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# The synthesis of a hydroazulen-2-one skeleton-determination of the diastereoselectivity of [3+2] cycloaddition of tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron with *E*/*Z*-η$^1$-(crotyl)Fp

Branislav Horváth [a], Andrej Boháč [a,*], Marta Sališová [a], Eva Solčániová [b], Myron Rosenblum [c]

[a] *Department of Organic Chemistry, Comenius University, Faculty of Natural Sciences, Mlynská dolina, 842 15 Bratislava, Slovakia*
[b] *Chemical Institute, Comenius University, Faculty of Natural Sciences, Mlynská dolina, 842 15 Bratislava, Slovakia*
[c] *Department of Chemistry, Brandeis University, Waltham, MA 02254-9110, USA*

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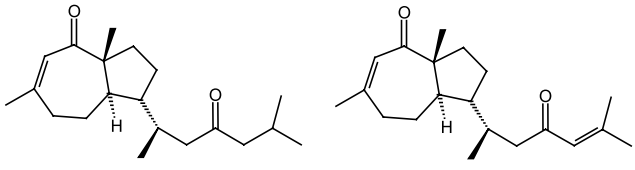
**Abstract**

The diastereoselectivity of [3+2] cycloaddition of tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron (**2**) with an *E*,*Z* isomeric mixture of η$^1$-(crotyl)Fp (**4*E*/4*Z***) [Fp: $C_5H_5Fe(CO)_2$ or $CpFe(CO)_2$] has been studied. By this cyclopentaanulation, four stereogenic centres are formed. The reaction occurs regioselectively and stereoselectively. The relative configurations of the cycloadducts **5a**, **5b** and **5c** were assigned on the basis of 2D and NOE NMR experiments. A mechanism for the stereoselective [3+2] cycloaddition has been proposed. The selectivity of the cycloaddition depends on the difference in steric discrimination approaches of the η$^1$-(crotyl)Fp **4E/4Z** to the tricarbonyl[(3,4,5,6,7-η)-1-trimethylsilyloxy-2-methyltropylium]iron **3** (repulsion of the methyl and methylene groups of **4** and the planar skeleton of **3**) and also upon the isomeric structure (*E* or *Z*) of the η$^1$-(crotyl)Fp reactant. The geometrical isomerism of the reagent (**4E/4Z**) is preserved in the products **5a**–**c**. 

*Keywords:* Regioselectivity; Stereoselectivity; Cyclopentaanulation; Cycloaddition; 2-Methyltroponeiron tricarbonyl; Ketohydroazulene; (crotyl)Fp; Reiswigin

## 1. Introduction

The terpenes constitute a large and structurally diverse group of natural products, many of which possess biological activity. We are currently involved in the synthesis of biologically active terpenoids. Reiswigin A and B (Scheme 1) are sesquiterpenes with a hydroazulene skeleton which have been isolated from deepwater marine organism (sponges *Epipolasis reiswigi* collected by submersible at 330 m). The Reiswigins have shown potent in-vitro antiviral activity against Herpes simplex type I virus and murine A59 hepatitis virus [1]. The present paper reports our studies directed toward the synthesis of hydroazulene skeletons related to this sesquiterpene.




Scheme 1.

Rosenblum described a facile cyclopentaanulation method for the synthesis of hydroazulenes through [3+2] *syn* cycloaddition of η$^1$-1-Fp(prop-2-ene) and η$^1$-1-Fp(prop-2-yne) complexes with tricarbonylcycloheptatrienyliumiron tetrafluoroborate [2]. It was subsequently shown, that the cycloaddition of E/Z η$^1$-(crotyl)Fp[1] on the tropylium salt derived from η$^4$-tricarbonyltroponeiron proceeds regioselectively. However, the cycloaddition yielded a mixture of diastereo-

* Corresponding author. Tel.: +421-2-602-96409; fax: +421-2-602-96690; www: http://www.fns.uniba.sk/ ~ bohac/
*E-mail address:* bohac@fns.uniba.sk (A. Boháč).

[1] Synonym: η$^1$-1-Fp(but-2-ene).

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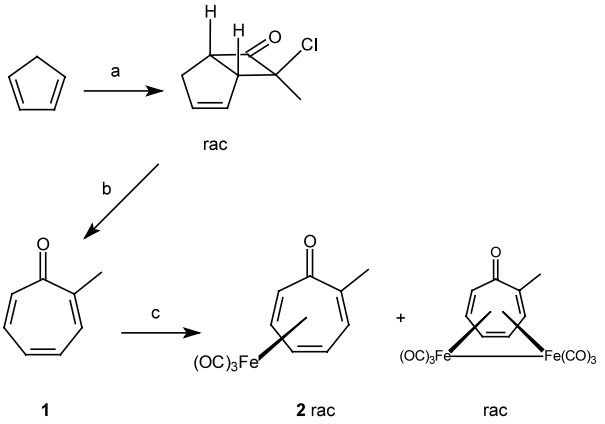



Scheme 2. Reagents and conditions: (a) (1) $Et_3N$, *n*-hexane, 0 °C; (2) $H_3CCHClCOCl$, −5 °C, 75 min; (3) overnight from −5 °C to r.t.; (b) reflux, 119 h, NaOAc, HOAc, $H_2O$, then r.t., NaOH, pH 10, 33% overall yield; (c) $Fe_2(CO)_9$ 2.49 mol eq., $C_6H_6$, 40 °C, 3 h, 74% of **2** and 8% of diiron by product.

isomers. The ratio of the diastereoisomers and their structures were not known [3]. As part of our research, we focused our study on the stereoselectivity of [3+2] cycloaddition of $\eta^1$-(crotyl)Fp (**4**) with the tropylium-iron tricarbonyl salt derived from 2-methyltropone (**1**).

## 2. Discussion

2-Methyltropone (**1**) was prepared from cyclopenta-1,3-diene through the intermediate $7_{exo}$-chloro-$7_{endo}$-methylbicyclo[3.2.0]hept-2-ene-6-one following the work of Brady and Hieble [4] in 33% overall yield. The desired tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron (**2**) was obtained in 74% yield by reaction of **1** with $Fe_2(CO)_9$ in degassed dry benzene at 40 °C, according to the described procedure [3]. A by-product, isolated after FLC was assigned as hexacarbonyl[μ-[(2,3,4-η:5,6,7-η)-2-methyltropone]]diiron in 8% yield [5] (Scheme 2).

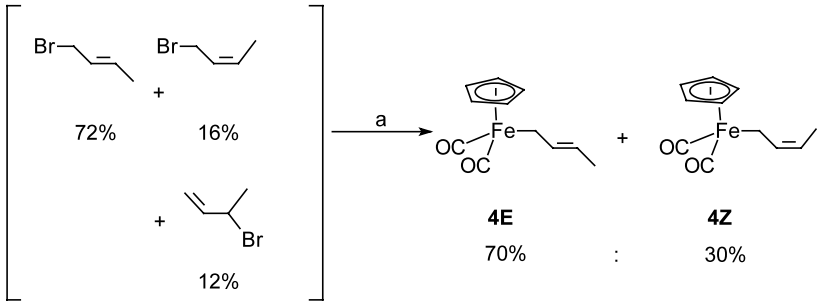
The *E*,*Z* mixture of $\eta^1$-(crotyl)Fp (**4**) was prepared from the commercially available crotyl bromide containing ca. 12% isomeric 3-bromobut-1-ene.[2] $\eta^5$-Dicarbonylcyclopentadienyliron dimer $Fp_2$ was prepared by heating dicyclopentadiene and $Fe(CO)_5$ with gentle reflux for 16 h, (yield 90%) [6]. The FpNa salt was obtained from $Fp_2$ and $NaHg_x$ in situ in THF at room temperature, then cooled to −80 °C and treated with crotyl bromide to give a ***4E/4Z*** mixture (70/30, respectively, determined by Cp singlet from $^1$H-NMR). It is known that the isomeric impurity, 3-bromobut-1-ene, present in commercial crotyl bromide is converted by treatment with FpNa to its FpR compound, which rearranges spontaneously to the desired mixture of $\eta^1$-(crotyl)Fp ***4E/4Z*** [7] (Scheme 3).

Tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron **2** was converted in situ to the fluxional tropyliumiron tricarbonyl salt **3** [3] by treatment with trimethylsilyl triflate. This electrophilic organoiron salt yielded ketohydroazulene cycloadducts in 80% yield on treatment with the mixture of ***4E/4Z*** $\eta^1$-(crotyl)Fp complexes. The crude product consisted of a mixture of the three diastereoisomers **5a**, **5b** and **5c** in the ratio of (57:26:17, respectively) (Scheme 4).

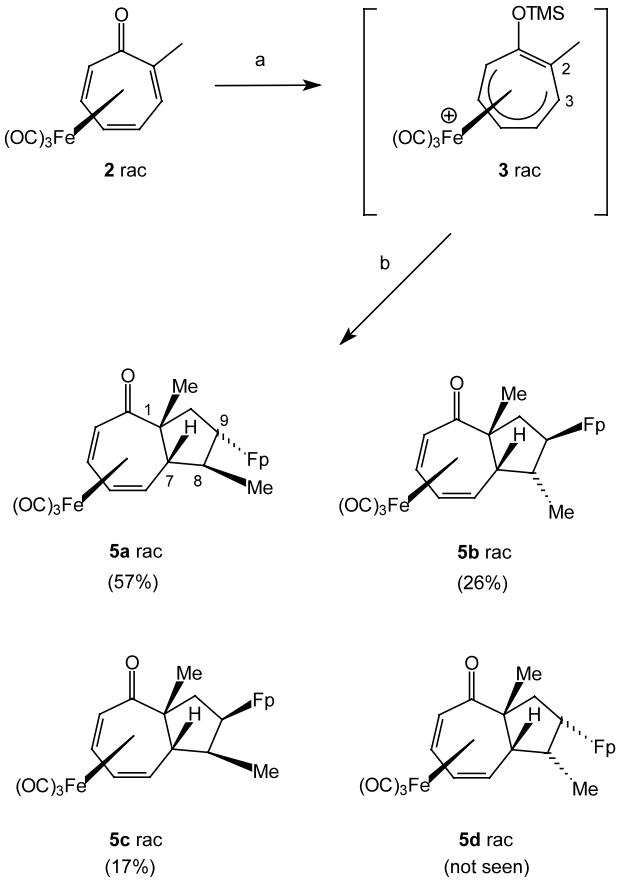
The relative configurations of products **5a**–**c** were determined by a combination of NOE and 2D NMR experiments and by use of the Karplus equation (correlation between coupling constants and estimated torsion angles of the rigid skeleton) [8]. The assignment of the relative configuration of the structures **5a**–**c** was complex because of the different observed conformation of the five-membered ring in the skeleton of the diastereoisomers. The proposed structures and estimated conformations (on the basis of observed coupling constants from $^1$H-NMR in $CDCl_3$ at room temperature) of the diastereoisomers **5a**–**c** are shown in Scheme 5. The results and conclusions of the NOE NMR experiments are summarised in Table 1.

The NOE experiments confirm that [3+2] cycloaddition, involving successive nucleophilic attack on the fluxional organoiron salt **3** by $\eta^1$-(crotyl)Fp (**4**), fol-

[2] Crotyl bromide, pract. ca. 85% (GC) Fluka (cat. no. 28100) containing: *E*-isomer (72%), *Z*-isomer (16%) and 3-bromobut-1-ene (12%) (determined by $^1$H-NMR). All the isomers above gave after the reaction with FpNa desired products: $\eta^1$-(crotyl)Fp ***4E/4Z***.




Scheme 3. Reagents and conditions: (a) FpNa in situ from $Fp_2$ and $NaHg_x$, −80 °C, 1 h, then r.t., distillation 150 °C/5 Pa, yield 22%, ***4E/4Z*** (*E*/*Z* 70/30).




Scheme 4. Reagents and conditions: (a) TMSTf, $CH_2Cl_2$, −80 °C, 3 h; (b) (1) $FpCH_2CH{=}CHCH_3$ (*E*/*Z* 70/30), −80 °C, 1 h, then 40 °C, 3 h; (2) THF, $NaHCO_3$ aq., r.t., 30 min, yield: 80%.

lowed by ring closure, proceeds regioselectively at C(3) and C(2) of the complex cation. The reaction also proceeds *trans*-stereoselectively at these centers with respect to the bulky $Fe(CO)_3$ group. In this manner, *syn*-stereogenic centers in the products **5a**–**c** at C(1) and C(7) are formed. Finally, each of these steps (nucleophilic attack and also ring closure) occurs *anti*-periplanar with respect to the activating Fp group [9]. Thus, the two remaining stereogenic centers in **5a**–**c** at C(8) and at C(9) are formed under this control as well as the effect of steric interactions associated with the reacting components. While the *E*-isomer gives a mixture of two products (**5a** and **5b**), the *Z*-isomer yields a single stereoisomer (**5c**). The relevant interactions of the reacting components are shown in Schemes 6 and 7 below and appear to give good account of the relative proportions of products observed in the reaction. Diastereomer **5d** is not formed in the reaction. This is best accounted for by the significantly greater steric interactions (methyl and methylene) of **4*Z*** with the complex tropylium ion in the first step of the cycloaddition reaction, which would give rise to this diastereomer.

## 3. Conclusions

The [3+2] cycloaddition reactions $\eta^1$-(crotyl)Fp (**4**) with complex tropylium ion **3** provides facile entry into the substituted hydroazulene skeleton, and has been shown to be highly diastereoselective at the four new stereogenic centers formed in these reactions. This stereoselectivity is accounted for in terms of known stereoelectronic demands of both organoiron reagents and of steric demands of the $\eta^1$-(crotyl)Fp reagent. Further study of these cycloaddition reactions and their application in sesquiterpene synthesis is in progress.

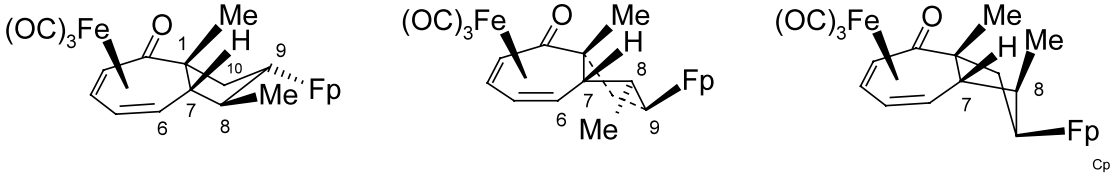
## 4. Experimental

### 4.1. General data

Dicyclopentadiene, 2-chloropropionyl chloride, crotyl bromide, trimethylsilyl triflate and $Fe(CO)_5$ are commercially available. $NaHg_x$, cyclopentadiene and $Fe_2(CO)_9$ [10] were prepared according to the known procedures.[3] All reactions were carried out under nitrogen or argon. The reaction apparatus was purged with argon prior to use. Benzene and THF were dried over sodium and redistilled under argon from sodium benzophenone ketyl. Triethylamine, dichloromethane and diethyl ether were dried over and distilled from $CaH_2$ under argon. Solvents were bubbled with argon for 15 min, prior to use [11].[4] Hexsol is a commercial

[3] Diiron nonacarbonyl was prepared by photolysis of iron pentacarbonyl in glacial acetic acid with a low pressure Hg lamp.

[4] 'The transferable gas container (TGC)' for introducing an inert gas into a reaction mixture, a solvent or a solution. TGC attached to a syringe allows convenient degassing of liquids.

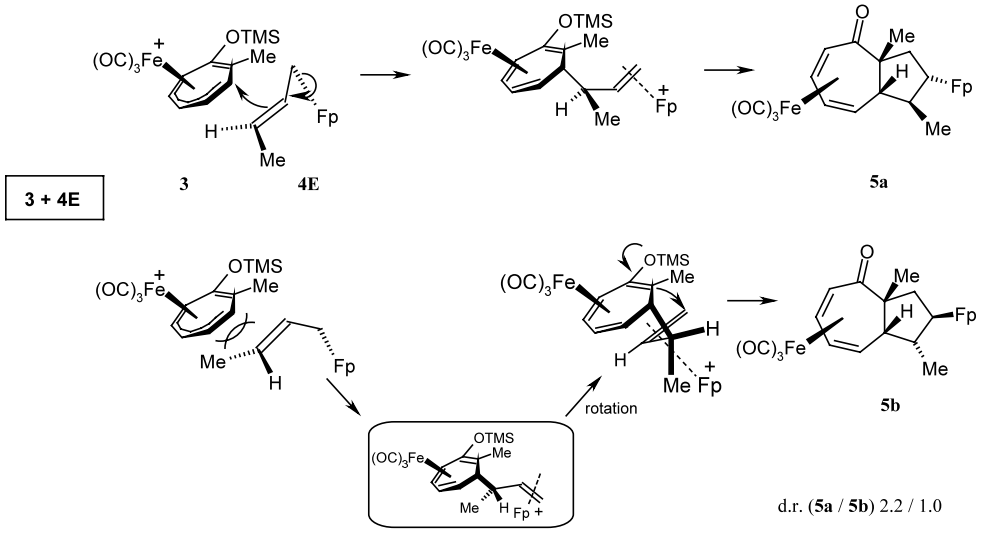



Scheme 5.

Table 1
The most important NOE NMR results confirming the assignment of the relative configurations of the diastereoisomers **5a**, **5b** and **5c**

| Diastereoisomer | Irradiated signal | Corresponding NOE signals [a] | Structure conclusions |
|---|---|---|---|
| **5a** | Me–C(1) | H–C(9) | Fp—down |
| | H–C(6) | H–C(8) | Me–C(8)—up |
| | H–C(9) | Me–C(1), Me–C(8), $H^{Me-C(1)}$–C(10) | Me–C(8)—up, Fp—down and an exact assignment for $H^{Me-C(1)}$–C(10) |
| **5b** | H–C(6) | Me–C(8) | Me–C(8)—down |
| | H–C(7) | H–C(8) | Me–C(8)—down |
| | Me–C(8) | H–C(6), H–C(9) | Me–C(8)—down, Fp—up |
| **5c** | Cp from Fp group | Me–C(8) | Me–C(8) and Fp are in the *syn* arrangement |
| | H–C(7) | Me–C(8) and also H–C(8) | The Fp preferred group conformation brings the Me–C(8) and Me–C(1) close to one another in **5c**. NOE signals for both groups at C(8) are observed when H–C(7) is irradiated. Me–C(8) up, Fp–up. |

[a] Upper index assigning nucleus for example $H^{Me-C(1)}$–C(10) means: the hydrogen at C(10) oriented towards to Me–C(1) (or looking at Me–C(1)); nomenclature introduced by Prof. Camille Ganter, ETH, Zürich, Switzerland.



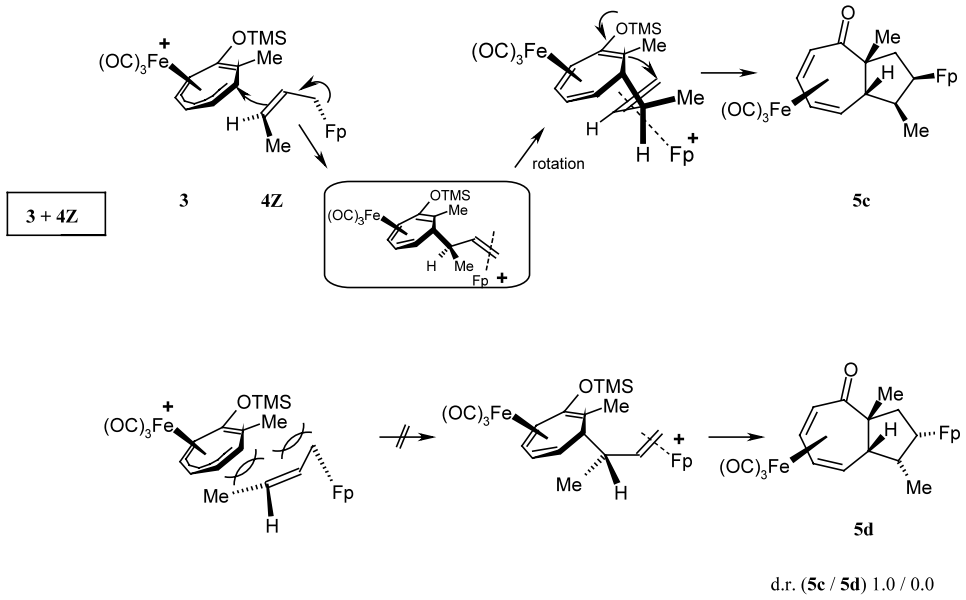

Scheme 6. Proposed mechanism for the stereoselective cycloaddition of the *E*-$\eta^1$-(crotyl)Fp **4*E*** on the organoiron salt **3**.

name for light hexane fraction of petrol (bp 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 and NOE techniques were used for exact assignments of the relative configuration of the products **5a**–**c**. IR spectra were recorded on a Perkin–Elmer spectrophotometer in 0.1 mm NaCl cell with the scale in $cm^{-1}$. Melting points were determined on a Kofler hot stage and are uncorrected. Elemental analyses (C, H, N) were performed on a Carlo Erba Instrumentazione analyzer.

### 4.2. 2-Methyltropone (*1*)[5]

2-Methyltropone was prepared following the procedure from the literature [4]. Yield: 11.8 g (98.2 mmol, 33% based on the starting cyclopentadiene), Kugelrohr distillation: oven temperature 105 °C (0.5 Torr) (lit. b.p. 70–72 °C/1 Torr) [4a]. $^1$H-NMR ($CDCl_3$) 7.36–7.30, 7.17–7.04 and 7.00–6.87 (1H, 2H and 2H, 3 × m, H–C(3), H–C(4), H–C(5), H–C(6), H–(7)), 2.28 (3H, d, $J$(3,Me–C(2)) = 1.0, Me–C(2)). $^{13}$C-NMR ($CDCl_3$) 187.4 (s, C(1)=O), 152.5 (s, C(2)), 139.9, 135.5, 135.1, 133.8 and 132.5 (5 × d, C(3), C(4), C(5), C(6) and C(7)), 22.8 (q, Me–C(2)). Anal. Calc. for $C_8H_8O$ (120.15): C, 79.97; H, 6.71. Found: C, 79.57; H 6.79%.

[5] Synonym: 2-methylcyclohepta-2,4,6-trien-1-one.




Scheme 7. Proposed mechanism for the stereoselective cycloaddition of the *Z*-$\eta^1$-(crotyl)Fp **4*Z*** on the organoiron salt **3**.

### 4.3. Tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron (**2**)[6]

2-Methyltropone irontricarbonyl was prepared following the procedure from the literature [3]. Yield: 7.63 g (29.3 mmol, 74%), red crystals, m.p. 68.5–70.0 °C [hexsol/$Et_2O$] (lit. 84%, m.p. 64 °C) [3]. $^1$H-NMR ($CDCl_3$) 6.39 (1H, dq, $J(3,4) = 8.2$, $J(Me,3) = 1.5$, 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, $J(Me,3) = 1.5$, 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 $cm^{-1}$. Anal. Calc. for $C_{11}H_8FeO_4$ (260.02): C, 50.81; H, 3.10. Found: C, 49.96; H, 3.00%.

Hexacarbonyl[μ-[(2,3,4-η:5,6,7-η)-2-methyltropone]]diiron,[7] red crystals, m.p. 112–120 °C (dec.) was observed as a by product. Yield 1.30 g (3.25 mmol, 8%). $^1$H-NMR ($CDCl_3$) 4.73 (1H, dddd, $J(4,5) = 7.7$, $J(5,6) = 6.9$, $J(5,7) = 1.4$, $J(3,5) = 0.8$, H–C(5)), 4.66 (1H, dd, $J(3,4) = 7.7$, $J(3,5) = 0.8$, H–C(3)), 4.57 (1H, ddd, $J(3,4) = 7.7$, $J(4,5) = 7.7$, $J(4,6) = 1.0$, H–C(4)), 4.50 (1H, ddd, $J(6,7) = 7.7$, $J(5,6) = 6.9$, $J(4,6) = 1.0$, H–C(6)), 3.38 (1H, dd, $J(6,7) = 7.7$, $J(5,7) = 1.4$, H–C(7)), 1.63 (3H, s, Me–C(2)). $^{13}$C-NMR ($CDCl_3$) 210.2 (s, 6 × CO from 2 × $Fe(CO)_3$), 189.6 (s, C(1)=O), 78.4 (d, C(3)), 75.9 (s, C(2)), 74.4 (d, C(6)) 62.9 (d, C(5)), 61.7 (d, C(7)), 57.1 (d, C(4)), 23.0 (q, Me–C(2)). IR ($CHCl_3$): 2070, 2025, 2010, 1590 (C(1) = O), 590, 580, 555. Anal. Calc. for $C_{14}H_8Fe_2O_7$ (399.90): C, 42.05; H, 2.02. Found: C, 42.50; H, 2.04%.

### 4.4. $\eta^5$-Dicarbonylcyclopentadienyliron dimer ($Fp_2$)

$Fp_2$ was prepared following the procedure from the literature [6]. Yield: 23.7 g (0.067 mol, 90%). $^1$H-NMR (80 MHz, $CDCl_3$): 4.78 (10H, s, 2 × Cp).

### 4.5. mixture of *E*/*Z* $\eta^1$-(crotyl)Fp (**4*E***, **4*Z***)[8]

A solid $NaHg_x$ (21.30 g, containing Na 2.8% w/w, 24.9 mmol, 1.14 mol eq.) was added to the solution of $Fp_2$ (4.00 g, 11.30 mmol, 1.03 mol eq.) in 65 ml of dry THF. The mixture was stirred 1 h at room temperature (r.t.). The solution of FpNa was decanted from the rest of Hg and $HgNa_x$. Crotyl bromide (72% *trans*, 16% *cis*, 12% 3-bromobut-1-ene) (see footnote 2) (2.95 g, 2.25 ml, 21.85 mmol) was added to the −80 °C cooled solution of FpNa within 15 min. The stirred mixture was allowed to warm up to r.t. during 1 h. The precipitate was removed by centrifugation and then the solid washed

[6] Other synonyms: 2-methyltroponeiron tricarbonyl or tricarbonyl[(4,5,6,-η)-2-methylcyclohepta-2,4,6-trien-1-one]iron; CAS: [54931-32-7] and [130853-98-4].

[7] Synonym: hexacarbonyl[μ-[(2,3,4-η:5,6,7-η)-2-methylcyclohepta-2,4,6-trien-1-one]]diiron.

[8] Other synonyms: *E*/*Z* $\eta^1$-1-Fp(but-2-ene) or *E*/*Z* dicarbonyl[$\eta^1$-(but-2-en-1-yl)-$\eta^5$-cyclopentadienyl]iron.

with ether (3 × 30 ml). The solvent was evaporated in vacuo. The crude oil was distilled on Kugelrohr (150 °C/5 Pa). Yield: 1.12 g (4.83 mmol, 22.1%) as the mixture of isomers **4*E*/4*Z*** (*E*:*Z* = 70:30 determined by $^1$H-NMR). Obtained brown oil was used in the next step without further purification. $^1$H-NMR (**4*E***, $CDCl_3$) 5.65 (1H, dt, *J*(2,3) = 15.5, *J*(1,2) = 8.4, H–C(2)), 5.31 (1H, dq, *J*(2,3) = 15.5, *J*(3, Me) = 6.4, H–C(3)), 4.68 (5H, s, Cp), 2.12 (2H, d, *J*(1,2) = 8.4, $-CH_2-$), 1.58 (3H, d, *J*(3, Me) = 6.4, Me–). $^1$H-NMR (**4*Z***, $CDCl_3$) 5.70 and 5.32 (2H, 2 × m, H–C(2) and H-C(3)), 4.74 (5H, s, Cp), 2.18 (2H, d, *J*(1,2) ≈ 9.2, $-CH_2-$), 1.60 (3H, d, *J*(3, Me) ≈ 6.0, Me–).

### 4.6. [3+2] Cycloaddition of tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron and E/Z η$^1$-(crotyl)Fp (**5a**–**d**)

A solution of tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron (1.00 g, 3.85 mmol) **2** in dry degassed $CH_2Cl_2$ (20 ml) was stirred and cooled to −80 °C under argon. Trimethylsilyl triflate (TMSTf) (0.7 ml, 0.853 g, 3.86 mmol) was added dropwise and the mixture was stirred 3 h at −80 °C. The solution of η$^1$-(crotyl)Fp (1.12 g, 4.83 mmol, 1.25 mol eq.) **4*E*/4*Z*** (70/30) in dry $CH_2Cl_2$ (5 ml) was added during 15 min. After stirring at −80 °C for 1 h the temperature was allowed to warm up to 40 °C for 3 h. After evaporation of the solvent, the red–brown residue was disolved in tetrahydrofuran (80 ml). The saturated aqueous $NaHCO_3$ (20 ml) was added and the mixture was stirred at r.t. for 30 min. The organic layer was separated. Water layer was washed with ether (3 × 10 ml). The combined organic layers were dried over magnesium sulphate. After filtration and evaporation of the solvent, the brown residue (2.28 g) was purified by flash column chromatography (FLC) on silica gel (450 g, 40/100 mesh, hexsol/$Et_2O$ (1:1)) to give **5**: (1.209 g, 2.457 mmol, 64% yield,[9] 78% conversion calculated on the used starting material). The ratio of the diastereoisomers in the crude product was determined by $^1$H-NMR ($CDCl_3$) based on the singlets of Cp signals of the Fp groups **5a**, **5b**, **5c**, **5d** in the ratio 57:26:17:0%; 4.74 δ (5H, s, **5a**–Cp) 4.70 δ (5H, s, **5b**–Cp), 4.77 δ (5H, s, **5c**–Cp), ? δ (5H, s, **5d**–Cp), respectively. The diastereoisomer **5d** was not observed. Part of the starting material **2** was also recovered (180 mg, 0.692 mmol, 18% mol).

Fraction 1: the diastereoisomeric mixture **5a** and **5b** (298 mg, 0.606 mmol)
Fraction 2: the mixture of **5a**, **5b** and **5c** (840 mg, 1.707 mmol)
Fraction 3: the pure diastereoisomer **5c** (71 mg, 0.144 mmol)
Fraction 4: starting material tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron **2** (180 mg, 0.692 mmol)

The mixture **5a**, **5b** and **5c** (840 mg, 1.707 mmol) was chromatographed again on silica gel (170 g, 40/100 mesh, hexsol/$Et_2O$ (1:1)) to give: **5a**, **5b** (502 mg, 1.020 mmol) and **5c** (99 mg, 0.201 mmol) (yellow red crystals m.p. 168–172 °C (dec)). Loss of material through decomposition during purification was observed (239 mg, 28% w/w). The pure **5a** (pale yellow crystals m.p. 177–180 °C (dec)) was obtained by crystallisation of the mixture **5a**, **5b** in ether/hexsol. The mother liquid gave enriched **5b** (70% **5b** + 30% **5a**).

**5a**: $^1$H-NMR ($CDCl_3$) 5.78 (1H, ddd, *J*(3,4) = 7.4, *J*(4,5) = 5.3, *J*(4,6) = 1.4, H–C(4)), 5.58 (1H, ddd, *J*(5,6) = 8.0, *J*(4,5) = 5.3, *J*(3,5) = 1.1, H–C(5)), 4.74 (5H, s, Cp), 3.17 (1H, dd, *J*(3,4) = 7.4, *J*(3,5) = 1.1, H–C(3)), 3.14 (1H, ddd, *J*(5,6) = 8.0, *J*(6,7) = 4.9, *J*(4,6) = 1.4, H–C(6)), 2.50 (1H, ddd, *J*(9,10$^{Fp}$) = 12.5, *J*(8,9) = 8.8, *J*(9,10 $^{Me-C(1)}$) = 6.3, H–C(9)), 2.28 (1H, ddd, *J*(6,7) = 4.9, *J*(7,8) = 4.3, *J*(7,10$^{Me-C(1)}$) = 1.4, H–C(7)), 1.89 (1H, dd, $J_{gem}$ = 12.3, *J*(9,10$^{Fp}$) = 12.5, H$^{Fp}$–C(10)), 1.84 (1H, dddq, *J*(8,9) = 8.8, *J*(8, Me–C(8)) = 6.9, *J*(7,8) = 4.3, *J*(8, 10$^{Me-C(1)}$) ≈ 1.4, H–C(8)), 1.50 (1H, ddm, $J_{gem}$ = 12.3, *J*(9,10 $^{Me-C(1)}$) = 6.3, $w_{1/2}$ = 2.8, among others, *J*(7,10 $^{Me-C(1)}$) = 1.4, *J*(8, 10$^{Me-C(1)}$) ≈ 1.4, H$^{Me-C(1)}$–C(10)), 1.15 (3H, d, *J*(8, Me–C(8)) = 6.9, Me–C(8)), 1.08 (3H, s, Me–C(1)). $^{13}$C-NMR ($CDCl_3$) 218.0, 217.7 (s, 2 × CO from Fp), 209.6 (s, 3 × CO from $Fe(CO)_3$), 209.4 (s, C(2)=O), 92.2 (d, C(4)), 89.3 (d, C(5)), 85.8 (s, Cp), 67.0 (d, C(7)), 66.0 (d, C(6)), 61.9 (d, C(8)), 60.2 (d, C(3)), 56.5 (t, C(10)), 55.3 (s, C(1)), 30.3 (d, C(9)), 25.6 (q, Me–C(1)), 22.60 (q, Me–C(8)). Anal. Calc. for $C_{22}H_{20}Fe_2O_6$ (492.08): C, 53.70; H, 4.10. Found: C, 53.35; H, 4.01%.

**5b**: $^1$H-NMR ($CDCl_3$) 5.69–5.62 (2H, m, H–C(4), H–C(5)), 4.70 (5H, s, Cp), 3.13 (1H, dd, *J*(3,4) = 6.6, *J*(3,5) = 1.7, H–C(3)), 2.93 (1H, ddd, *J*(5,6) = 7.6, *J*(6,7) = 4.3, *J*(4,6) = 2.1, H–C(6)), 2.54 (1H, ddm, *J*(7,8) = 5.8, *J*(6,7) = 4.3, $w_{1/2}$ ≈ 1.9, H–C(7)), 2.21 (1H, dd, *J*(9,10$^{H-C(9)}$) = 9.6, *J*(9,10$^{Me-C(1)}$) = 8.8, H–C(9)), 2.14 (1H, dq, *J*(8, Me–C(8) = 6.1, *J*(7,8) = 5.8, H–C(8)), 2.06 (1H, ddm, $J_{gem}$ = 14.2, *J*(9,10) = 9.6, $w_{1/2}$ ≈ 1.8, H$^{C(9)}$–C(10)), 1.21 (1H, ddm, $J_{gem}$ = 14.2, *J*(9,10) = 8.8, $w_{1/2}$ ≈ 1.5, H$^{Me-C(1)}$–C(10)), 1.13 (3H, s, Me–C(1)), 1.10 (3H, d, *J*(8, Me–C(8)) = 6.1, Me–C(8)). $^{13}$C-NMR ($CDCl_3$) 217.5 and 217.2 (s, 2 × CO from Fp), 209.5 (s, 3 × CO from $Fe(CO)_3$), 209.2 (s, C(2)=O), 91.2 and 90.2 (2 × d, C(4) and C(5)), 86.0 (s, Cp), 63.7 (d, C(7)), 59.1 (2 × d, C(3) and C(6)), 54.5 (t, C(10)),

[9] When 1.86 mol eq. of η$^1$-(crotyl)Fp (instead of 1.25 mol eq.) was used the yield of cycloadducts increased from 64 to 80%.

54.0 (s, C(1)), 51.7 (d, C(8)), 27.3 (q, Me–C(1)), 26.7 (d, C(9)), 17.0 (q, Me–C(8)).

**5c**: $^{1}$H-NMR ($CDCl_3$) 5.66 (1H, ddd, $J(3,4) = 7.4$, $J(4,5) = 5.2$, $J(4,6) = 1.7$, H–C(4)), 5.53 (1H, ddd, $J(5,6) = 8.0$, $J(4,5) = 5.2$, $J(3,5) = 1.2$, H–C(5)), 4.77 (5H, s, Cp), 3.30 (1H, dd, $J(3,4) = 7.4$, $J(3,5) = 1.2$, H–C(3)), 3.24 (1H, ddd, $J(9,10^{Me-C(1)}) = 12.9$, $J(9,10^{H-C(9)}) = 8.1$, $J(8,9) = 7.0$, H–C(9)), 3.23 (1H, ddd, $J(5,6) = 8.0$, $J(6,7) = 5.6$, $J(4,6) = 1.7$, H–C(6)), 2.50 (1H, dd, $J(6,7) = 5.6$, $J \approx 0.6$, H–C(7)), 1.97 (1H, dqm, $J(8, Me–C(8)) = 7.5$, $J(8,9) = 7.0$, $w_{1/2} \approx 3$, H–C(8)), 1.84 (1H, dddm, $J_{gem} = 14.2$, $J(9,10^{H-C(9)}) = 8.1$, $w_{1/2} = 1.8$, $H^{H-C(9)}$–C(10)), 1.52 (1H, ddm, $J_{gem} = 14.2$, $J(9,10^{Me-C(1)}) = 12.9$, $w_{1/2} = 1.2$, $H^{Me-C(1)}$–C(10)), 1.27 (3H, s, Me–C(1)), 1.11 (3H, d, $J(8, Me–C(8)) = 7.5$, Me–C(8)). $^{13}$C-NMR ($CDCl_3$) 217.8 and 217.4 (2 × s, 2 × CO from Fp), 209.5 (s, 3 × CO from $Fe(CO)_3$), 208.8 (s, C(2)=O), 91.1 (d, C(4)), 88.8 (d, C(5)), 85.8 (s, Cp), 66.5 (d, C(6)), 64.3 (d, C(7)), 62.3 (d, C(3)), 56.6 (d, C(8)), 54.7 (t, C(10)), 54.5 (s, C(1)), 29.7 (q, Me–C((1)), 22.6 (d, C(9)), 22.5 (q, Me–C(8)). Anal. Calc. for $C_{22}H_{20}Fe_2O_6$ (492.08): C, 53.70; H, 4.10. Found: C, 53.48; H, 4.08%.

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## References

[1] Y. Kashman, S. Hirsch, F. Koehn, S. Cross, Tetrahedron Lett. 28 (1987) 5461.
[2] N. Greco, D. Marten, S. Raghu, M. Rosenblum, J. Am. Chem. Soc. 98 (1976) 848.
[3] M. Rosenblum, J.C. Watkins, J. Am. Chem. Soc. 112 (1990) 6316.
[4] (a) W.T. Brady, J.P. Hieble, J. Am. Chem. Soc. 94 (1972) 4279;
(b) W.T. Brady, J.P. Hieble, Tetrahedron Lett. 37 (1970) 3205.
[5] N. Morita, T. Asao, A. Tajiri, H. Sotokawa, M. Hatano, Chem. Lett. (1985) 1879.
[6] R.B. King, Organometallic Syntheses: Transition Metal, vol. 1, Academic Press, New York, 1965, p. 90.
[7] (a) A. Cutler, D. Ehntholt, W.P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, D. Wells, J. Am. Chem. Soc. 98 (1976) 3495;
(b) A. Bucheister, P Klemarczyk, M. Rosenblum, Organometallics 1 (1982) 1679.
[8] E. Pretsch, T. Clerc, J. Seibl, W. Simon, Tables of Spectral Data for Structure Determination of Organic Compounds, Springer-Verlag, Berlin, 1983, p. H25.
[9] M. Rosenblum, J. Organometal. Chem. 300 (1986) 191.
[10] G. Brauer, Handbuch der Präparativen Anorganischen Chemie, vol. 3, Ferdinand Enke Verlag, Stuttgart, 1981, p. 1827.
[11] A. Boháč, J. Chem. Educ. 72 (1995) 263.