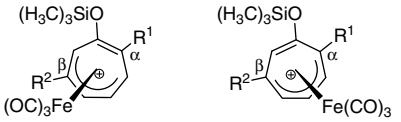


4a R^1: CH_3; R^2: H **4b** R^1: CH_3; R^2: H
5a R^1: H; R^2: CH_3 **5b** R^1: H; R^2: CH_3
6a R^1: CH_3; R^2: CH_3 **6b** R^1: CH_3; R^2: CH_3

Chart 2. Cations of *C*-protonized tricarbonyl(η^4-tropone)iron complexes.



Scheme 2.



7a R^1: CH_3; R^2: H **7b** R^1: CH_3; R^2: H
8a R^1: H; R^2: CH_3 **8b** R^1: H; R^2: CH_3
9a R^1: CH_3; R^2: CH_3 **9b** R^1: CH_3; R^2: CH_3

Chart 3. Cations of *O*-trimethylsilylated tricarbonyl(η^4-tropone)iron complexes.

bond with $NaHCO_3$. The excellent stereoselectivity of cycloaddition results from the approach of Fp-reagent from the *exo*-side with respect to $Fe(CO)_3$ group in both stages of the cycloaddition. Therefore, the hydroazulenone product possesses exclusively the *syn* configuration of annulated ring at C1 and C7. Actually, the mixture of two epimers was obtained because the stereogenic center at C9 is not generated stereoselectively [24b].

The *O*-silylated tricarbonyltropyliumiron cations derived from the tricarbonyl(2-methyltropone)iron **1** and tricarbonyl(4-methyltropone)iron complexes react with Fp-reagents regioselectively. The mechanism of cycloaddition was proposed upon the detailed analysis of configuration of the diastereoisomeric cycloadducts formed by the addition of *E*/*Z* (η^1-but-2-enyl)Fp mixture to **3** *via* corresponding *O*-trimethylsilylated cations **9a,b** (Chart 3) [25]. According to conclusions of Lewis [20], based on the site-preferences observed in tricarbonyl(η^5-methyltropylium)iron complex, the cation derived from the tricarbonyl(4-methyltropone)iron appeared to be thermodynamically more stable when the ligand was coordinated in (η^5-3,4,5,6,7) pattern to the iron [24b]. Despite of that fact, exclusively the (η^5-2,3,4,5,6) form was reactive which was explained in terms of the steric hindrance imposed by methyl in the predominant regioisomer.

This paper is outlined as follows. The computational details used in this study are described in the next section. Section 3 is divided into three subsections. Subsection 3.1 is devoted to experimental and theoretical investigations of tricarbonyl(η^4-tropone)iron complexes. The *C*-protonized forms of these complexes are discussed in Subsection 3.2. Subsection 3.3 concerns with the corresponding *O*-silylated tricarbonyl(η^5-tropylium)iron cationic complexes. Conclusions are given in Section 4 and experimental details are discussed in Section 5.

2. Computational details

Since then significant differences in compositions of regiosomers of neutral complexes are not clarified satisfactorily assuming exclusively the electronic effects these compounds were investigated also at the theoretical level. In the case of *C*-protonized and *O*-silylated complexes the conclusions were drawn based on the differences in reactivity between regioisomeric pairs. The calculations were carried out by means of the density functional theory (DFT) using GAUSSIAN98 program [26]. Two hybrid non-local DFT functionals, the B3LYP [27,28] and B3P86 [27,29] functionals, were employed in this study. The 6-311+G* split-valence basis set has been used. The geometries of free 2-methyltropone (and its anion at the B3P86/6-311+G* level), 3-methyltropone, and 2,6-dimethyltropone as well as both of their regioisomeric tricarbonyliron complexes **1a,b**, **2a,b**, and **3a,b**, respectively, were completely optimized and characterized as the true minima on potential energy hypersurface. The reason for involving free tropones and in the case of 2-methyltropone also its anion was to get insight into the interactions between iron and tropone ligands in these compounds.

The selected functionals, especially B3P86, turned out to be adequate for optimization, of the ground state geometry of organometallic compounds [30]. In many cases the DFT approach leads to geometries comparable with the MP2 geometries if not even closer to the experimental ones [31]. The DFT functionals provide also reasonable energetic parameters.

3. Results and discussion

3.1. Neutral tricarbonyl(η^4-tropone)iron complexes

In this section we are focusing on the tricarbonyliron complexes of 2-methyltropone, 3-methyltropone, and 2,6-dimethyltropone **1**, **2**, and **3**, respectively (Chart 1). Appropriate ligands were prepared by known procedures. Synthesis of 2-methyltropone was accomplished using the procedure of Brady and Hieble [32]. 3-Methyltropone and 2,6-dimethyltropone were prepared from 2-methylcyclohexanone and 2,6-dimethylcyclohexanone, respectively, employing the procedure developed by our group [33]. The desired complexes **1**, **2**, and **3** were prepared on treatment of $Fe_2(CO)_9$ with appropriate substituted tropones in benzene at 40 °C.

The equilibrium mixtures of regioisomers of tricarbonyliron complexes **1a**,**b**, **2a**,**b**, and **3a**,**b** were always accompanied by small amounts of binuclear complexes **1c**, **2c**, and **3c**, respectively. The composition of equilibrium mixtures and thermodynamic parameters (*K* and ΔG) were determined from ^{1}H NMR and HPLC analyses and are presented in Table 1.

The presence of methyl group at C2 (α-position) in complexes **1** and **3** has a crucial influence on the regioisomeric stability and site preference of the $Fe(CO)_3$ moiety. The composition of the equilibrium regioisomeric mixture is extensively shifted in favor of the structure possessing the methyl-substituted carbon C2 outside the coordination sphere of iron. The influence of methyl substituent at β-position on the stability of regioisomers seems to be less significant. The above is obvious from the comparable abundance of regioisomers **1b** (2.9%) without β-methyl-substitution and **3b** (3.7%) with β-methyl-substitution in their equilibrium mixtures. The thermodynamically more stable form **2b** with the methyl group attached to carbon outside the coordination sphere of iron differs only moderately from the less stable regioisomer **2a** (ΔG^{323} = 1.8 kJ mol^{-1}). On the other hand the differences between the regioisomers of complexes involving methyl group at α-position **1a,b** and **3a,b** are much greater (ΔG^{297} = 8.6 kJ mol^{-1} and 8.0 kJ mol^{-1}, respectively).

The equilibration of the mixtures enriched by thermodynamically less stable isomers **1b** and **3b,** respectively, was monitored by dynamic ^{1}H NMR spectroscopy in $CDCl_3$ at constant temperature. The reaction half-times and rate constants of regioisomerization of complexes **1** and **3** are summarized in Table 2. The preparation of disequilibrium mixtures of **1a**,**b** and **3a**,**b** will be discussed below.

The activation enthalpies, entropies, and Gibbs energies of regioisomerization for complexes **1** and **3** are presented in Table 3. The corresponding values for complex **2** determined by Morita et al. [17] are also included for comparative purposes. Listed values are related to conversion of the thermodynamically less stable to the thermodynamically more stable regioisomers.

Table 1
Thermodynamic parameters of tricarbonyl(η^4-tropone)iron complexes **1**–**3**

Regioisomeric complexes	The ratio of regioisomers in equilibrium	*K*	ΔG [kJ mol^{-1}]
1a:**1b**[a]	97.1:2.9	33.48	8.6
2a:**2b**[b]	33.9:66.1	1.95	1.8
3a:**3b**[a]	96.3:3.7	26.00	8.0

[a] Measured at T = 296 K in $CDCl_3$.
[b] measured at T = 323 K in $CDCl_3$, taken from Ref. [17].

Table 2
Kinetic parameters of regioisomerization of complexes **1a,b** and **3a,b**

T [K]	**1b** X **1a**			**3b** X **3a**		
	$\tau_{1/2}$ [h]	k_1 [s^{-1}]	k_{-1} [s^{-1}]	$\tau_{1/2}$ [h]	k_1 [s^{-1}]	k_{-1} [s^{-1}]
296	12.8	1.50×10^{-5}	4.44×10^{-7}	26.5	7.28×10^{-6}	2.78×10^{-7}
306	3.5	5.52×10^{-5}	1.64×10^{-6}	6.1	3.14×10^{-5}	1.19×10^{-6}
316	0.8	2.41×10^{-4}	7.19×10^{-6}	1.6	1.19×10^{-4}	4.56×10^{-6}

Table 3
Activation parameters of isomerization to thermodynamically more stable isomer

Regioisomerization	$\Delta H^{\neq}$ [kJ mol^{-1}]	$\Delta S^{\neq}$ [J K^{-1} mol^{-1}]	$\Delta G^{\neq}$ [kJ mol^{-1}]
1b → **1a**[a]	105.2	18.0	99.9
2a → **2b**[b]	114.6	28.5	105.4
3b → **3a**[a]	106.0	14.8	101.6

[a] Measured at T = 296 K in $CDCl_3$.
[b] Measured at T = 323 K in $CDCl_3$, taken from Ref. [17].

In thermodynamically less stable isomers **1b** and **3b** the diene fragment coordinated to the iron comprises, from the steric viewpoint, an extremely inconvenient methyl-substituted peripheral carbon. The iron is forced to coordinate the diene substituted at inner carbon in thermodynamically more stable form of tricarbonyl(2,6-dimethyltropone)iron complex **3a**. Even though the composition of equilibrium isomeric mixtures of complexes **1** and **3** is similar, the isomerization of complex **3b** proceeds approximately twice slower than the isomerization of complex **1b**. The presence of methyl at the peripheral position of coordinated diene in the minor isomers (**1b**, **3b**) raises their energy level and thus lowers the activation barrier. This is the crucial driving force for the isomerization. In the prevailing isomer **3a** iron experiences steric interactions analogous to those in thermodynamically less stable isomer **2a**. In the case of complex **2** the $Fe(CO)_3$ group is released to coordinate more convenient unsubstituted diene moiety leading to isomer **2b**. Because the difference between energy levels of the isomers **2a** and **2b** is not so significant and both represent thermodynamically suitable structures the activation energy is about 5 kJ mol^{-1} higher and isomerization rate is markedly lower than in the complexes **1** and **3**.

3.1.1. Theoretical results on tricarbonyl(η^4-tropone)iron complexes

The geometries of both regioisomers of complexes **1**, **2**, and **3** optimized at B3LYP/6-311+G* and B3P86/6-311+G* levels are sketched in Supplementary material. All complexes possess quasi-tetragonal pyramidal arrangement around the iron with two basal and one apical CO ligands. Some relevant structural parameters are provided in Supplementary material. The corresponding parameters of free 2-methyl, 3-methyl, and 2,6-dimethyltropones are also included to show their structural variations resulting from coordination to the iron. The experimental bond lengths and bond angles of tricarbonyl(η^4-tropone)iron are: C1C2 = 1.447 Å, C2C3 = 1.343 Å, C3C4 = 1.463 Å, C4C5 = 1.435 Å, C5C6 = 1.396 Å, C6C7 = 1.442 Å, C1C7 = 1.492 Å, C1O = 1.248 Å, FeC4 = 2.149 Å, FeC5 = 2.042 Å, FeC6 = 2.067 Å, FeC7 = 2.114 Å, FeC(O) = 1.759 Å, $(CO)_{av}$ = 1.115 Å, C2C1C7 = 123°, C1C2C3 = 124°, C2C3C4 = 127°, C3C4C5 = 122°, C4C5C6 = 121°, C5C6C7 = 120°, C1C7C6 = 127° (the atom numbering is consistent with the numbering of free tropone, it starts at the carbonyl carbon and follows through the uncoordinated part toward the coordinated diene) [34].

Apart from the bonds containing Fe both functionals produce structural parameters that are very similar, the agreement in bond lengths is found within the range of 0.01 Å. The differences become more noticeable for C–Fe bond distances. The B3P86 functional is prone to yield systematically shorter bonds as well as modestly larger puckering of tropone ligands and appears to provide values closer to the experimental estimates than the B3LYP functional. Except for the Fe–C(O) distances the differences between the DFT and experimental estimates are less than 2%. Our Fe-C(diene) bond distances of complexes **1** and **3** calculated at B3LYP/6-311+G* level are found to agree within less than 0.01 Å with the corresponding values of Ariafard and Lin calculated at B3LYP level with the basis set of double-zeta quality augmented with a set of polarization functions [14]. The experimentally observed reverse ordering of bond lengths within the diene coordinated to $Fe(CO)_3$ (the central bond being shorter than the two peripheral bonds) with respect to free tropone is uniformly reproduced by both of the theoretical approaches. In the optimized structures the iron takes position closer to the inner carbons consistently with experimental findings.

The essentially planar optimized geometries of all mono- and dimethyl-substituted tropones become bent by about 50–60° upon coordination to $Fe(CO)_3$. Hence two planar fragments (coordinated and uncoordinated) of tricarbonyl(η^4-tropone)iron complexes are recognizable. Upon complexation the CO and CC double bonds outside the coordination sphere of iron are contracted by about 0.02 Å and 0.01 Å, respectively. The puckering of tropone plane is also reflected on the elongated single bonds between both split conjugated fragments by about 0.03–0.04 Å. The bond length alteration (BLA) of the coordinated diene fragments is reduced and changes sign with respect to the free tropones. Contrariwise, as a result of overall conjugation breaking caused by the tropone distortion, the BLA of the remaining uncoordinated unit involving C=O bond increases in complexes. However, this part undergoes less pronounced changes. It is worth noticing that if carbon C2 bearing CH_3 group is incorporated into the coordination sphere of iron an increase in Fe–C2 distance by about 0.07–0.08 Å is calculated. Analogous incorporation of methyl group at carbon C3 in the coordination sphere of iron increases the Fe–C3 distance only by about 0.01–0.02 Å. In the less stable regioisomers **1b** and **3b,** the methyl substituent gets close to one basal CO group. The distance between the carbon of methyl group and carbon of this CO ligand is 3.04 Å. In the more stable regioisomers **1a** and **3a** the distance between the carbons of methyl group and the nearest (apical) CO ligand is around 4.56 Å. Thus the repulsive interactions of CH_3 and CO groups in **1b** and **3b** are responsible for their destabilization. The less significant discrimination of regioisomer **2a** with respect to **2b** might be connected with the smaller differences in the distances between methyl group and CO groups in both regioisomeric forms. The carbon of methyl group is 4.22 Å far away from the carbon of apical CO ligand in the more stable isomer **2b**, while in less stable complex **2a** the carbon of methyl group is found at the distance of 3.28 Å from the carbon of the nearest basal CO ligand.

Other useful information on complexes **1**–**3** may be obtained from the charge distribution analysis and character of molecular orbitals. The partial charges of iron, tropone, and carbonyl ligands obtained from the natural population analysis (NPA) are presented in Table 4. Iron atom and tropone ligands in all complexes attain partial negative charges and CO ligands attain partial positive

Table 4
Partial NPA charges and relative energies including ZPE correction of complexes **1**–**3**[a]

		1a	1b	2a	2b	3a	3b
Q(Fe)	B3LYP	−0.247	−0.236	−0.248	−0.246	−0.252	−0.238
	B3P86	−0.272	−0.289	−0.300	−0.298	−0.303	−0.291
Q(tropone)	B3LYP	−0.251	−0.247	−0.261	−0.262	−0.247	−0.245
	B3P86	−0.239	−0.235	−0.247	−0.248	−0.233	−0.233
Q(CO)[b]	B3LYP	0.166	0.161	0.170	0.169	0.166	0.161
	B3P86	0.170	0.175	0.182	0.182	0.179	0.175
ΔE	B3LYP	3.16[c]	17.77[c]	2.11[c]	0.00[c]	0.00[d]	11.99[d]
	B3P86	3.00[c]	17.10[c]	2.15[c]	0.00[c]	0.00[d]	11.27[d]

[a] Energies are given in kJ mol^{-1} and charges in e.
[b] The values averaged over all CO bonds.
[c] Relative energy with respect to **2b**.
[d] Relative energy with respect to **3a**.

charge. Although, 2-methyltropone gets altogether far less than one electron upon the coordination to $Fe(CO)_3$ the coordinated diene fragment in complexes **1a** and **1b** also experiences the same structural modification as in the free anion while the remaining O=C−C=C fragment behaves similarly to the free neutral 2-methyltropone. The coordinated diene parts of the HOMO orbitals of all investigated complexes strongly resemble the corresponding part of the LUMO orbitals of free tropone ligands. The characters of HOMO orbitals of all compounds are qualitatively very similar and are located at Fe, tropones, and partly on CO ligands. The only difference that can be found between the regioisomers lies in the extent to which the methyl group is involved into the HOMO. It appears that the bonding contribution due to CH_3 group to HOMO is more intensive when methyl is attached to the carbon outside the coordination sphere of iron (in more stable regioisomers **1a**, **2b**, and **3a**). This tendency is more pronounced for methyl at C2. This may partly render an explanation for the larger energy difference between the pairs of regioisomers of complexes **1** and **3** compared to **2**.

The relative stabilities within both sets (with mono- and dimethyltropone ligands) of investigated positional isomers were evaluated using the electronic energies including the zero point vibrational corrections and are given in Table 4. In line with experimental findings it is apparent that the regioisomers with methyl group appended to carbon outside the coordination sphere of iron are lower in energy than those with methyl group at carbon within the coordination sphere of iron (**1a** versus **1b** or **2b** versus **2a**). The propensity of carbon bearing methyl group to be repelled from the iron coordination sphere is more significant for 2-methyltropone as is evidenced by the larger energy differences between regioisomers **1a** and **1b** than between **2b** and **2a** as well as enhanced stability of regioisomer **3a** with respect to **3b**.

Although, the free 3-methyltropone is higher in energy than the 2-methyltropone by about 5.17 kJ mol^{-1} and 6.40 kJ mol^{-1}, respectively, according to the B3LYP and B3P86 models the situation in complexes becomes reversed. As Table 4 shows the pair of regioisomers with 3-methyltropone (**2a**, **2b**) is more stable than the pair of regioisomers with 2-methyltropone (**1a**, **1b**). Considering the preferred regioisomers (**1a**, **2b**), one can estimate that the stabilization effect due to the methyl group at carbon C3 in **2b** exceeds the stabilization effect of the methyl group at carbon C2 in **1a** by about 5.17 + 3.16 = 8.33 kJ mol^{-1} and 6.40 + 3.00 = 9.40 kJ mol^{-1} at B3LYP and B3P86 levels, respectively.

The reverse pattern of stability of free 2-methyl- and 3-methyltropone with respect to their tricarbonyliron complexes may be explained in terms of different degrees of conjugation loss. In the free 2-methyltropone the favorable position of methyl group allows to involve it through its hyperconjugation effect into overall conjugation with the tropone framework. On contrary in the free 3-methyltropone, the hyperconjugation interaction of methyl group is restricted only over 2 double bonds, namely the C1=O and C2=C3 and partially depletes the conjugation between the O=C1−C2=C3 and C4=C5−C6=C7 fragments. This is reflected on the lower stability of free 3-methyltropone related to free 2-methyltropone. Thus bending of 3-methyltropone upon coordination to iron, which requires a reduction of conjugation, is promoted by methyl at C3 and is energetically less demanding than bending of 2-methyltropone.The situation with the free 2,6-dimethyltropone is analogous to the 2-methyltropone. The energy differences between **1b** and **2a** are even more pronounced and cannot be accounted for by the loss of delocalization energy. The larger destabilization of methyl group at C2 in **1b** with respect to methyl group at C3 in **2a** might be attributed to the steric interactions. The methyl group at C2 in **1b** gets closer to Fe than the methyl group at C3 in **2a** by about 0.03 Å.

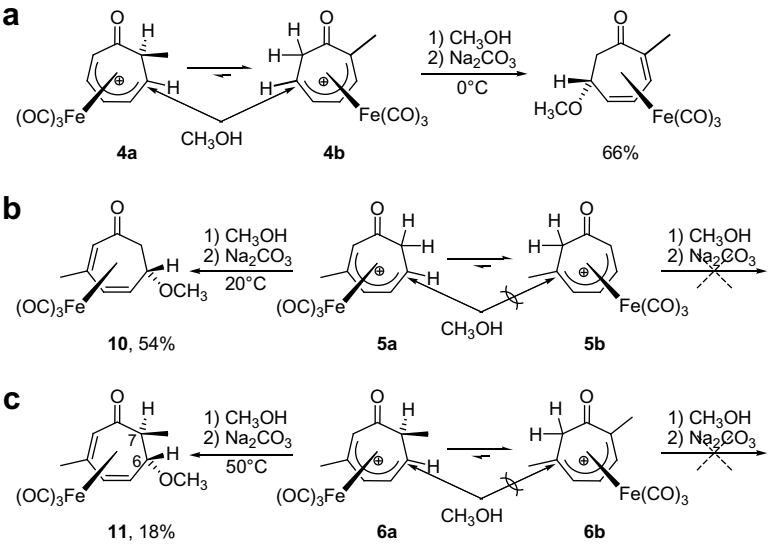
3.2. C-Protonized cationic forms of tricarbonyl(η^4-tropone)iron complexes

Since in the neutral complexes discussed above the conjugation between the iron-coordinated diene moiety and α,β-unsaturated ketone moiety is broken, the enone CC double bond is a potential site for the addition of nucleophile in acidic media. Reactivity of protonized cationic complexes **5** and **6** (Chart 2) was examined by the nucleophilic addition of methanol in concentrated H_2SO_4.

As it was not possible to assess the composition of mixtures of protonized complexes directly, the composition was determined indirectly from the composition of corresponding mixtures of neutral complexes immediately after deprotonization. The protonization of complexes **1** and **3** using concentrated H_2SO_4 or HBF_4 in Ac_2O followed by their neutralization with Na_2CO_3 or triethylamine gave the disequilibrium mixtures of regioisomers considerably enriched by the thermodynamically less stable isomers **1b** and **3b**, resulting from the more stable cations **4b** and **6b**. These mixtures were exploited for the determination of kinetic parameters of regioisomerization of complexes **1** and **3**. Similarly, starting from the equilibrium mixture of **2a** and **2b**, the mixture enriched by the thermodynamically more stable isomer **2b** related to cation **5b** was prepared. In all cases of major complex cations **4b**, **5b** and **6b** the methyl group(s) occupies the peripheral positions of the coordinated pentadienylium systems and stabilizes them through an electron-donation. The strongest stabilization effect is expected in cation **6b** due to the presence of methyl group at both peripheral carbons in the coordinated pentadienylium fragment. Indeed, the $Fe(CO)_3$ group of protonized complexes **4** and **6** was shifted almost completely to the opposite side during 1 h at 0 °C. After deprotonization, the obtained neutral complexes **1b** and **3b** rearranged slowly at ambient temperature until the equilibrium distribution of **1a,b** and **3a,b** was restored (Scheme 2).

The next aim of our research was to compare the reactivity of complexes **5** and **6** toward the nucleophilic addition of methanol with reactivity of complex **4** described earlier by Eisenstadt [35]. In concentrated H_2SO_4, complex **1a** is protonized at uncoordinated enone α-carbon. Thus formed cation **4a** isomerizes quickly by 1,2-haptotropic shift to thermodynamically preferred isomer **4b**. Nucleophile attacks the peripheral β-carbon of pentadienylium system stabilized by η^5-coordination to iron. Only one isomeric product of methanol addition to complex **4** at 0 °C was isolated in 66% yield (Scheme 3a) This is not surprising as the equilibrium of mixture is strongly shifted in favor of isomer **4b**.

After the protonization, complexes **2** and **3** tend to rearrange to the forms in which the methyl bearing carbons constitute the peripheral positions of coordinated pentadienylium chains. However, as a consequence of stabilization of the pentadienylium system the reaction center in preferred isomers is blocked by the methyl group. As supposed, only the less abundant regioisomeric



Scheme 3.

forms **5a** and **6a** undergo the nucleophilic attack of CH_3OH to give the products **10** and **11**, respectively.

The reaction of methanol with **5** required an extended reaction time (16 h) at ambient temperature. The adduct **10** was isolated in 54% yield as a single product. The residual starting material was recovered in the form **2b**. The nucleophilic attack of CH_3OH proceeds regioselectively and stereoselectively from the *exo*-side with respect to $Fe(CO)_3$ (Scheme 3b).

Due to the two methyl substituents in cationic complex **6** the equilibrium is even more shifted in favor of non-reactive isomer **6b** and even more substantial decrease in reactivity with CH_3OH was expected. The reaction temperature had to be elevated to 50 °C. Adduct **11** was isolated as a single product in 18% yield and 75% of starting material was recovered in the form **3b** (Scheme 3c). The interaction constant ($^3J_{6,7}$ = 10.2 Hz) of protons at C6 and C7 suggests that compound **11** is a product of *cis*-addition. Both, H–(C7) and CH_3O–(C6), approach the double bond from the *exo*-side. This observation contradicts the result of the CH_3OH addition to complex **4a** in FSO_3H at −78 °C obtained by Eisenstadt where a proton approaches the double bond from the *endo*-side of complex. [35] The attempts to add (–)-menthol in order to separate enantiomers of complexes **5** and **6** failed under the same conditions due to greater steric demands of the bulky alcohol. No traces of desired products were observed.

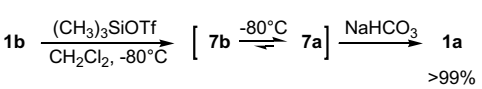
3.3. O-Trimethylsilylated cationic forms of tricarbonyl(η^4-tropone)iron complexes

The cationic tricarbonyl(η^5-trimethylsilyloxytropylium)iron complexes **7**–**9** (Chart 3) were formed upon the reaction of the corresponding neutral complexes **1**–**3** with trimethylsilyltriflate ($(CH_3)_3SiOTf$) at low temperature (−80 °C). Compared with the protonized complexes **4**–**6** discussed formerly these cations are selectively silylated at the oxygen and therefore they occur exclusively in their enol ether forms. The positive charge is again spread over the pentadienylium system and stabilized by an enhanced hapticity of iron. The enol ether double bond is outside the coordination sphere of iron and thermodynamic stability increases when this double bond is terminated by methyl group. On the other side, methyl substituent at the peripheral carbons of pentadienylium chain stabilizes the cationic structure through its electron-donation as in previously discussed *C*-protonized cations **4**–**6**. In complexes **7** and **9** with C2-substituted ligands these two competing tendencies lead to the opposite regioisomeric preferences.

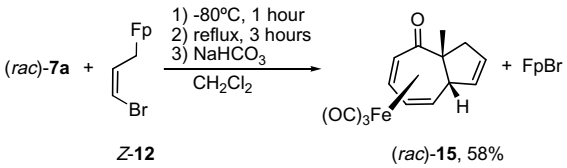
Tricarbonyl(η^5-trimethylsilyloxytropylium)iron triflates decomposed at higher temperature and were not isolated. The composition of equilibrium mixtures of regioisomers **7**–**9** was determined indirectly from the composition of corresponding neutral tricarbonyl(η^4-tropone)iron complexes **1**–**3** obtained immediately after hydrolysis with the saturated solution of $NaHCO_3$. The regioisomerization of complexes **7**–**9** proceeds at considerably higher rates than the regioisomerizations of neutral complexes **1**–**3** or *C*-protonized complexes **4**–**6**. This was proven by the silylation of chromatographically separated complex **1b**. The rearrangement to thermodynamically more stable isomer **7a** was completed within 1 h at −80 °C (Scheme 4). *O*-Trimethylsilylated cation derived from 2-methyltropone complex **1** occurs preferentially in form **7a** in which the carbon bearing methyl substituent is a part of the enol ether system. The abundance of this regioisomer in the equilibrium mixture was more than 99%. The stabilization effect of methyl group by its electron-donation at the peripheral position in isomer **7b** on the pentadienylium fragment is almost negligible.

The cycloaddition of cation **7a** with *Z*-(η^1-3-bromoprop-2-enyl)Fp **12** proceeded stereoselectively from the accessible *exo*-side. After the spontaneous elimination of FpBr from the resulting cycloadduct, complex **15** was obtained in 58% yield (Scheme 5).

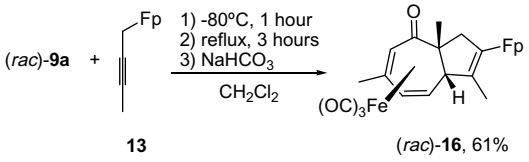
The equilibrium of cations formed by the trimethylsilylation of tricarbonyl(η^4-3-methyltropone)iron complexes **2** is strongly shifted in favor of the regioisomer **8b**, in which the stabilization by an electron-donation of methyl substituent at the peripheral position of the coordinated pentadienylium system is feasible. However, at the same time the introduction of a nucleophile is blocked by methyl group present at the reaction center in isomer **8b**. Hence, the cationic complex **8** is completely inert toward the [3+2] cycloadditions with Fp-reagents *Z*-**12**, **13**, and *E*/*Z*-**14** defined in Schemes 5–7, respectively. The preference of methyl to occupy



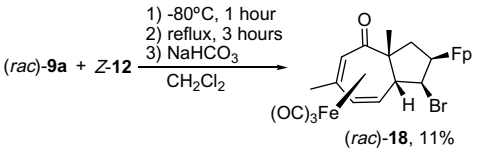
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 8.

the peripheral position of pentadienylium system in **8b** is, however, surprising compared to results of Lewis et al. [20] who observed that the substitution at carbon C2 of the coordinated pentadienylium moiety of tricarbonyl(η^5-methyltropylium)iron cation is considerably more suitable than the substitution at carbon C1.

Though isomer **9b** is favorably stabilized by the electron-donating effects of both methyl substituents at peripheral positions of the coordinated pentadienylium chain, complex **9** occurs preferentially in regioisomeric form **9a** stabilized by the formation of methyl-substituted enol ether double bond. This effect has a major influence on the equilibrium regioisomeric composition which consists of 92.8% of isomer **9a** and 7.2% of isomer **9b** (determined from ^{1}H NMR of **3a**,**b** mixture obtained after hydrolysis; $\Delta G^{193} = 4.1$ kJ mol^{-1}). Due to the steric hindrance of methyl group at β-position the minor regioisomer **9b** did not give the [3+2] cycloadditions with Fp-reagents and observed products were selectively the cycloadducts of regioisomeric complex **9a**. The relative configurations of cycloadducts were assigned by NOE difference experiments.

The [3+2] cycloaddition of **9a** with (η^1-but-2-inyl)Fp-reagent **13** resulted in the product of anticipated *exo*-addition of Fp-reagent. Hydroazulenone adduct **16** was isolated in 61% yield (Scheme 6).

Reaction of **9a** with the 70:30 *E*/*Z* mixture of (η^1-but-2-enyl)Fp **14** afforded three different stereoisomers **17a**–**c** in overall 31% yield (Scheme 7). According to the mechanism proposed for the analogous reaction with complex **7a,b** [25], the absolute configurations at stereogenic centers C1 and C7 are determined by the absolute configuration of planar chirality of the starting tropylium complex **9a**. The configuration of double bond of Fp-reagent is preserved on the relative configuration of stereogenic centers C8 and C9 in the products **17a–c**. Therefore adducts **17a** and **17b** are related to the addition of *E*-**14** and adduct **17c** comes from *Z*-**14**.

The cycloaddition of complex **9a** with *Z*-(η^1-3-bromoprop-2-enyl)Fp *Z*-**12** provided only the single stereoisomer **18** with the anticipated relative configuration in 11% yield (Scheme 8). Trace amount of eliminated FpBr was also observed. However, the elimination proceeded slower than in the case of cycloadduct **15**.

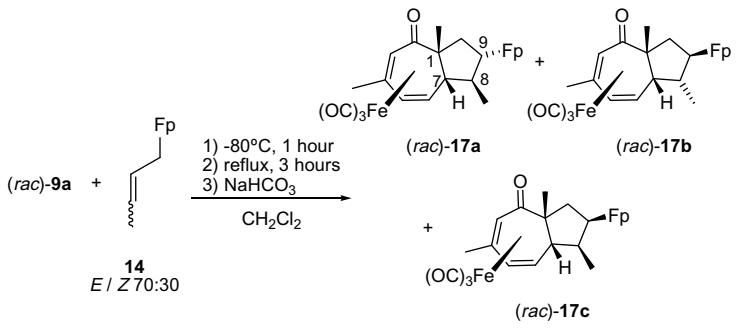
The assumption of reduced reactivity of the dimethylated tropylium complex **9**, compared to the reactivity of monomethylated complex **7**, due to the more significant ratio of the unreactive isomer **9b** was approved. The cycloadducts **17a–c** derived from the tricarbonyl(η^4-2,6-dimethyltropone)iron complex **3** are relatively less stable than the corresponding cycloadducts of the tricarbonyl(η^4-2-methyltropone)iron complex **1**.

4. Conclusion

4.1. Neutral tricarbonyl(η^4-tropone)iron complexes **1**–**3**

The methyl-substituted carbon C2 in tropone ligands of complexes **1** and **3** is preferentially situated out of the coordination sphere of iron. Methyl substituent at the peripheral position of the coordinated diene system has stronger destabilization effect than the methyl at the inner position. The methyl-substituted β-carbon (**2a,b**) is prone to arrange itself outside the coordination sphere of iron. Methyl at β-position causes increase of activation enthalpy of isomerization of complexes **2** and **3**.

According to the DFT calculations the contribution of methyl group to the character of HOMO orbitals is found to be more substantial in the more stable regioisomers. Bending of 2-methyltropone in complex **1a** is energetically more demanding than bending of 3-methyltropone in complex **2b**. This is responsible for greater thermal stability of regioisomer **2b** with respect to regioisomers **1a**. Even greater difference in energy between regioisomers **1b** and **2a** may be associated with greater steric interaction of CH_3 substituent with $Fe(CO)_3$ group in **1b**. The theoretically predicted relative stabilities of complexes **1**–**3** are in qualitative agreements with the experimental counterparts.



Scheme 7.

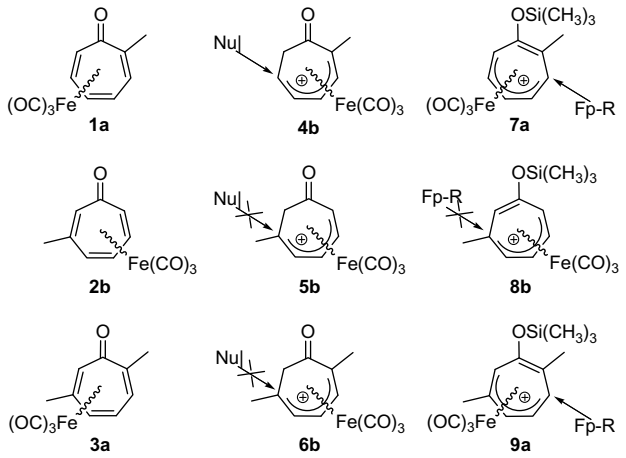


Chart 4. Structures of the thermodynamically more stable forms of neutral complexes **1**–**3**, *C*-protonized complexes **4**–**6**, and *O*-trimethylsilylated complexes **7**–**9**.

*4.2. C-Protonized cationic forms of tricarbonyl(η^4-tropone)iron complexes **4**–**6***

In the major regioisomers of complexes **4–6** methyl substituent is preferentially oriented at the peripheral position of the iron-coordinated pentadienylium system where it participates in the stabilization through the electron-donation. Complex **4** reacts with nucleophiles selectively in prevailing regioisomeric form **4b**, whereas the protonized complexes **5** and **6** react only in their minor forms **5a** and **6a**, respectively, because the reaction centers in major regioisomers **5b** and **6b** are sterically hindered by β-methyl group (Chart 4). The addition of CH_3OH is slow and gives only low yields (Scheme 3). The reaction with more bulky nucleophiles does not proceed at all.

*4.3. O-Trimethylsilylated cationic forms of tricarbonyl(η^4-tropone)iron complexes **7**–**9***

O-Trimethylsilylated cation **7** derived from complex **1** occurs almost exclusively in the regioisomeric form **7a** with the thermodynamically more stable methyl-substituted enol ether double bond. Complex **7a** undergoes [3+2] cycloaddition with various Fp-reagents in good yields. Methyl substituent of *O*-trimethylsilylated cation **8** derived from complex **2** stabilizes the pentadienylium system in prevailing form **8b** by its electron-donation but, at the same time, hinders the reaction center. This complex does not give [3+2] cycloadditions. In the equilibrium mixture of cation **9** the reactive regioisomer **9a** prevails (almost 93%). Described results indicate that the stabilization through the electron-donation of methyl group is more effective at the enol ether double bond than at the peripheral carbons of the coordinated pentadienylium system (Chart 4). The cycloadditions of complex **9a** with Fp-reagents proceeded with lower yields in comparison with complex **7a**.

5. Experimental

5.1. General experimental details

Trimethylsilyltriflate ($(CH_3)_3SiOTf$) was commercially available. 2-Methyltropone was prepared from cyclopenta-1,3-diene following the procedure of Brady and Hieble [32]. 3-Methyltropone and 2,6-dimethyltropone were prepared from 2-methylcyclohexanone and 2,6-dimethylcyclohexanone, respectively, using the method developed by our group [33]. The corresponding tricarbonyl(η^4-tropone)iron complexes **1** [24b,36], **2** [17], and **3** [12] were prepared according to published procedures. The equilibrium mixtures **1a**/**1b** (97:3), **2a**/**2b** (34:66) or **3a**/**3b** (96:4) were used as starting materials. *Z*-(η^1-3-Bromoprop-2-enyl)Fp (*Z*-**12**) reagent was prepared by the bromination of (η^1-allyl)Fp complex. (η^1-But-2-inyl)Fp (**13**), *E*/*Z*-(η^1-but-2-enyl)Fp (*E*/*Z*-**14**), and (η^1-allyl)Fp were prepared from corresponding allylbromides and Fp_2 following the published procedures [37]. The reaction apparatus was flame dried under vacuum and purged by argon prior to the usage. All reactions were carried out under an argon atmosphere. Benzene was dried by the distillation from sodium-benzophenone ketyl under an argon atmosphere. Dichloromethane and hexane were dried over and distilled from CaH_2 under argon atmosphere. Methanol was dried by the distillation from magnesium turnings under argon. The solvents were bubbled by argon for 15 min prior to use. The column chromatography was performed on 40/100 mesh silica gel. HPLC analyses were made on LiChrospher RP-8 column by CH_3OH/H_2O 1:1 (flow rate: 0.75 mL min^{-1}) and UV detection. The NMR spectra were recorded on a Varian Gemini 2000 spectrometer at 300 MHz (^1H) and 75 MHz (^{13}C) in $CDCl_3$. TMS was used as an internal standard. The chemical shift values are given in ppm and the listed coupling constants are in Hz. The IR spectra were recorded on a Perkin–Elmer spectrophotometer in a 0.1 mm NaCl cell with the scale in cm^{-1}. The elemental analyses were performed on a Carlo Erba Instrumentazione analyzer. The melting points were measured on Barnstead Electrothermal IA9200 apparatus and are uncorrected.

*5.2. Preparation of tricarbonyl(η^4-6-methoxy-3-methylcyclohepta-2,4-dienone)iron **10***

The mixture of complexes **2a**,**b** (100.0 mg, 0.39 mmol, **2a**/**2b** 34:66) was dissolved in concentrated H_2SO_4 (320 μL, 5.77 mmol) at 0 °C and the resulting brown-red solution was stirred for 45 min. Anhydrous CH_3OH (340 μL, 8.36 mmol) was added. The reaction mixture was removed from the ice bath and stirred at r.t. for 16 h. CH_2Cl_2 (5 mL) and anh. powdered Na_2CO_3 (1.0 g) were added slowly. The inorganic salts were filtered off and the solvent removed by the distillation under vacuum. The crude mixture was purified by column chromatography (SiO_2, hexane/Et_2O 1:2). The product **10** (60.1 mg, 54%) was isolated as an yellow oil. Anal. Calc. for $C_{12}H_{12}FeO_5$: C, 49.35; H, 4.14. Found: C, 49.72; H, 4.07%. ^1H NMR ($CDCl_3$, 300 MHz): 5.46 (dd, 1H, $^3J_{4,5}$ = 7.6, $^4J_{2,4}$ = 1.2, *H*C(4)), 3.87 (ddd, 1H, $^3J_{6,7endo}$ = 10.8, $^3J_{6,7exo}$ = 5.5, $^3J_{5,6}$ = 1.9, *H*C(6)), 3.36 (s, 3H, C*H*$_3$O), 3.30 (dd, 1H, $^4J_{2,7exo}$ = 1.9, $^4J_{2,4}$ = 1.2, *H*C(2)), 3.19 (ddd, 1H, $^3J_{4,5}$ = 7.6, $^3J_{5,6}$ = 1.9, $^4J_{5,7exo}$ = 1.9, *H*C(5)), 2.45 (dddd, 1H, ^2J = 11.1, $^3J_{6,7exo}$ = 5.5, $^4J_{5,7exo}$ = 1.9, $^4J_{2,7exo}$ = 1.9, H^{exo}C(7)), 2.29 (s, 3H, C*H*$_3$C(3)), 1.89 (dd, 1H, ^2J = 11.1, $^3J_{6,7endo}$ = 10.8, H^{endo}C(7)). ^{13}C NMR ($CDCl_3$, 75 MHz): 195.5 (s, C(1)), 103.9 (s, C(3)), 84.1 (d, C(4)), 77.7 (d, C(2)), 56.0 (d, C(5)), 51.0 (d, C(6)), 50.9 (q, *C*H$_3$O), 38.8 (t, C(7)), 18.5 (q, *C*H$_3$C(3)) (signals of Fe(*C*O)$_3$ carbons were not resolved).

*5.3. Preparation of tricarbonyl(η^4-6-methoxy-3,7-dimethylcyclohepta-2,4-dienone)iron **11***

The mixture of complexes **3a**,**b** (100.0 mg, 0.36 mmol, **3a**/**3b** 96:4) was dissolved in conc. H_2SO_4 (270 μL, 4.86 mmol). The mixture was cooled in an ice bath and stirred for 20 min, then removed from the bath and anh. CH_3OH (285 μL, 7.02 mmol) was added. The reaction mixture was heated to 50 °C and stirred for 5 h. After cooling to r.t. CH_2Cl_2 (5 mL), anh. powdered Na_2CO_3 (1.0 g) were added slowly. The final mixture containing complex **3b** and adduct **11** was filtered and the solvent evaporated under vacuum. The crude mixture was purified by column chromatography (SiO_2, hexane/Et_2O 1:1). The product **11** (20.3 mg, 18%) was isolated as an yellow

crystalline compound. Anal. Calc. for $C_{13}H_{14}FeO_5$: C, 51.01; H, 4.61. Found: C, 50.67; H, 4.54%. ^{1}H NMR ($CDCl_3$, 300 MHz): 5.46 (dd, 1H, $^3J_{4,5}$ = 7.6, $^4J_{2,4}$ = 1.3, *H*C(4)), 3.41 (s, 3H, C*H*$_3$O), 3.39 (dd, 1H, $^3J_{6,7}$ = 10.2, $^3J_{5,6}$ = 1.9, *H*C(6)), 3.33 (d, 1H, $^4J_{2,4}$ = 1.3, *H*C(2)), 3.15 (dd, 1H, $^3J_{4,5}$ = 7.6, $^3J_{5,6}$ = 1.9, *H*C(5)), 2.26 (s, 3H, C*H*$_3$C(3)), 2.00 (dq, 1H, $^3J_{6,7}$ = 10.2, $^3J_{CH3-C(7),7}$ = 6.6, *H*C(7)), 0.99 (d, 3H, $^3J_{CH3-C(7),7}$ = 6.6, C*H*$_3$C(7)). ^{13}C NMR ($CDCl_3$, 75 MHz): 207.3–208.1 (br, Fe(*C*O)$_3$), 202.1 (s, C(1)), 108.4 (s, C(3)), 88.7, 88.6 (2 × d, C(2) and C(4)), 60.8 (d, C(5)), 55.7 (d, C(6)), 54.1 (q, *C*H$_3$O), 46.3 (d, C(7)), 23.0 (q, *C*H$_3$C(3)), 10.9 (q, *C*H$_3$C(7)).

5.4. Preparation of cycloadduct **15**

The solution of complexes **1a**,**b** (150.0 mg, 0.58 mmol, **1a**/**1b** 97:3) in anh. CH_2Cl_2 (5 mL) was cooled to −80 °C and $(CH_3)_3SiOTf$ (135.5 mg, 0.61 mmol) was added slowly. The resulting dark brown solution was stirred at −80 °C for 3 h. The solution of freshly prepared Fp-reagent *Z*-**12** (500.0 mg, 1.68 mmol) in anh. CH_2Cl_2 (4 mL) was filtered through Celite and dropwise added within 10 min. The solution was stirred for 1.5 h at −80 °C, removed from bath and let to warm to r.t. and refluxed for 2 h. The volatile parts were removed under vacuum. THF (5 mL) and satd. $NaHCO_3$ solution (5 mL) were added. The mixture was extracted with Et_2O (3 × 15 mL) and purified by column chromatography (SiO_2, hexane/Et_2O 1:1) The cycloadduct **15** (100.1 mg, 58%) was isolated as an orange crystalline compound. Anal. Calc. for $C_{14}H_{12}FeO_4$: C, 56.03; H, 4.03. Found: C, 56.40; H, 4.14%. M.p.: 85–87 °C [hexane/Et_2O]. ^{1}H NMR ($CDCl_3$, 300 MHz): 5.79–5.73 (m, 1H, *H*C(8)), 5.70 (ddd, 1H, $^3J_{3,4}$ = 7.3, $^3J_{4,5}$ = 5.5, $^4J_{4,6}$ = 1.4, *H*C(4)), 5.52–5.59 (m, 1H, *H*C(9)), 5.40 (ddd, 1H, $^3J_{5,6}$ = 5.6, $^3J_{4,5}$ = 5.5, $^4J_{3,5}$ = 1.0, *H*C(5)), 3.31 (dd, 1H, $^3J_{3,4}$ = 7.3, $^4J_{3,5}$ = 1.0, *H*C(3)), 3.10–3.20 (m, 2H, *H*C(6) and *H*C(7)), 2.42 (dd, 1H, ^2J = 16.9, $^3J_{9,10}$ = 2.3, *H*C(10)), 1.88 (dd, 1H, ^2J = 16.9, $^3J_{9,10}$ = 2.8, *H*C(10)), 1.07 (s, 3H, C*H*$_3$C(1)). ^{13}C NMR ($CDCl_3$, 75 MHz): 209.0, 208.9 (2 × s, Fe(*C*O)$_3$), 199.2 (s, C(2)), 136.7 (d, C(8)), 126.9 (d, C(9)), 92.6 (d, C(4)), 88.7 (d, C(5)), 63.5, 62.2 (2 × d, C(6) and C(7)), 59.5 (d, C(3)), 51.8 (s, C(1)), 44.9 (t, C(10)), 25.2 (q, *C*H$_3$C(1)). IR ($CHCl_3$): 2250s, 1990s, 1630s, 1435m, 1355w, 1325w, 1265m, 1125w, 990m, 685m, 675m.

5.5. Preparation of cycloadduct **16**

To the stirred and cooled (−80 °C) solution of complexes **3a**,**b** (50.0 mg, 0.18 mmol, **3a**/**3b** 96:4) in anh. CH_2Cl_2 (2 mL), $(CH_3)_3SiOTf$ (42.0 mg, 0.19 mmol) has been added. Resulting dark brown mixture was stirred at −80 °C for 3 h. The filtered solution of Fp-reagent **13** (174.0 mg, 0.76 mmol) in anh. CH_2Cl_2 (1 mL) was added dropwise during 10 min. The mixture was stirred for 1 h at −80 °C, removed from bath, let to warm to r.t., and refluxed for 3 h. The volatile parts were evaporated under vacuum. THF (2 mL) and satd. $NaHCO_3$ solution (2 mL) were added. The aqueous part was diluted with H_2O (10 mL) and extracted with Et_2O (3 × 5 mL). The product **16** (55.0 mg, 61%) was isolated by column chromatography (SiO_2, hexane/Et_2O 1:1) as an yellow crystalline compound. Anal. Calc. for $C_{23}H_{20}Fe_2O_6$: C, 54.80; H, 4.00. Found: C, 55.13; H, 4.06%. M.p.: 202–205 °C [hexane/Et_2O]. ^{1}H NMR ($CDCl_3$, 300 MHz): 5.25 (ddd, 1H, $^3J_{5,6}$ = 8.0, $^4J_{3,5}$ = 1.5, $^4J_{5,7}$ = 0.5, *H*C(5)), 4.78 (s, 5H, H^{Cp}), 3.30 (d, 1H, $^4J_{3,5}$ = 1.5, *H*C(3)), 3.24 (dd, 1H, $^3J_{5,6}$ = 8.0, $^3J_{6,7}$ = 3.9, *H*C(6)), 2.81 (ddd, 1H, $^3J_{6,7}$ = 3.9, $^4J_{7,10exo}$ = 1.7, $^4J_{5,7}$ = 0.5, *H*C(7)), 2.47 (ddq, 1H, ^2J = 15.9, $^4J_{CH3\text{-}C(1),10exo}$ = 2.3, $^4J_{7,10exo}$ = 1.7, $H^{exo}C(10)$), 2.21 (s, 3H, C*H*$_3$C(4)), 1.89 (1H, dq, ^2J = 15.9, $^4J_{CH3-C(1),10endo}$ = 1.8, $H^{endo}C(10)$), 1.85 (dd, 3H, $^4J_{CH3-C(1),10exo}$ = 2.3, $J_{CH3-C(1),10endo}$ = 1.8, C*H*$_3$C(1)), 1.00 (s, 3H, C*H*$_3$C(8)). ^{13}C NMR ($CDCl_3$, 75 MHz): 215.8, 215.5 (2 × s, $(CO)^{Fp}$), 209.8 (s, C(2)), 209.0–209.9 (br, Fe(*C*O)$_3$), 148.0 (s, C(8)), 130.4 (s, C(9)), 110.1 (s, C(4)), 87.7 (d, C(5)), 85.3 (d, Cp), 69.9 (d, C(7)), 62.6 (d, C(3)), 62.1 (t, C(10)), 60.0 (d, C(6)), 54.0 (s, C(1)), 25.3 (q, *C*H$_3$C(4)), 23.9 (q, *C*H$_3$C(1)), 18.2 (q, *C*H$_3$C(8)). IR ($CHCl_3$): 2100s, 2060s, 2040s, 1980s, 1650w, 1620w, 1540w, 1500w, 1440m, 1070m, 1050m, 950m, 900w, 870m, 720m, 710s, 685m, 650w.

5.6. Preparation of cycloadducts ***17a–c***

To the stirred and cooled (−80 °C) solution of complexes **3a**,**b** (40.0 mg, 0.15 mmol, **3a**/**3b** 96:4) in anh. CH_2Cl_2 (1 mL), $(CH_3)_3SiOTf$ (35.0 mg, 0.16 mmol) was added. The dark brown mixture was stirred at −80 °C for 1 h. The filtered solution of Fp-reagent *E*/*Z*-**14** (48.7 mg, 0.21 mmol, *E*/*Z* mixture 70:30) in anh. CH_2Cl_2 (0.5 mL) was added dropwise. The mixture was stirred for 1 h at −80 °C, removed from bath, let to warm to r.t., and refluxed for 3 h. The solvent was evaporated under vacuum and THF (2 mL) and satd. $NaHCO_3$ solution (1 mL) were added. The mixture was extracted with Et_2O (3 × 1 mL) and purified by column chromatography (SiO_2, hexane/Et_2O 1:1). The inseparable mixture of the cycloadducts **17a**,**b** (20.1 mg, 27%, **17a**/**17b** 75:25) and cycloadduct **17c** (4.0 mg, 5%) was isolated. **17a**: ^{1}H NMR ($CDCl_3$, 300 MHz): 5.57 (dd, 1H, $^3J_{5,6}$ = 8.1, $^4J_{3,5}$ = 1.2, *H*C(5)), 4.69 (s, 5H, H^{Cp}), 3.19 (d, 1H, $^4J_{3,5}$ = 1.2, *H*C(3)), 2.77 (dd, 1H, $^3J_{5,6}$ = 8.1, $^3J_{6,7}$ = 4.0, *H*C(6)), 2.24 (s, 3H, C*H*$_3$C(4)), 1.54 (d, 3H, $^3J_{CH3-C(8),8}$ = 6.9, C*H*$_3$C(8)), 1.07 (s, 3H, C*H*$_3$C(1)) (characteristic signals resolved in spectrum of **17a**,**b** mixture 75:25). **17b**: ^{1}H NMR ($CDCl_3$, 300 MHz): 5.49 (dd, 1 H, $^3J_{5,6}$ = 8.1, $^4J_{3,5}$ = 1.3, *H*C(5)), 4.74 (s, 5 H, H^{Cp}), 3.24 (d, 1 H, $^4J_{3,5}$ = 1.3, *H*C(3)), 2.98 (dd, 1H, $^3J_{5,6}$ = 8.1, $^3J_{6,7}$ = 4.8, *H*C(6)), 2.27 (s, 3H, C*H*$_3$C(4)), 1.11 (s, 3H, C*H*$_3$C(1)), 1.10 (d, 3H, $^3J_{CH3-C(8),8}$ = 6.9, C*H*$_3$C(8)) (characteristic signals resolved in spectrum of **17a**,**b** mixture 75: 25). **17c**: Anal. Calc. for $C_{23}H_{22}Fe_2O_6$: C, 54.58; H, 4.38. Found: C, 54.29; H, 4.45%. ^{1}H NMR ($CDCl_3$, 300 MHz): 5.44 (dd, 1H, $^3J_{5,6}$ = 7.9, $^4J_{3,5}$ = 1.2, *H*C(5)), 4.75 (s, 5H, H^{Cp}), 3.37 (d, 1H, $^4J_{3,5}$ = 1.2, *H*C(3)), 3.21 (ddd, 1H, $^3J_{8,9}$ = 13.2, $^3J_{9,10exo}$ = 8.1, $^3J_{9,10endo}$ = 6.1, *H*C(9)), 3.08 (dd, 1H, $^3J_{5,6}$ = 7.9, $^3J_{6,7}$ = 5.7, *H*C(6)), 2.43 (d, 3H, $^3J_{6,7}$ = 5.7, *H*C(7)), 2.28 (s, 3H, C*H*$_3$C(4)), 1.41–1.99 (m, 3H, *H*C(8), 2 × *H*C(10)), 1.26 (d, 3H, $^4J_{CH3-C(1),10}$ = 1.6, C*H*$_3$C(1)), 1.09 (d, 3H, $^3J_{8,CH3-C(8)}$ = 7.6, C*H*$_3$C(8)).

5.7. Preparation of cycloadduct ***18***

To the stirred and cooled (−80 °C) solution of complexes **3a**,**b** (100.0 mg, 0.36 mmol, **3a**/**3b** 96:4) in anh. CH_2Cl_2 (4 mL) $(CH_3)_3SiOTf$ (86.4 mg, 0.39 mmol) was added slowly. The dark brown mixture was stirred at −80 °C for 2 h. The solution of freshly prepared Fp-reagent *Z*-**12** (202.0 mg, 0.68 mmol,) in anh. hexane (6 mL) was added dropwise. The mixture was stirred at −80 °C for 1.5 h, removed from bath, let to warm to r.t., and refluxed overnight. The solvents were evaporated under vacuum. THF (10 mL) and satd. $NaHCO_3$ solution (10 mL) were added and the mixture was stirred for 1 h. The layers were separated and aqueous part was extracted with Et_2O (3 × 15 mL). The cycloadduct **18** (22 mg, 11%) was isolated by column chromatography (SiO_2, hexane/Et_2O 1:1). The complex **18** is unstable compound and decomposes at an ambient temperature. Anal. Calc. for $C_{22}H_{19}BrFe_2O_6$: C, 46.28; H, 3.35. Found: C, 46.88; H, 3.47%. ^{1}H NMR ($CDCl_3$, 300 MHz): 5.55 (d, 1H, $^3J_{5,6}$ = 8.0, *H*C(5)), 4.76 (s, 5H, H^{Cp}), 3.16 (s, 1H, *H*C(3)), 3.02 (m, 1H, *H*C(9)), 2.73 (dd, 1H, $^3J_{5,6}$ = 8.0, $^3J_{6,7}$ = 3.8, *H*C(6)), 2.60 (dd, 1H, $^3J_{6,7}$ = 3.8, $^3J_{7,8}$ = 3.8, *H*C(7)), 2.29 (s, 3H, C*H*$_3$C(4)), 1.97(dd, 1H, ^2J = 13.2, $^3J_{9,10endo}$ = 2.0, $H^{endo}C(10)$), 1.77 (dd, 1H, ^2J = 13.2, $^3J_{9,10exo}$ = 6.6, $H^{exo}C(10)$), 1.04 (s, 3H, C*H*$_3$C(1)). ^{13}C NMR ($CDCl_3$, 75 MHz): 217.2 a 217.0 (2 × s, $(CO)^{Fp}$), 210.0 (s, C(2)), 208.8–209.8 (br s, Fe(*C*O)$_3$), 107.0 (s, C(4)), 90.1 (d, C(5)), 85.3 (d, Cp), 61.3 (d, C(6)), 60.3 (d, C(7)), 59.5 (d, C(3)), 53.8 (d, C(8)), 53.2 (t, C(10)), 51.0 (s, C(1)), 29.7 (d, C(9)), 26.4 (q, *C*H$_3$C(4)), 23.8 (q, *C*H$_3$C(1)) (the signal of quaternary carbon C(9) was not resolved).

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Appendix A. Supporting information available

Structures of compounds **1a**, **1b**, **2a**, **2b**, **3a**, **3b** optimized at B3LYP/6-311+G* and B3P86/6-311+G* levels (Figure S1-S6); selected theoretical structural parameters for regioisomers **1a**, **1b** (Table S1), **2a**, **2b** (Table S2) and **3a**, **3b** (Table S3). Supplementary data associated with this article can be found, in the online version. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.07.014.

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