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# Synthesis of tricarbonyliron cyclohexa-2,4-dienone complexes from tosylhydrazones of acyclic dienone complexes.

## A novel ansa dicarbonyliron complex by intramolecular trapping of reaction intermediates of the cyclocarbonylation reaction

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### Abstract

Cyclohexa-2,4-dienones stabilized by coordination to tricarbonyliron are obtained when tosylhydrazones of tricarbonyliron complexed dienones are submitted to the conditions of the Bamford-Stevens reaction (thermolysis in the presence of strong bases). This cyclocarbonylation reaction proceeds most likely via  $\alpha$ -diazodiene complexes, and from there via carbenes, which react intramolecularly with a CO ligand, the coordinatively unsaturated iron species so formed being finally stabilized by an external two-electron ligand. The existence of two such hypothetical intermediates could be proven by intramolecular trapping experiments (1,3-dipolar cycloadducts **3**, ansa Fe(CO)<sub>2</sub> complex **6**, structures confirmed by X-ray diffraction).

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### 1. Introduction

Stable cyclohexadienone complexes are formed by thermal decomposition, in presence of strong bases, of tosylhydrazones of tricarbonyliron complexes of dienal and dienylmethylketones [1].

### 2. Results and discussion

In view of previous results [2] with tosylhydrazones of  $\alpha$ -ketoesters, we proposed for this cyclocarbonylation reaction a mechanism via an  $\alpha$ -diazodiene complex, with a carbenic intermediate and intramolecular carbonyla-

tion by a CO ligand, followed by cyclization within the coordination sphere.

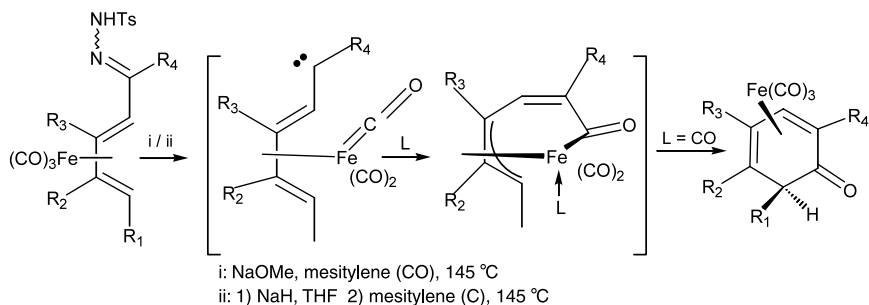
However, under the rather drastic conditions (ca. 145 °C), necessary for the reaction to proceed in the general case (i.e. with non stabilized diazocompounds), the diazodiene complexes could never be observed, and attempts to trap them, when performing the reaction in the presence of dipolarophiles, failed.

We could now prove that such diazocompounds are real intermediates, by means of an intramolecular 1,3-dipolar cycloaddition trapping reaction [3]. Two unsaturated dienone complexes, bearing respectively an  $\omega$ -pentenyl and an  $\omega$ -butenyl chain on the ketocarbonyl,<sup>1</sup>

<sup>1</sup> The 6-penten-4-yl- and 6-buten-3-yl-hexa-2,4-dien-6-one-Fe(CO)<sub>3</sub> complexes **1** and **4** were obtained in 85% yield by oxidation with 1,1'-(azodicarbonyl)-dipiperidine [4] of the magnesium alcoholates resulting from the reactions of pent-4-enyl magnesium bromide and, respectively, but-3-enyl magnesium bromide, with the iron tricarbonyl complex of sorbaldehyde.

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were synthesized and the thermal decomposition of the sodium salts of their tosylhydrazones studied.

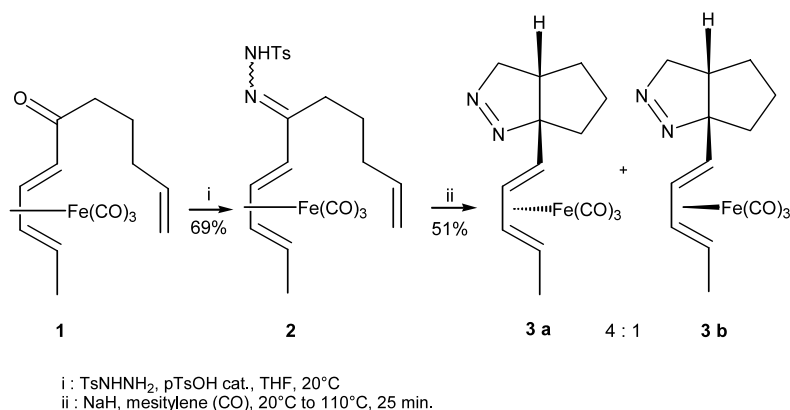
The tosylhydrazone **2** of the dienone complex **1**, with the pentenyl chain, was treated with 1.3 equivalents NaH and heated in mesitylene from 20 to 110 °C. After 25 min., the sole reaction product was a mixture of two difficult to separate acyclic diene-Fe(CO)<sub>3</sub> complexes, with the nitrogen still present as an azo group ( $\Delta^1$ -pyrazolines **3a** and **3b**, isolated 51%, ca. 4:1, three CO ligands as a sharp band at 2044 cm<sup>-1</sup>, and a broad band at 1973 cm<sup>-1</sup>; no  $\omega$ -C=C bond;  $\nu$ N=N at 1550 cm<sup>-1</sup>). However, single crystals of the major pyrazoline **3a** could be obtained after chromatographic enrichment, allowing confirmation of the structure by X-ray diffraction.

Amazingly the intramolecular cyclocarbonylation

was favored by the strongly electron donating diene tricarbonyl iron substituent.

Under the same thermolysis conditions, the tosylhydrazone **5** of the dienone complex **4**, with the shorter butenyl chain, gave the unusual ansa cyclohexadienone Fe(CO)<sub>2</sub> complex **6**, as sole organometallic species.

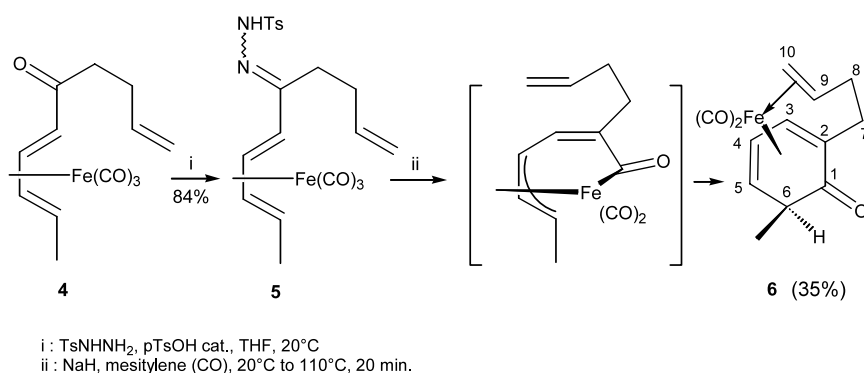
Obviously, an intramolecular 1,3 dipolar cycloaddition was no longer favoured and the cyclocarbonylation reaction took place anew, leading this time to a coordinatively unsaturated Fe(CO)<sub>2</sub> complex, which was not stabilized by an external ligand (CO), but by intramolecular coordination with the butenyl C=C bond. The structure of **6** resulted from the IR and H<sup>1</sup>-NMR spectra (only two CO ligands as sharp bands at 1957 and 2010 cm<sup>-1</sup>; metal coordinated vinyl group: 3H at 0.95, 3.43 and 4.25 ppm), and was confirmed by X-



reaction was postponed in favour of an intramolecular cycloaddition reaction of the diazo dipole, which yet could have been considered as thermally highly desta-

ray diffraction.

When the  $\omega$ -unsaturated chain was directly located on the metal coordinated diene, opposite to the keto group,



no such intramolecular stabilization was observed, in spite of the fact that at first look the Fe (CO)<sub>2</sub> group and the unsaturated chain would be close: the cyclohexadienone Fe (CO)<sub>3</sub> complexes **9a** and **9b** (three CO ligands; uncoordinated vinyl group) were the sole organometallic products obtained from the tosylhydrazones **8a** and **8b** of the 6-buten-3-yl- and 6-penten-4-yl-hexa-3,5-dien-2-one complexes **7a** and **7b**.

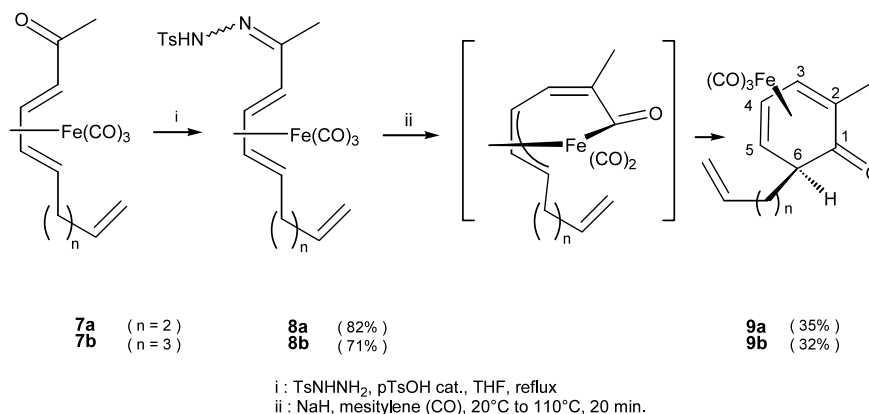
The ω-unsaturated chain must apparently be linked to the terminal carbon atom (C2) of the diene fragment of the cyclohexadienone complex, in order to stabilize intramolecularly the coordinatively unsaturated Fe (CO)<sub>2</sub> species (pseudo six-membered ring for the substructure C3–C10, p orbitals of the double bond C9–C10 pointing symmetrically towards the iron). As can be seen on molecular models, when the ω-unsaturated chain is linked to the sp<sup>3</sup> carbon C6 of the cyclohexadienone complex, α to the diene unit, the distance between the terminal double bond and the region above C4 becomes more important, making such a coordination less probable. Also the orientation of the p orbitals of the terminal double bond in relation to the iron seems

less favourable. Therefore the stabilization consists most probably in the replacement of an equatorial CO ligand of the equivalent Fe (CO)<sub>3</sub> complex by the C=C double bond.

### 3. Experimental

#### 3.1. Tosylhydrazone (5)

Anhydrous magnesium sulphate (3.00 g) was added to a solution of the dienone complex **4** (158 mg, 0.54 mmol), tosylhydrazine (142 mg, 0.76 mmol) and p-toluenesulfonic acid (10 mg, 0.05 mmol) in THF (50 ml). The mixture was refluxed for 14 h. Diethyl ether (50 ml) and water (100 ml) were added and the organic phase was washed successively with an aqueous saturated solution of NaHCO<sub>3</sub> and brine, and dried over MgSO<sub>4</sub>. The solvents were removed by evaporation (30 °C, 15 Torr) and the residue was purified by chromatography on a silica gel column (15 g, Merck Si 60, eluent hexane with 30% dichloromethane). Thirty-



four milligrams of the dienone complex **4** (0.12 mmol, 21%) was recovered as well as 165 mg tosylhydrazone **5** ( $C_{20}H_{22}N_2O_5SFe$ , 0.36 mmol, 66%, yellow solid). Yield **5** based on consumed **4**: 84%.

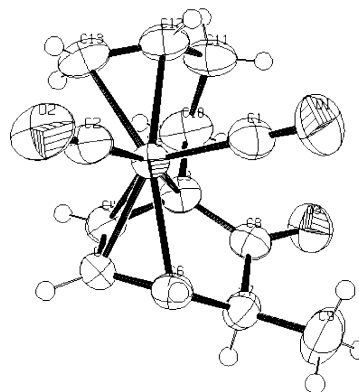
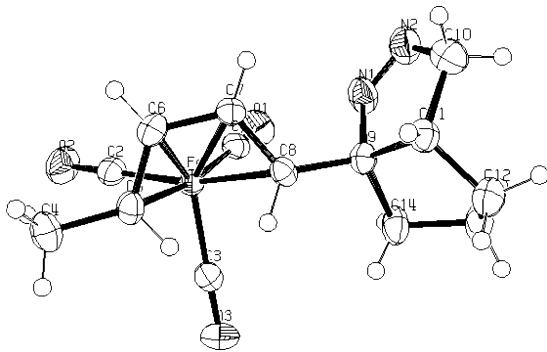
### 3.2. Cyclocarbonylation

NaH (10 mg, 0.4 mmol) was added to a stirred solution of the tosylhydrazone (**5**, 143 mg, 0.31 mmol) in mesitylene (20 ml). The air atmosphere over the mixture was replaced by carbon monoxide (several degassings under vacuo) and the temperature was gradually raised from room temperature (r.t.) to 110 °C in 20 min. About 80% of the solvent was evaporated (30 °C, 0.1 Torr), and the resulting solution was chromatographed on  $SiO_2$  (20 g, eluent hexane with 1–20% ether). Thirty-one milligrams of the cyclohexadienone complex **6** ( $C_{13}H_{14}O_3Fe$ , 0.11 mmol, 35%) was obtained.

### 3.3. Cyclohexadienone complex **6**

Yellow crystals, m.p. 102–104 °C; IR ( $CH_2Cl_2$ )  $\nu$  2010, 1957, 1646 (CO);  $^1H$ -NMR (300 Mhz,  $CDCl_3$ ):  $\delta$  0.94 (dddd, 1 H,  $J = 18.5, 12.8, 7.5$  and  $5.7$  Hz), 1.38 (d, 3H,  $J = 7.0$  Hz), 2.00 (q, 1H,  $J = 7.0$  Hz), 2.19 (d, 1H,  $J = 9.5$  Hz), 2.25–2.41 (m, 2H), 2.72 (dddd, 1H,  $J = 15.3, 12.2, 7.2$  and  $4.8$  Hz), 2.89 (ddd, 1H,  $J = 5.5, 2.0$  and  $1.6$  Hz), 3.43 (d, 1H,  $J = 13.5$  Hz), 4.25 (dddd, 1H,  $J = 13.6, 9.0, 4.6$  and  $2.0$  Hz), 5.82 (dd, 1H,  $J = 4.6$  and  $2.1$  Hz), 5.88 (td, 1H,  $J = 4.8$  and  $1.0$  Hz);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  15.44 ( $CH_3$ ), 23.59 ( $CH_2$ ), 38.23 (CH), 39.07 ( $CH_2$ ), 45.60 ( $CH_2$ ), 53.43 (CH), 81.02 (CH), 84.35 (CH), 89.42 (C), 98.80 (CH), 192.96 (C), 211.99 (C), 222.19 (C); MS ( $ES^+$ ):  $m/z$  275.0 [ $M+H^+$ ] (100%); HRMS ( $FAB^+$ ) Calc. for [ $M+H^+$ ]  $C_{13}H_{15}O_3Fe$  275.03706. Found 275.03679.

The details of the X-ray structure determination will be given in the full paper (Service Communs de Rayon X de l'Institut de Chimie de l'ULP).



**9a**: IR ( $CH_2Cl_2$ )  $\nu$  2059, 1989, 1663 (CO);  $^1H$  NMR (300 Mhz,  $CDCl_3$ ):  $\delta$  1.44 (m, 1H), 1.53 (s, 3 H), 2.07–2.32 (m, 4H), 3.02 (ddd, 1H,  $J = 1.6, 2.0$  and  $6.2$  Hz), 4.97 (tdd, 1H,  $J = 1.3, 2.0$  and  $10.2$ Hz), 5.03 (tdd, 1H,  $J = 1.4, 2.0$  and  $17.2$ Hz), 5.54 (dd, 1H,  $J = 6.5$  and  $4.6$  Hz), 5.78 (ddt, 1H,  $J = 17.2, 10.2$  and  $6.5$  Hz), 5.87 (dd, 1H,  $J = 2.2$  and  $4.6$  Hz);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  17.38 ( $CH_3$ ), 30.22 ( $CH_2$ ), 32.00 ( $CH_2$ ), 41.15 (CH), 56.73 (CH), 75.82 (C), 82.73 (CH), 91.64 (CH), 115.30 ( $CH_2$ ), 137.91 (CH), 196.25(C), 209.51 (C).

The 6-buten-3-yl- and 6-penten-4-yl-hexa-3,5-dien-2-one- $Fe(CO)_3$  complexes **7a** and **7b** were obtained by complexation ( $Fe_2(CO)_9$ , refluxing benzene) of (*E,E*)-3,5,9-decatrienone-2 and (*E,E*)-3,5,10-undecatrienone-2, prepared by crotonization with acetone ( $Ba(OH)_2$ , ca. 80%) of (*E*)-2,6-heptadienal [5], respectively, (*E*)-2,7-octadienal [6].

### Acknowledgements

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