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Thermodynamic and kinetic parameters associated with the fluxional behavior of 2-methyl- and 2,6-dimethyltroponeiron tricarbonyl complexes

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Abstract

The kinetic and thermodynamic parameters for regioisomerisation of 2-methyl- and 2,6-dimethyl-derivatives of tricarbonyl[η^4-troponelliron complexes have been studied by ^{1}H NMR spectrometry over a range of 40 °C. Regioisomerisation of these complexes proceeds by an intramolecular first-order process and results in the almost complete conversion of the less stable complexes (**4**, **8**) to more stable regioisomers (**1**, **5**). The activation energies and half lifes for the conversion (**4** → **1**) and (**8** → **5**) were found to be $\Delta G^{\#} = 92$ kJ mol^{-1}; $\tau_{1/2} = 12.8$ h, and $\Delta G^{\#} = 107$ kJ mol^{-1}; $\tau_{1/2} = 26.8$ h, respectively, at 23 °C. Complex **1** reacts with (1R,2S,5R)-menthol in sulphuric acid solution, followed by neutralisation with sodium carbonate to give a separable mixture of diastereomeric tricarbonyl[(2,3,4,5-η)-(1R′,2S′,5R′)-6-menthyloxy-2-methyltropone]iron complexes, **9** and **10**. The corresponding dimethylated complex **5** fails to react under these conditions.

Keywords: Troponeiron tricarbonyls; Fluxional behavior; Regioisomerisation; Thermodynamic and kinetic parameters; Dynamic ^{1}H NMR spectroscopy; (1R,2S,5R)-menthol

1. Introduction

Tropones are useful synthetic intermediates for incorporation of a seven-membered ring into polycyclic systems. They have found use as dienophiles in Diels Alder [1] and other electrocyclisation reactions [2] and in the preparation of heterocycles [3]. Iron tricarbonyl complexes of tropones, which are readily available by treatment of tropones with $Fe_2(CO)_9$ [4], have been used in the synthesis of hydroazulenes related to the pseudoguaianolide class of terpenes by [3 + 2] cycloaddition reactions [5].

In this latter context, it was of interest to examine the fluxional behavior of iron tricarbonyl complexes of 2-methyltropone [6] and of 2,6-dimethyltropone [7] as well as their derived tropylium salts. Rapid haptotropic interconversion of transition metal complexes through movement of the metal around the periphery of a polyolefin ring by aseries of 1,2 shifts with or without concomitant π-bond reorganisation is a well-recognised phenomenon in transition metal organometallic chemistry [8]. The fluxional behavior of monosubstituted tropyliumiron tricarbonyl complexes, $RC_7H_6Fe(CO)_3^+$ (R = methyl, isopropyl, cyclopropyl and phenyl) has been studied in detail by Brookhart [9]. Using variable temperature ^{1}H- and ^{13}C NMR, the rates and energies of activation associated with fluxional behavior in these complexes and their low temperature isomer distribution were determined.

Eisenstadt [10] found that 2-monosubstituted tropones (R = Me-, Cl-, Ph-) gave iron tricarbonyl complexes in which the metal group was exclusively coordinated to those double bonds, which do not bear

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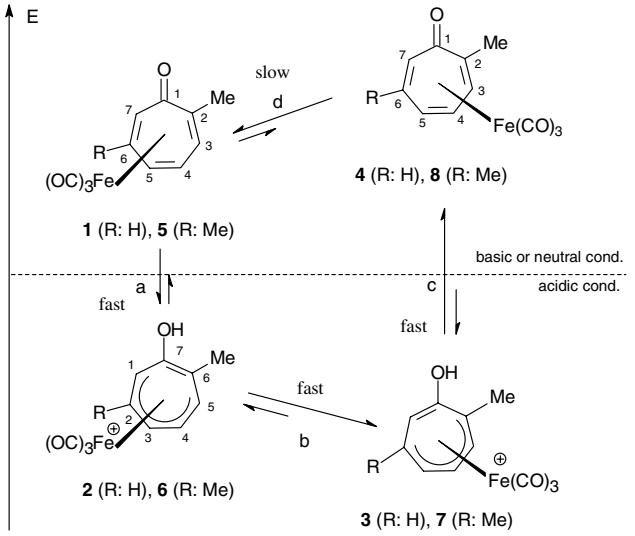
the substituent. Protonation of these complexes takes place at the uncoordinated double bond in unsubstituted and 2-substituted troponeiron tricarbonyl complexes, and this is followed by rapid haptotropic shift of the $Fe(CO)_3$ moiety. Within 15–30 min, only one regioisomer of the cation, in which the substituent R is at C-1 of the pentadienyl ligand, is observed. Replacement of one carbon monoxide ligand by PPh_3, decelerates the ring fluxional process to 68 h, probably by enhancing the stability of the iron diene bond [11].

Resolution of tricarbonyl[η^4-tropone]iron has allowed determination of the activation energy associated with racemisation of the optically active complex ($\Delta G^{\#} = 107$ kJ mol^{-1}) which takes place through 1,3-haptotropic rearrangement [12]. Similar kinetic studies have been carried out on 2-acetoxy- and 2-benzoyloxy-derivatives of tricarbonyl[η^4-tropone]iron regioisomers by Morita and Asao [13]. Kinetic studies of the interconversion of the regioisomeric iron tricarbonyl complexes derived from 4-bromotropone have also been carried out [14]. In both of these latter studies, the activation enthalpies and entropies as well as the equilibrium constants for these reversible intramolecular first-order processes were determined. In contrast to the fluxional behavior of these complexes, the iron tricarbonyl complex of 3-bromotropone does not isomerise to its regioisomer [14].

Recently we described the strong effect of the fluxional character on the regioselective outcome of [3 + 2] cycloaddition reactions involving tricarbonyl[η^4-2-methyltropone]iron and the *E*- or *Z*-isomers of (η^1-crotyl)Fp [5].

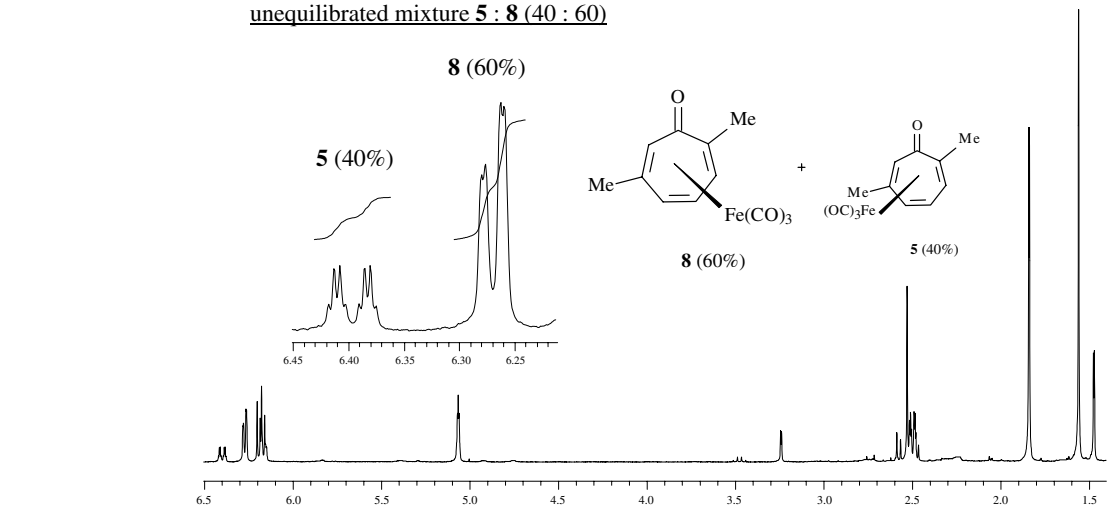
2. Results and discussion

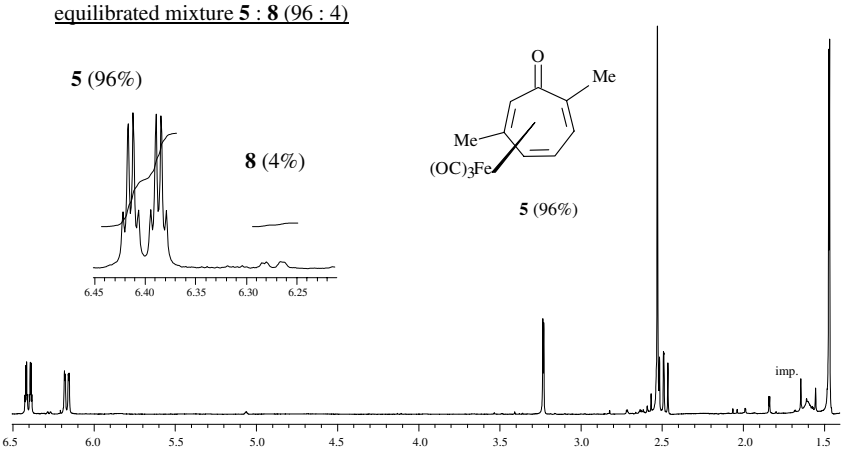
Regioisomerisation of 2-methyl- or 2,6-dimethyl-derivatives of tricarbonyl[η^4-tropone]iron was followed by ^{1}H NMR in $CDCl_3$ at different temperatures (13, 23, 33, 43 and 53 °C). Regioisomerisation of these complexes proceeds slowly at room temperature in $CDCl_3$ ($\tau_{1/2}$: 12.8 and 26.8 h, respectively). The thermodynamically more stable (4,5,6,7-η) regioisomers (**1** or **5**) were obtained by complexation of 2-methyl- or 2,6-dimethyltropone with $Fe_2(CO)_9$ in benzene at 40 °C in high yields. These were converted to their tetrafluoroborate salts by treatment with HBF_4 in Ac_2O at r.t. (Scheme 1). These salts consisting mostly of the thermodynamically more stable complexes (**3** or **7**) were converted to mixtures enriched in the thermodynamically less stable (2,3,4,5-η) regioisomers (**4** or **8**) by quenching with Et_3N. These inter-conversions are summarised in Scheme 1.



Scheme 1. (a) 1.6 M HBF_4 in Ac_2O, r.t., Ar, 30 min; (b) fast, r.t. (isomerisation **2** to **3** completed within 15 min, (c) Et_3N, r.t., Ar, 15 min); (d) slow in $CDCl_3$ at r.t. ($\tau_{1/2}(4 \rightarrow 1) = 12.8$ h; $\tau_{1/2}(8 \rightarrow 5) = 26.8$ h).

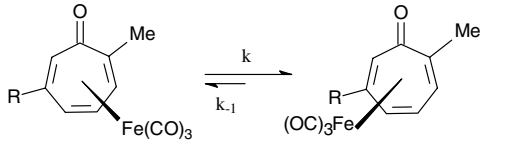
The difference in stability of regioisomers (**1**, **4** or **5**, **8**) were calculated from the experimentally determined equilibrium constants $K_{(\mathbf{1}/\mathbf{4})}$ and $K_{(\mathbf{5}/\mathbf{8})}$ [15]. From these measurements, values of $K_{(\mathbf{1}/\mathbf{4})} = 33.5$ and





$K_{(\mathbf{5}/\mathbf{8})} = 26.0$ were determined. For both regioisomeric systems **1**, **4** and **5**, **8** the difference in stabilities were determined to be $\Delta G(\mathbf{1},\mathbf{4}) = 8.8\ \mathrm{kJ\,mol^{-1}}$ and $\Delta G(\mathbf{5},\mathbf{8}) = 8.4\ \mathrm{kJ\,mol^{-1}}$. These results are summarised below in Scheme 2.

The methyl group at C(6) has lower influence on the ratio of regioisomers in the equilibrium. However, in both cases, the most stable regioisomers are those which have the $Fe(CO)_3$ group coordinated to the double bonds not bearing Me–C(2).



4 (R: H), **8** (R: Me) — thermodynamically less stable

1 (R: H), **5** (R: Me) — thermodynamically more stable

The fluxional regioisomerisation can be considered as reversible intramolecular first-order process.

For this kind of reaction, the kinetic equation can be deduced [16] (Eq. (3)):

$$\mathrm{A} \underset{k_{-1}}{\overset{k}{\rightleftharpoons}} \mathrm{B}$$

$$v = \mathrm{d}x/\mathrm{d}t = k(A_0 - x) - k_{-1}(B_0 + x), \tag{1}$$

$$\mathrm{d}x/\mathrm{d}t = kA_0 - k_{-1}B_0 - x(k + k_{-1}),$$

$$\mathrm{d}x/\mathrm{d}t = (k + k_{-1})[(kA_0 + k_{-1}B_0)/(k + k_{-1}) - x]$$

in equilibrium $K = [\mathrm{B}]/[\mathrm{A}] = k/k_{-1}$.

$$\mathrm{d}x/\mathrm{d}t = (k + k_{-1})[(KA_0 + B_0)/(K + 1) - x]$$

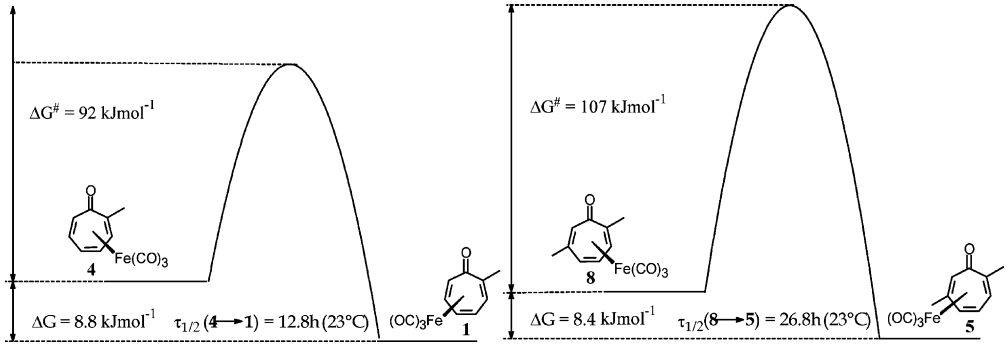
for simplification $Y = (KA_0 + B_0)/(K + 1)$.

$$\mathrm{d}x/\mathrm{d}t = (k + k_{-1})[Y - x], \tag{2}$$

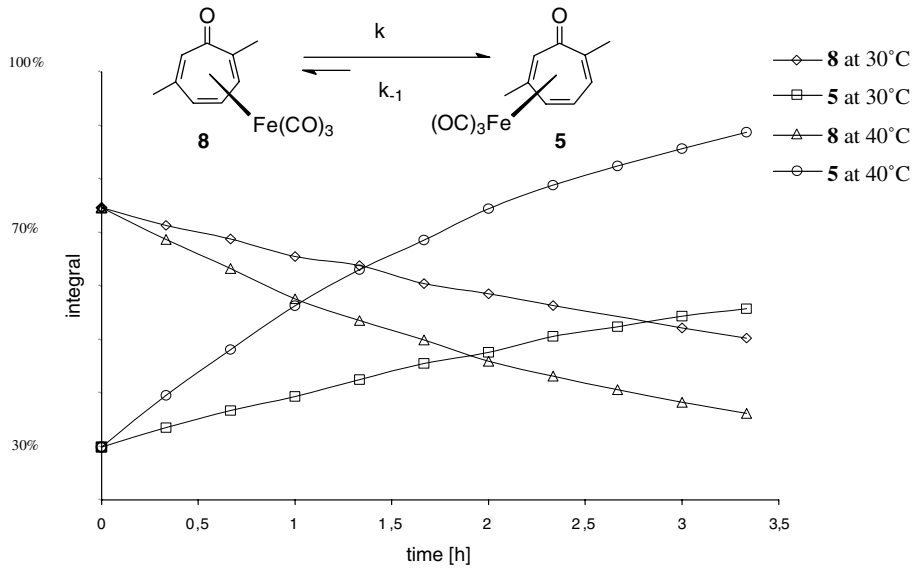
integration yields

$$\ln(Y/(Y - x)) = (k + k_{-1})t,$$
$$\ln(Y/(Y - x)) = k(1 + 1/K)t,$$
$$k = \ln(Y/(Y - x))/(1 + 1/K)t,$$
$$k_{-1} = k/K,$$

The kinetic equation (Eq. (3)) for the intramolecular reversible first-order fluxional regioisomerisation is



Scheme 2. The thermodynamic stabilities (ΔG), activation energies ($\Delta G^{\#}$) and half lifes ($\tau_{1/2}$) determined for 2-methyl- (**1**,**4**) and 2,6-dimethyl- (**5**,**8**) derivatives of tricarbonyl[η^4-tropone]iron fluxional complexes.

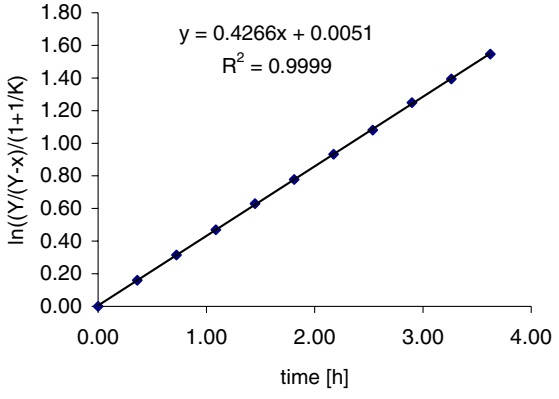


Scheme 3. Examples of the time depending integral values of hydrogen signals in the unequilibrated mixture of regioisomers **5** and **8**. ^{1}H NMR spectra were taken at 30 and 40 °C.

$$k = \ln(Y/Y - x)/(1 + 1/K)t, \quad (3)$$

where $Y = (KA_0 + B_0)/(K + 1)$.

The rate constants k and $k - 1$ for both fluxional systems (**4** ↔ **1** and **8** ↔ **5**) were determined from observed conversion rates of ^{1}H NMR spectra [17], Scheme 3.



Scheme 4. Example of the solution of Eq. (3) for regioisomerisation of **8** to **5** at 43 °C.

The determination of k was done by linear regression analysis using the "least squares" method to fit a line through a set of values. The rate constant $k = 0.4266$ was obtained with a very good correlation coefficient ($R^2 = 0.9999$) (cf. Scheme 4).

The half lifes for each regioisomerisation and temperature are calculated from appropriate values of rate constants k. The rate constants k, k_{-1} and half lifes $\tau_{1/2}$ for each regioisomerisations were determined and are collected Table 1.

To determine the activation energies for regioisomerisations, the known Eq. (4) was used [16]:

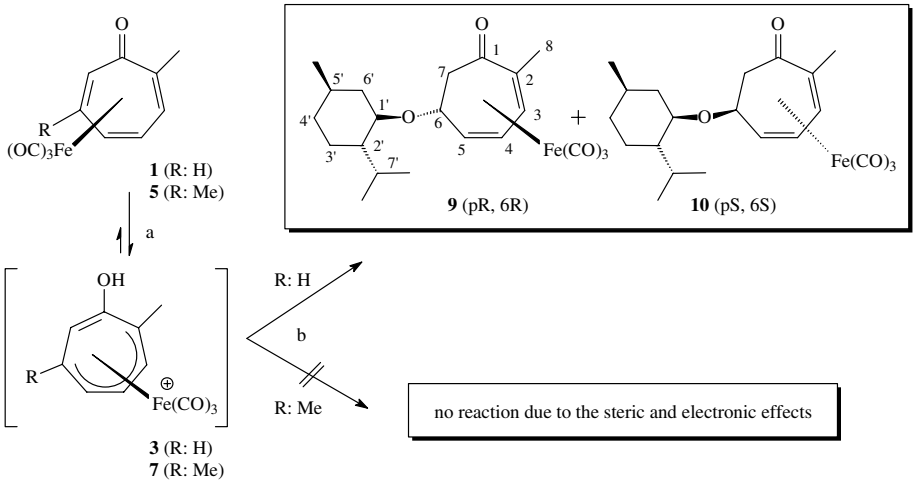
$$\Delta G^{\#} = (RT_1T_2 \ln k_1/k_2)/(T_1 - T_2)$$
(valid for close temperatures). (4)

The activation energy of isomerisation was obtained as an average of activation energies obtained by combinations of k and T. We determined the activation energy of regioisomerisation (2-methyl-) $\Delta G^{\#}_{(\mathbf{1/4})} = 92$ kJ mol^{-1} and for (2,6-dimethyl-) derivative of tricarbonyl[η^4-tropone]iron $\Delta G^{\#}_{(\mathbf{5/8})} = 107$ kJ mol^{-1}.

The preferred regioselectivity of the salt formation was the same for both 2-methyl- and 2,6-dimethyl-

Table 1
Calculated rate constants and half lifes of the fluxional regioisomerisations

(2-Methyl-) 4 ↔ 1				(2,6-Dimethyl-) 8 ↔ 5		
T (K)	k (h^{-1})	$10^2 k_{-1}$ (h^{-1})	$\tau_{1/2}$ (h)	k (h^{-1})	$10^2 k_{-1}$ (h^{-1})	$\tau_{1/2}$ (h)
286	0.0154	0.05	45.0	–	–	–
296	0.0540	0.16	12.8	0.0262	0.10	26.5
306	0.1986	0.59	3.5	0.1132	0.43	6.1
316	0.8660	2.59	0.8	0.4266	1.64	1.6
326	–	–	–	1.4439	5.54	0.5



Scheme 5. (a) H_2SO_4 conc., 0 °C, 60 min, then (1R,2S,3R)-menthol, r.t., 4 h; (b) Na_2CO_3 (powder), dichloromethane. Yield: 77%.

derivatives of tricarbonyl[η^4-tropone]iron (**1** and **5**). In each case, the main regioisomers (**3** and **7**) were formed in the equilibrium when these were dissolved in sulphuric acid. However, the reactivity of these salts to addition of (1R,2S,5R)-menthol is different due to the increased steric hindrance and decreased electrophilic reactivity properties of (**7**) compared to (**3**). Thus, addition of (1R,2S,5R)-menthol to solutions of **3**, followed by quenching with sodium carbonate, gave separable mixtures of diastereomers **9** and **10** (scheme 5). However, the resolution of tricarbonyl[(4,5,6,7-η)-2,6-dimethyltropone]iron (**5**) by these means was unsuccessful, and **5** was recovered unchanged. The observed thermodynamic and kinetic properties of troponeiron tricarbonyls (**1** and **5**) allowed us to explain why the resolution of dimethyl derivate (**5**) did not proceed. The first formed and expected more reactive salt (**6**) is rapidly converted to the more stable but unreactive regioisomer (**7**). This complex salt has methyl substituents at both termini of the dienylium ligand which serve to inhibit access of menthol and lower the positive charge at these sites.

On the other hand, the reactivity of cation **3** to addition of menthol is high due to the absence of the second methyl group. Interestingly only adducts (**9** and **10**) were obtained in the high yield. No other regioisomer was detected. The addition of menthol to the ligand proceeds regiospecifically and stereospecifically as shown in Scheme 5.

3. Experimental

2-Methyltropone was prepared from cyclopenta-1,3-diene [18], 2,6-dimethyltropone [7] and $Fe_2(CO)_9$ [19] were prepared according to the known procedures. All reactions were carried out under nitrogen or argon. The reaction apparatus was purged with argon prior to use. Solvents were bubbled with argon for 15 min, prior to use [20]. Hexsol is a commercial name for light hexane fraction of petrol (b.p. 62–65 °C). TLC was carried out on silica plates and spots were detected by UV ($\lambda = 254$ nm light), or in the iodine vapours. Flash liquid chromatography FLC was performed on SiO_2 (40/100 mesh). NMR spectra were recorded on a Varian Gemini 2000 spectrometer at 300 MHz for protons and 75 MHz for carbons, in $CDCl_3$ unless otherwise noted. TMS was used as an internal standard. Listed coupling constants are in Hz. The Hetcor, HMQC, NOE and homodecoupling techniques were used for exact assignments of the relative configuration of the listed compounds. In NMR data, special descriptors were used: the upper index assigning nucleus for example H^{MentO}–C(7) means: the hydrogen at C(7) oriented towards to menthyloxy group (or hydrogen at C(7) "looking" at the menthyloxy functionality). IR spectra were recorded on a Perkin–Elmer spectrophotometer in 0.1 mm NaCl cell with scale in cm^{-1}. Melting points were determined on a Kofler hot stage and are uncorrected. Elemental analyses (C, H) were performed on a Carlo Erba Instrumentazione analyser.

3.1. Synthesis of tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron (thermodynamically more stable isomer)

Synthesis of **1** was performed by complexation of 2-dimethyltropone with $Fe_2(CO)_9$ in benzene at 40 °C following the recipe from the literature. The yield after FLC purification (silica, Hexsol/Et_2O, 1/2): 74%, m.p. 68.5–70.0 °C [Hexsol/Et_2O] (lit. 84%, m.p. 64 °C) [5] ^1H NMR ($CDCl_3$) 6.39 (1H, dq, $J(3,4) = 8.2$, $J(\mathrm{Me},3) = 1.5$, H–C(3)), 6.32 (1H, ddd, $J(6,7) = 7.6$, $J(5,6) = 4.7$, $J(4,6) = 1.5$, H–C(6)), 6.30 (1H, ddd, $J(4,5) = 7.3$, $J(5,6) = 4.7$, $J(5,7) = 1.4$, H–C(5)), 3.17 (1H, dd, $J(6,7) = 7.6$, $J(5,7) = 1.4$, H–C(7)), 2.68 (1H,

ddd, $J(3,4) = 8.2$, $J(4,5) = 7.3$, $J(4,6) = 1.5$, H–C(4)), 1.48 (3H, d, $J(\mathrm{Me},3) = 1.5$, Me–C(2)). ^{13}C NMR ($CDCl_3$) 208.2 (s, 3× CO from $Fe(CO)_3$), 198.9 (s, C(1)=O), 143.0 (d, C(3)), 129.3 (s, C(2)), 95.1 and 91.3 (d, C(5)) and (d, C(6)), 61.2 and 51.5 (d, C(4)) and (d, C(7)), 17.0 (q, Me–C(2)). IR ($CHCl_3$): 2065, 2007, 1993, 1632, 1610, 968, 607, 600 cm^{-1}. Calc. for $C_{11}H_8FeO_4$(260.02): C, 50.81; H, 3.10. Found: C, 50.50; H, 3.08%.

3.2. Synthesis of unequilibrated mixture of regioisomeric complexes **4** and **1** (35/65, respectively)

Tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron **1** (150.0 mg, 0.577 mmol, 1.0 mol eq.) was dissolved in 1.6 M solution of HBF_4 conc. aq. in acetanhydride (550 μl). The mixture was stirred at room temperature under argon for 30 min. Under this conditions, the first formed tricarbonyl [(1,2,3,4,5-η)-1-methyl-7-oxocyclohepta-2,4-dien-1-yl]-iron(1+) tetrafluoroborate **2** rapidly isomerised to the thermodynamically more stable tricarbonyl[(1,2,3,4,5-η)-1-methyl-7-oxocyclohepta-2,4-dien-1-yl]iron(1+) tetrafluoro-borate **3**. The obtained tricarbonyliron salts **3** and **2** were precipitated by addition of dry Et_2O (4.0 ml) to the reaction mixture. The formed suspension was filtered off through Celite. The solid product was washed with dry Et_2O to yield pale yellow powder (178.5 mg, 0.514 mmol, 89%).

To the crude mixture of the salts **3** and **2** (20.7 mg, 0.06 mmol), dry Et_3N (5.0 ml) was added. The mixture was stirred at room temperature under argon for 15 min. The excess of Et_3N was removed on RVE to yield dense red oil which was dried under high vacuum and then dissolved in degassed $CDCl_3$ (800 μl). Obtained solution was filtered through Celite directly into the NMR tube filled with argon. The composition of unequilibrated mixture of 2-methyltropone complexes **4**, **1** was determined by ^{1}H NMR (the initial ratio of regioisomers was determined to be 35/65, respectively).

3.2.1. Tricarbonyl[(2,3,4,5-η)-2-methyltropone]iron **4** (thermodynamically less stable isomer)

^{1}H NMR ($CDCl_3$): 6.48 (1H, dd, $J(6,7) = 10.9$, $J(5,6) = 7.9$, H–C(6)); 6.30 (2H, m, H–C(3) and H–C(4)), 5.11 (1H, dd, $J(6,7) = 10.9$, $J(5,7) = 1.4$, H–C(7)), 2.62 (1H, ddd, $J(4,5) = 9.3$, $J(5,6) = 7.9$, $J(5,7) = 1.4$, H–C(5)), 1.55 (3H, s, Me–C(2)).

3.3. Synthesis of tricarbonyl[(4,5,6,7-η)-2,6-dimethyltropone]iron **5** (thermodynamically more stable isomer)

The mixture of 992 mg (7.39 mmol, 1.0 mol eq.) of 2,6-dimethyltropone, 6.72 g (18.47 mmol, 2.5 mol eq.) of $Fe_2(CO)_9$ and 20 ml of dry benzene was stirred at 40 °C under argon for 2.5 h (until the starting material disappeared). Then the mixture was cooled down and filtered through Celite. Product was separated by flash chromatography on silica with Hexsol/Et_2O (1:2). Tricarbonyl[η^4-2,6-dimethyltropone]iron was prepared in form of red oil, which is possible to purified by vacuum distillation (120 °C/10 Pa). Yield: 1.34 g (4.88 mmol, 66%).

^{1}H NMR ($CDCl_3$): 6.41 (1H, dq, $J(3,4) = 8.4$, $J(\mathrm{Me–C}(2),3) = 1.5$, H–C(3)), 6.18 (1H, dd, $J(4,5) = 7.4$, $J(5,7) = 1.7$, H–C(5)) [21], 3.23 (1H, d, $J(5,7) = 1.7$, H–C(7)), 2.53 (3H, s, Me–C(6)), 2.50 (1H, dd, $J(3,4) = 8.4$, $J(4,5) = 7.4$, H–C(4)), 1.47 (3H, d, $J(\mathrm{Me–C}(2),3) = 1.5$, Me–C(2)). ^{13}C NMR ($CDCl_3$) [22]: not detectable at ca 208 (s, 3× CO from $Fe(CO)_3$), 198.8 (s, C=O), 144.2 (d, C(3)), 128.3 (s, C(2)), 108.5 (s, C(6)), 94.9 (d, C(5)), 65.2 (d, C(7)), 47.8 (d, C(4)), 24.1 (q, Me–C(2)), 16.9 (q, Me–C(6)). Calc. for $C_{12}H_{10}FeO_4$ (274.05): C, 52.59; H, 3.68. Found: C, 52.40; H, 3.55%.

3.4. Synthesis of unequilibrated mixture of regioisomeric complexes **8** and **5**

Tricarbonyl[(4,5,6,7-η)-2,6-dimethyltropone]iron **5** (20.0 mg, 0.073 mmol, 1.0 mol eq.) was dissolved in 1.6 M solution of HBF_4 conc. aq. in acetanhydride (76 μl). The mixture was stirred at room temperature under argon for 30 min. Under this conditions, the first formed [(1,2,3,4,5-η)-2,6-dimethyl-7-oxocyclohepta-2,4-dien-1-yl]tricarbonyliron(1+) tetrafluoroborate **6** isomerised to the thermodynamically more stable [(1,2,3,4,5-η)-1,5-dimethyl-6-oxocyclohepta-2,4-dien-1-yl]tricarbonyliron(1+) tetrafluoroborate **7**. The obtained salts were precipitated by addition of dry Et_2O (500 μl). The obtained suspension was filtered through the Celite and solid product washed with dry Et_2O (3 × 1 ml) to yield pale yellow solid mixture of **7** and **6** (19.4 mg, 0.071 mmol, 97%).

Dry Et_3N (1.0 ml) was added to the crude solid mixture **7** and **6** (19.4 mg, 0.071 mmol) and stirred at room temperature under argon for 15 min to liberate unequilibrated mixture of regioisomers **8** and **5**. The excess of Et_3N was removed on RVE. The obtained red oil was dried under high vacuum to give tricarbonyl[η^4-2,6-dimethyltropone]irons **8** and **5**. The obtained mixture was dissolved in degased $CDCl_3$ (800 μl) and filtered through Celite directly into the NMR tube filled with argon. The initial ratio of regioisomers **8** and **5** was determined by ^{1}H NMR to be 70/30, respectively.

3.4.1. Tricarbonyl[(2,3,4,5-η)-2,6-dimethyltropone]iron **8** (thermodynamically less stable isomer)

^{1}H NMR ($CDCl_3$): 6.28 (1H, dd, $J(3,4) = 5.2$, $J(3,5) = 1.1$, H–C(3)), 6.19 (1H, dd, $J(4,5) = 7.5$, $J(3,4) = 5.2$, H–C(4)), 5.06 (1H, dq, $J(5,7) = 1.7$, $J(\mathrm{Me–C}(6),7) = 1.3$, H–C(7)), 2.50 (1H, ddd, $J(4,5) = 7.5$, $J(5,7) = 1.7$, $J(3,5) = 1.1$, H–C(5)), 1.84 (3H, d, $J(\mathrm{Me–C}(6),7) = 1.3$, Me–C(6)), 1.55 (3H, s, Me–C(2)).

^{13}C NMR ($CDCl_3$): not detectable at ca. 208 (s, 3× CO from $Fe(CO)_3$), 198.7 (s, C=O), 157.8 (s, C(6)), 120.6 (d, C(7)), 98.7 and 90.7 (2× d, C(3) and C(4)), 72.6 (s, C(2)), 54.9 (d, C(5)), 26.1 and 25.4 (2× q, Me–C(2) and Me–C(6)).

3.5. Synthesis of diastereoisomeric mixture of tricarbonyl[(2,3,4,5-η)-(1R′,2S′,5R′)-6-menthyloxy-2-methyltropone]irons **9** and **10**

A racemic mixture of tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron 300 mg (1.168 mmol) was dissolved in 320 μl of H_2SO_4 conc. The solution was stirred under argon for 2 h at 0 °C. To the fresh formed hydrogensulphate salt of tropone tricarbonyliron, 1.46 g (9.3 mmol) of (1R,2S,5R)-menthol was added portionwise. The mixture was stirred at room temperature for 4 h. The reaction was quenched by adding of Na_2CO_3 1.22g (11.5 mmol) in 4.0 ml of CH_2Cl_2. After neutralisation, 20 ml of water was added, layers were separated and water layer extracted with 3 × 15 ml CH_2Cl_2. Combined organic layers were washed with 10 ml of water and dried over $MgSO_4$. The solvent and excess of menthol were removed by vacuum distillation and sublimation on Büchi. Both diastereoisomers **9** and **10** were obtained in the mixture in the ratio ca 1/1. The remaining mixture was separated by flash chromatography on SiO_2 with Hexsol/Et_2O 3:1. The first eluted complex tricarbonyl[(2,3,4,5-η)-(2pR,6R,1R′,2S′,5R′)-6-menthyloxy-2-methylcyclohepta-2,4-dien-1-one]iron **9** as yellow crystalline compound (m.p. = 127–129 °C [Hexsol]). As the second fraction came tricarbonyl[(2,3,4,5-η)-(2pS,6S,1R′,2S′,5R′)-6-menthyloxy-2-methylcyclohepta-2,4-dien-1-one]iron **10** (m.p. = 90–92 °C [Hexsol]). The latest crystallised very slowly and formed yellow needles. It is also possible to separate the diastereomeric products by the fractional crystallisation from Hexsol by inoculating with a crystal of the pure diastereoisomer as a seed. Total yield of prepared menthyloxy adducts was 375.1 mg (0.901 mmol, 77%).

3.5.1. Tricarbonyl[(2,3,4,5-η)-(2pR,6R,1R′,2S′,5R′)-6-menthyloxy-2-methyltropone]iron **9** [23]

m.p. = 127–129 °C [Hexsol], yellow ^{1}H NMR ($CDCl_3$): 5.79 (1H, d, $J(3,4) = 5.8$, H–C(3)); 5.36 (1H, dd, $J(4,5) = 7.7$, $J(3,4) = 5.8$, H–C(4)); 4.07 (1H, ddd , $J(6,7^{Fe}) = 11.0$, $J(6,7^{MentO}) = 5.5$, $J(5,6) = 1.6$, H–C(6)); 3.26–3.17 (2H, m, H–C(5), H-C(1′)); 2.42 (1H, ddd, $J_{gem} = 11.0$, $J(6,7^{MentO}) = 5.5$, $J(5,7^{MentO}) = 1.9$, H^{MentO}–C(7)); 2.24 (m, 2H); 1.94 (2H, dd, $J_{gem} = 11.0$, $J(6,7^{Fe}) = 11.0$, H^{Fe}–C(7)); 1.64 (3H, s, Me–C(2)); 1.70 – 0.70 (7H, m); 0.93 (3H, d, $J(Me,5') = 7.1$, Me–C(5′)); 0.90 (3H, d, $J(Me,7') = 6.6$, Me–C(7′)); 0.81 (3H, d, $J(Me,7') = 7.1$, Me–C(7′)).

^{13}C NMR (75 MHz, $CDCl_3$): 209.0 (s, 3× CO from$Fe(CO)_3$); 199.9 (s, C=O); 97.4 (d,C(3)); 85.9 (d, C(4)); 80.9 (d, C(6)); 79.4 (d,C(1′)); 72.2 (s,C(2)); 61.2 (d,C(5)); 48.7; 46.9; 42.2; 34.5; 31.8; 25.5; 23.4; 23.2; 22.4; 21.5; 16.2.

IR($CHCl_3$): 3000m, 2960m, 2930m, 2870m, 2070s, 2010s, 1650m, 1460m, 1440w, 1380m, 1340m, 1280w, 1200w, 1180w, 1100w, 1080w, 1040m, 1005w, 910w, 620w, 610m, 590m, 580m. Calc. for $C_{21}H_{28}FeO_5$ (416.29): C, 60.59; H, 6.78. Found: C, 60.36; H, 6.66%.

3.5.2. Tricarbonyl[(2,3,4,5-η)-(2pS,6S,1R′,2S′,5R′)-6-menthyloxy-2-methyltropone]iron **10**

m.p. = 90–92 °C [Hexsol], yellow ^{1}H NMR ($CDCl_3$): 5.79 (1H, d, $J(3,4) = 5.5$, H–C(3)); 5.39 (1H, dd, $J(4,5) = 7.9$, $J(3,4) = 5.5$, H–C(4)); 4.09 (1H, ddd, $J(6,7^{Fe}) = 10.7$, $J(6,7^{MentO}) = 5.5$, $J(5,6) = 1.6$, H–C(6)); 3.18–3.09 (2H, m, H–C(5), H–C(1′)); 2.44 (1H, ddd, $J_{gem} = 11.0$, $J(6,7^{MentO}) = 5.5$, $J(5,7^{MentO}) = 1.9$, H^{MentO}–C(7)); 2.09–2.02 (2H, m); 1.85 (1H, dd, $J_{gem} = 11.0$, $J(6,7^{Fe}) = 10.7$, H^{Fe}–C(7)); 1.64 (3H, s, Me–C(2)); 1.7 – 0.7 (7H, m); 0.94 (3H, d, $J(Me,7') = 6.6$, Me–C(7′)); 0.86 (3H, d, $J(Me,5') = 6.9$, Me–C(5′)); 0.69 (3H, d, $J(Me,7') = 6.9$, Me–C(7′)).

^{13}C NMR (75 MHz, $CDCl_3$): 209.0 (s, 3× (CO) from $Fe(CO)_3$); 199.8 (s, C=O); 97.2 (d, C(3)); 86.0 (d, C(4)); 80.0 (d, C(6)); 78.6 (d, C(1′)); 72.4 (s, C(2)); 62.3 (d, C(5)); others: 48.6; 45.4; 42.2; 34.6; 31.8; 25.3; 23.4; 23.2; 22.5; 21.4; 16.1.

IR($CHCl_3$): 3000m, 2960m, 2930m, 2800m, 2070s, 2010s, 1650m, 1460m, 1440w, 1380m, 1340m, 1280w, 1200w, 1180m, 1140m, 1105w, 620m, 610m, 590m, 580m. Calc. for $C_{21}H_{28}FeO_5$ (416.29): C, 60.59; H, 6.78. Found: C, 60.16; H, 6.71%.

4. Conclusion

The preparation, fluxional behavior, kinetic properties and thermodynamic parameters for the fluxional isomerisation of complexes (**1**, **4**, and **5**, **8**) have been described. The regioisomerisation proceeds as a reversible intramolecular first-order process leads to the almost complete formation of the thermodynamically more stable complexes **1** or **5** in the equilibrated mixtures. These complexes are present in equilibrated mixtures in high ratio (97% and 96%, respectively). The difference in thermodynamic stabilities of regioisomeric tricarbonyl[η^4-2-methyltropone]iron ($\Delta G(\mathbf{1},\mathbf{4}) = 8.8$ kJ mol^{-1}) and tricarbonyl[η^4-2,6-dimethyltropone]iron ($\Delta G(\mathbf{5},\mathbf{8}) = 8.4$ kJ mol^{-1}) have been determined. While the methyl group at C(2) appears to be responsible for the lower stability of **4** and **8** compared with **1** and **5**, the Me substituent at C(6) appears to have smaller effect on the energy balance between regioisomers. Instead, the Me group at C(6) influences the rate of isomer exchange by raising the activation energy for regioisomerisation from 92 kJ mol^{-1} for **4** → **1** to 107 kJ mol^{-1} for **8** → **5**.

Thus, the regioisomerisation of **4** to **1** ($\tau_{1/2} = 12.8$ h) is approximately two times faster than the rate of isomerisation of **8** to **5** ($\tau_{1/2} = 26.8$ h) at r.t.

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