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Intramolecular Friedel–Crafts acylation of acyclic (η^4-diene)$Fe(CO)_3$ complexes

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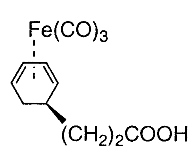
Abstract

Intramolecular cyclization of (η^4-diene)$Fe(CO)_3$ complexes bearing a carboxylic acid chloride functionality at the terminal side chain of the diene ligand produces (σ, η^3-allyl)$Fe(CO)_3$ complexes, whereas treatment of the acid chloride complexes with Et_3N and $AlCl_3$ provides (η^4-diene)$Fe(CO)_3$ complexes containing a cyclopentanone moiety. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Diene; Friedel–Crafts acylation; Intramolecular; Cyclopentanone

1. Introduction

The chemistry of (η^4-diene)$Fe(CO)_3$ complexes is a subject of continuing interest. Numerous synthetically useful carbon–carbon forming reactions using the complexes are based on the fact that diene ligands bonded to the electrophilic irontricarbonyl moiety are activated toward addition by reactive carbon nucleophiles [1] and ketyl anion radicals [2]. However, activation of dienes toward electrophilic attack by complexation with irontricarbonyl has been limited to intermolecular Friedel–Crafts acylation [3]. Only limited examples of intramolecular nucleophilic reactions of the tricarbonylmyrceneiron(0) complex with carbon electrophiles have been reported [4]. The reactions involved protonation or acylation of the pendant free double bond of the tricarbonylmyrceneiron(0) complex to generate the carbonium ion or the acyl chloride intermediate. Intramolecular nucleophilic addition of the diene ligand to the electron-deficient carbon centers gave cyclized products. Recently, we have found that the diene ligand of acyclic (η^4-butadiene)$Fe(CO)_3$ complexes is also capable of addition at the pendant chromium carbene carbon center to produce hydrofuran derivatives in fair yields [5]. Only one example of intramolecular cyclization of a cyclic (η^4-diene)$Fe(CO)_3$ complexes, for example **1**, afforded the bicyclic ketone **2** upon treating **1** with oxalyl chloride, Et_3N and $AlCl_3$ in methylene chloride. Complex **1** presumably underwent double bond migration in the presence of $AlCl_3$ to give **3**. Intramolecular Friedel–Crafts acylation of **3** provided **2** [5]. In this paper, we report in full detail that intramolecular cyclization of acyclic (η^4-diene)$Fe(CO)_3$ complexes bearing an acid chloride at the terminal position of the diene ligand using $AlCl_3$ and Et_3N generates iron–diene complexes containing a cyclopentanone ring.



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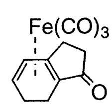

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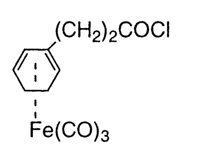

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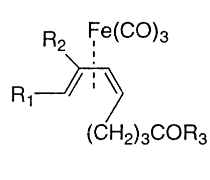

4a : R_1= H, R_2 = H, R_3 = OH
4b : R_1= CH_3, R_2 = H, R_3 = OH
4c : R_1= H, R_2 = CH_3, R_3 = OH
4d : R_1= Ph, R_2 = H, R_3 = OH
4e : R_1= Naphthyl, R_2 = H, R_3 = OH
4f : R_1= H, R_2 = H, R_3 = Cl
4g : R_1= H, R_2 = H, R_3 = OEt

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2. Results and discussion

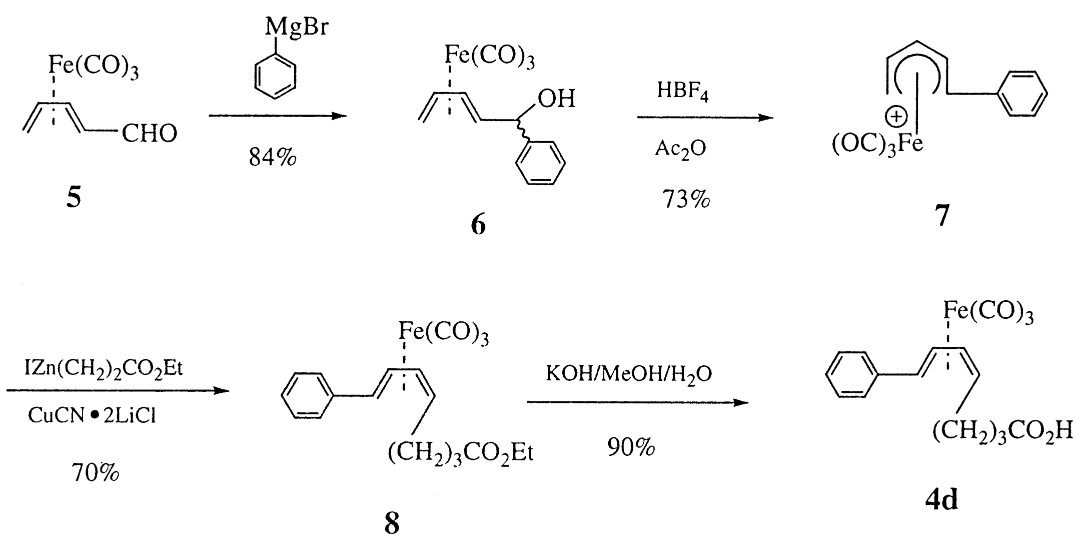
2.1. Synthesis of starting acid complexes

The starting complexes **4a–c** were prepared by the addition of the corresponding ester functionalized zinc–copper reagents to the (η^5-pentadienyl)$Fe(CO)_3$ cation salt followed by hydrolysis of the resulting ester complexes to the acid complexes according to the literature procedures [2,6]. Complex **4d** bearing a phenyl moiety at the terminal position of the diene ligand was synthesized as follows (Scheme 1). Addition of the phenyl Gringard reagent to (η^4-*trans*-2,4-pentadien-1-al)$Fe(CO)_3$ (**5**) [7] produced an alcohol (**6**) in 84% yield. The reaction of **6** with tetrafluoroboric acid and acetic anhydride yielded a cation (**7**) in 73% yield [8]. Addition of the zinc–copper reagent [9], derived from ethyl 3-iodopropionate, to cation **7** gave an ester complex **8** in 70% yield. Hydrolysis of **8** using KOH in MeOH–THF–H_2O furnished acid complex **4d** in 90% yield. Complex **4e** bearing a naphthyl moiety was synthesized in the similar sequence starting from the naphthyl Gringard reagent and complex **5** in 41% overall yield (four steps) (Scheme 1).

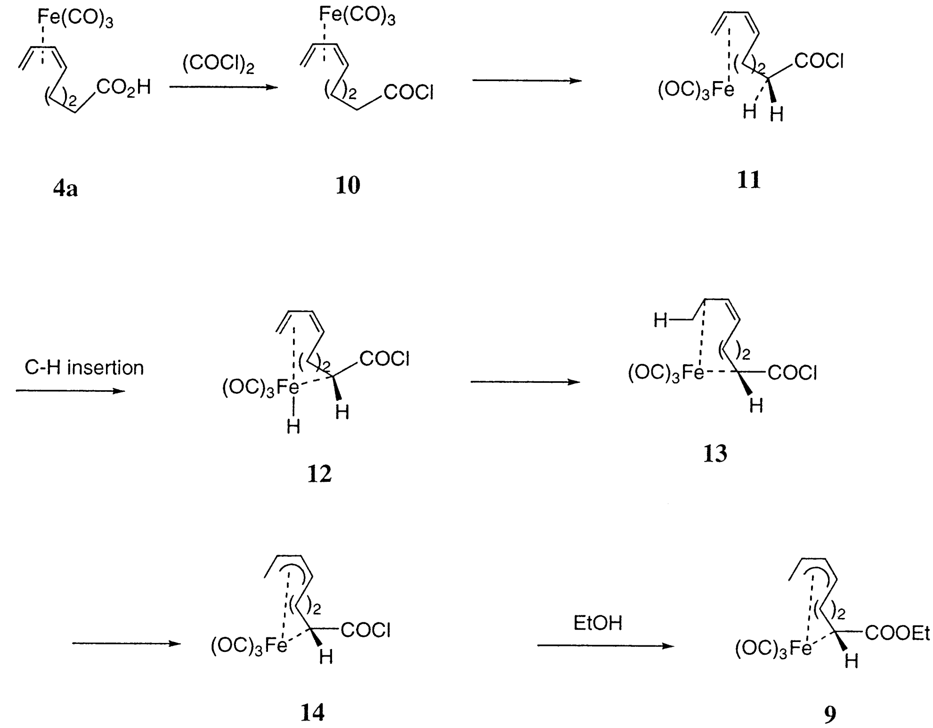
2.2. Formation of (σ, η^3-allyl)$Fe(CO)_3$ complexes

Our cyclization study began with complex **4a**. Oxalyl chloride (two molar equivalents) was added to a solution of acid complex **4a** in CH_2Cl_2 at 0°C and the reaction mixture was stirred at 0°C for 30 min. The reaction was performed in the expectation that acid chloride **4f** would be generated in situ before the addition of $AlCl_3$. However, TLC analysis showed that the expected ester complex **4g** [5] was not present upon quenching an aliquot with ethanol, and the reaction led instead to a new iron complex. Thus, the reaction was quenched with an excess of ethanol to give an iron complex, identified as (σ, η^3-allyl)$Fe(CO)_3$ complex (**9**) (Scheme 2). Complex **9** was isolated as the only diastereomeric isomer in 88% yield after regular aqueous work-up and flash column chromatography. Complex **9** was obtained previously from $TiCl_4$-assisted intramolecular cyclization of the ester–irondiene complex **4g** [5]. It is important to mention that the isolation of (σ, η^3-allyl)$Fe(CO)_3$ complex (**9**) is different from those found in Pearson's group for the intramolecular cyclization of the tricarbonylmyrceneiron complex [4]. Reaction of the tricarbonylmyrceneiron(0) with oxalyl chloride gave an acid chloride intermediate. Aluminum chloride-assisted intramolecular acylation of the diene ligand produced cyclized ketone. However, addition of oxalyl chloride followed by $AlCl_3$ to complex **4a** using Pearson's protocols also provided (σ, η^3-allyl)$Fe(CO)_3$ complex (**9**) in 80% yield. None of the cyclized ketone can be found. The different reaction path of complex **4a** may be due to the position of the side chain. Complex **3** and the intermediate derived from tricarbonylmyrceneiron(0) bearing an acid chloride side chain at the internal position of the diene ligand underwent Friedel–Crafts acylation, while complex **4a** with an acid chloride side chain at the terminal position produced (σ, η^3-allyl)$Fe(CO)_3$ complex.

The isolation of ester (σ, η^3-allyl)$Fe(CO)_3$ complex (**9**) may indicate that acid chloride **10** was formed initially (Scheme 2). Detachment of the olefin ligand would give the unsaturated-16-electron metal species **11**. For steric reasons, the acid chloride functional group will point away from the metal center in the transition-state conformation. *Endo* C–H bond insertion at the α-carbon of **11** into the iron center would generate the iron–hydride intermediate with the relative



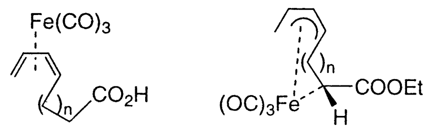
Scheme 1.



Scheme 2.

stereochemistry depicted in **12**. Hydride addition to the olefin ligand produced **13**. Reattachment of the pendant double bond to the metal center led to the formation of **14**, which upon quenching with ethanol produced **9**. It is important to note that two new stereogenic centers (the α- and allylic carbons) of **9** are created; however, only the single diastereomer shown was isolated.

Using the same approach, we are able to obtain (σ, η^3-allyl)$Fe(CO)_3$ complexes (**18**–**20**) in good yields (80–88%) via addition of oxalyl chloride to acid complexes **15**–**17** [5], respectively, followed by quenching the reaction mixture with ethanol.



15 n = 1
16 n = 3
17 n = 4

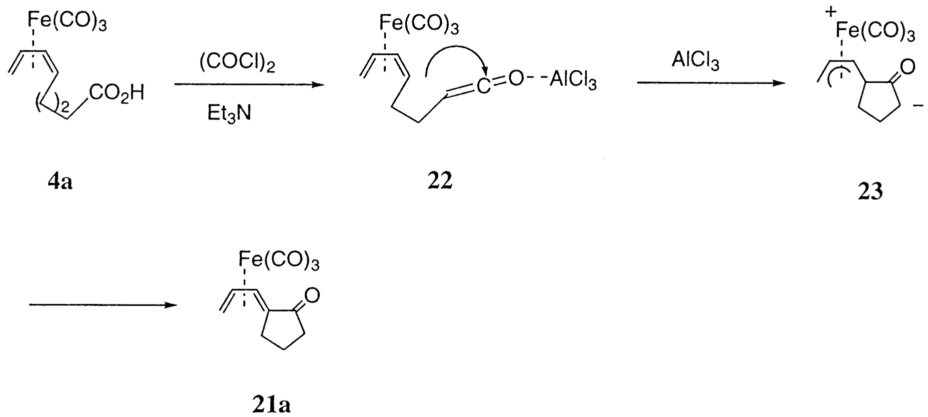
18 n = 1
19 n = 3
20 n = 4

2.3. Intramolecular Friedel–Crafts acylation

The intramolecular acylation of the acyclic (η^4-diene)$Fe(CO)_3$ complexes using the acid chloride functionality failed as stated above; thus, a more electrophilic carbon center must be considered. We then turned our effort to the more electrophilic ketene functionality. The acid was converted to the ketene by the reaction of **4a** with oxalyl chloride (1.2 molar equivalents) and Et_3N (1.2 molar equivalents) in CH_2Cl_2 at 0°C for 45 min. Addition of $AlCl_3$ (1.5 molar equivalents) in CH_2Cl_2 to the ketene intermediate at 25°C for 1 h gave a major product in 85% yield, identified as complex **21a**. The ^{13}C-NMR spectrum of complex **21a** has the usual ironcarbonyl chemical shift at 210 ppm. However, the CO of the ketone is not present in the ^{13}C-NMR spectrum between the 190–230 ppm region. The reason for not observing the CO of the ketone peak in the ^{13}C-NMR spectrum of **21a** may be due to the paramagnetic effect caused by the iron center. Nevertheless, the infrared spectrum of complex **21a** shows a sharp ketone stretch at 1676 cm^{-1} and the usual ironcarbonyl bands at 2056 and 1987 cm^{-1}. The ^{1}H-NMR spectrum of **21a** has the characteristic chemical shifts at 5.62 and 5.51 ppm for the internal vinyl protons. The chemical shifts of the vinyl protons stated above are consistent with those found for most acyclic (η^4-diene)$Fe(CO)_3$ complexes.

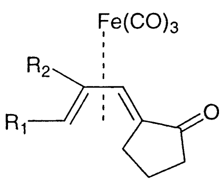
The ketene intermediate **22** formed presumably upon treatment of **4a** with oxalyl chloride and triethylamine (Scheme 3). The formation of **21a** may have started from the $AlCl_3$-assisted nucleophilic addition of the diene ligand of **22** at the ketene carbon center to give the cyclized intermediate **23**, which led to the formation of complex **21a** upon deprotonation at the α-carbon.

Under the same reaction conditions, intramolecular cyclization of complexes **4b**–**e** using oxalyl chloride, $AlCl_3$ and Et_3N also produced the expected cyclopen-



Scheme 3.

tanone derivatives **21b**–**e** in fair to modest yields (**21b**, 64%; **21c**, 76%; **21d**, 46% and **21e**, 33%). The structure of complex **21d** is further secured by X-ray diffraction analysis. The ORTEP structure (supplementary material) of **21d** clearly indicates that the carbonyl of the cyclopentanone moiety is in the closed proximity of the iron center. Due to the paramagnetic effect caused by the iron, the carbonyl of the cyclopentanone is not present in the ^{13}C-NMR spectrum of **21d** and the observation is consistent with those found for **21a**–**c** and **21e**.



21a : R_1= H, R_2 = H
21b : R_1= CH_3, R_2 = H
21c : R_1= H, R_2 = CH_3
21d : R_1= Ph, R_2 = H
21e : R_1= Naphthyl, R_2 = H

It is important to mention that the intramolecular Friedel–Crafts acylation of acyclic $(\eta^4\text{-diene})Fe(CO)_3$ complexes is limited to the formation of cyclopentanone derivatives. Attempted intramolecular acylation using ether other than three methylene groups, for example complexes **15**–**17**, failed to give cyclized products. The starting acid complexes were recovered upon quenching the reaction mixture with saturated aqueous NH_4Cl solution.

3. Conclusions

The reactions of the iron–diene complexes bearing an acid functionality with oxalyl chloride afford $(\sigma, \eta^3\text{-allyl})Fe(CO)_3$ complexes in diastereoselective fashion, in which C–H insertion at the α-carbon into the iron center takes place. Intramolecular Friedel–Crafts acylation occurs upon treating the acid complexes with oxalyl chloride and $AlCl_3$ in the presence of triethylamine to afford diene–iron complexes containing a cyclopentanone moiety.

4. Experimental

4.1. General

All reactions were run under a nitrogen atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Diethyl ether (ether) and tetrahydrofuran (THF) were distilled under nitrogen from a deep blue sodium benzophenone ketyl solution. Methylene chloride was distilled from calcium hydride. Complexes **4a**–**c** were synthesized according to the literature procedures [5,6]. Flash column chromatography, following the method of Still et al. [10], was carried out with Merck silica gel (Kieselgel 60, 230–400 mesh) using the indicated solvents. Analytical thin-layer chromatography was performed with silica gel 60 F254 plastic plates of 0.2 mm thickness from Merck. The term concentration refers to the removal of solvent with an aspirator pump (Yamato instrument Co. Model WP-15) with a Buchi Rotovapor-R. The term under nitrogen implies that the apparatus was evacuated (oil pump) and then filled with nitrogen three times. Melting points were determined in open capillaries with a Thomas–Hoover apparatus and are uncorrected. ^{1}H nuclear magnetic resonance (NMR) spectra were obtained with a JEOL EX 400 instrument (400 MHz). Chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or $CHCl_3$ (7.26 ppm) as internal standard. ^{13}C-NMR spectra were recorded with a JEOL EX 400 spectrometer (100.4 MHz) with $CDCl_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (*m*/*e*) with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Taichung, Taiwan.

4.2. General procedure I: formation of (σ η^3-allyl)Fe(CO)$_3$ complexes from acid complexes

To a 50 ml Schlenk flask was added 1.0 molar equivalent of an acid complex and 10 ml of CH_2Cl_2. The mixture was degassed three times. The reaction was cooled to 0°C under nitrogen and added slowly 2.0 molar equivalents of oxalyl chloride. The reaction was stirred at 0°C for 2 h and then quenched with 5.0 ml of ethanol. The reaction mixture was concentrated on rotary evaporator to give the crude mixture.

4.3. General procedure II: intramolecular Freidel–Crafts acylation of acyclic diene–irontricarbonyl complexes

To a 50 ml Schlenk flask was added 1.0 molar equivalent of an acid complex and 10 ml of CH_2Cl_2. The mixture was degassed three times. The reaction was cooled to 0°C under nitrogen and added slowly 1.2 molar equivalents of oxalyl chloride and 1.2 molar equivalents of triethylamine. The reaction was stirred at 25°C for 45 min. The reaction mixture was cooled to 0°C and was added 1.5 molar equivalents of $AlCl_3$ in 10 ml of CH_2Cl_2. The reaction was stirred at 25°C for 1 h and then quenched with saturated aqueous NH_4Cl solution. The reaction mixture was diluted with 100 ml of CH_2Cl_2. The organic solution was washed with water (3 × 100 ml) and brine (3 × 100 ml), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture.

4.4. Synthesis of complex **4d**

To a 50 ml Schlenk flask under nitrogen was added complex **5** (1.48 g, 6.60 mmol) and 20 ml of ether. The reaction was cooled to −78°C and 4.0 ml (2.0 M, 8.0 mmol) of phenyl Grignard reagent in ether was added slowly. The reaction was stirred at −78°C for 1 h. The reaction mixture was quenched with 10 ml of saturated aqueous NH_4Cl solution. The reaction mixture was diluted with 50 ml of CH_2Cl_2. The organic solution was washed with water (3 × 100 ml) and brine (3 × 100 ml), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. Flash column chromatography (silica gel, 5% ethylacetate–hexane) of the crude mixture gave complex **6** (1.25 g, 84%) as an orange oil. Complex **6** was used for the next step without further purification. To a 50 ml Schlenk flask under nitrogen at 5°C was added complex **6** (1.25 g, 4.3 mmol) and 10 ml of Ac_2O. To the reaction mixture at 5°C was added 0.54 ml (8.6 mmol) of tetrafluoroboric acid. The reaction was stirred at 5°C for 1 h followed by the addition of 20 ml of ether. The yellow precipitate was filtered and dried via vacuo to give cation **7** (0.92 g, 73%) as a yellow solid. Cation **7** was used for the next step without further purification. To 100 ml of Schlenk flask at 5°C under nitrogen was added cation **7** (0.65 g, 1.76 mmol) and 20 ml of THF. To the reaction mixture was added via syringe the zinc–copper reagent [Zn-(CuCN)$(CH_2)_2CO_2Et$] [9] (7.23 mmol) in 10 ml of THF. The reaction was stirred at 25°C for 3 h. The reaction mixture was quenched with 15 ml of saturated aqueous ammonium chloride solution. The reaction mixture was diluted with 100 ml of 5% ethylacetate–hexanes. The organic solution was washed with water (3 × 100 ml) and brine (3 × 100 ml), dried over anhydrous magnesium sulfate (15 g), and concentrated to give the crude mixture. Flash column chromatography (silica gel, 10% ethylacetate–hexane) of the crude mixture gave ester complex **8** as a deep red oil. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.18 (t, $J=7.1$ Hz, 3H); 1.36 (m, 1H); 1.55–1.65 (m, 1H); 1.73–1.75 (m, 2H); 2.21–2.25 (m, 2H); 2.49 (m, 1H); 3.2 (d, $J=9.8$ Hz, 1H); 4.05 (q, $J=3.1$ Hz, 2H); 5.23 (dd, $J=7.1$, 5.6 Hz, 1H); 5.92 (dd, $J=9.6$, 5.4 Hz, 1H); 7.10–7.19 (m, SH). To 100 ml round bottom flask, at 5°C under nitrogen, was added complex **8** (0.39 g, 1.01 mmol), KOH (0.29 g, 5.05 mmol), 10 ml of THF, 10 ml of water and 10 ml of MeOH. The reaction was stirred at 25°C for 1 h. The reaction mixture was quenched with 15 ml of 5% HCl solution and then diluted with 100 ml of 20% ethylacetate–hexane. The organic solution was washed with water (3 × 100 ml) and brine (3 × 100 ml), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. Flash column chromatography (silica gel, 50% ethylacetate–hexane) of the crude mixture gave acid complex **4d** (0.32 g, 90%) as a light yellow powder. The overall yield (four steps) for the synthesis of complex **4d** from complex **5** was 39%. m.p. (dec.) 103°C; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.36 (m, 1H); 1.55–1.66 (m, 1H); 1.78 (m, 2H); 2.36–2.38 (m, 2H); 2.56 (m, 1H); 3.60 (d, $J=9.8$ Hz, 1H); 5.29 (dd, $J=7.6$, 5.4 Hz, 1H); 5.99 (dd, $J=9.8$, 5.1 Hz, 1H); 7.17–7.26 (m, 5H). ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 27.8; 29.1; 33.2; 58.4; 60.7; 87.5; 89.0; 126.0; 126.5; 128.6; 140.1; 178.6; 210.9. IR (CH_2Cl_2): 3397; 3062; 3052; 3048; 2987; 2307; 2044; 1974; 1748; 1709; 1604; 1452 cm^{-1}. EI MS m/z (%) of major fragments: 342 (M^+, 1.2%); 314 (20); 286 (100); 200 (24); 198 (13).

4.5. Synthesis of complex **4e**

Complex **4e** was synthesized starting from complex **5** and naphthyl Grignard reagent according to the procedure stated above. The overall yield (four steps) for the synthesis of complex **4e** (an orange powder) from complex **5** was 41%. m.p. 115–124°C; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.26 (m, 1H); 1.66 (m, 1H); 1.88 (m, 2H); 2.38 (m, 2H); 2.70 (m, 1H); 3.80 (d, $J=10$ Hz, 1H); 5.40 (dd, $J=8.2$, 5 Hz, 1H); 6.26 (dd, $J=10$, 5 Hz, 1H); 7.27–8.14 (m, 7H). ^{13}C-NMR ($CDCl_3$, 400 MHz):

δ 28.8; 30.3; 41.7; 54.4; 58.4; 83.6; 88.3; 121.0; 123.0; 125.9; 126.5; 126.9; 127.8; 129.6; 131.6; 134.7; 136.9; 183.0; 212.8. IR (CH_2Cl_2): 3053; 2993; 2974; 1747; 1711; 1606; 1423; 1361; 1298; 1126 cm^{-1}. EI MS m/z (%) of major fragments: 406 (M^+, 1%); 322 (100); 266 (46); 193 (40); 179 (88). High-resolution MS for $C_{18}H_{18}O_2Fe(M^+)$: Anal. Calc.: 322.0556. Found: 322.0658.

4.6. Formation of (σ, η^3-allyl)Fe(CO)$_3$ complex (**9**)

The crude mixture obtained from intramolecular cyclization of complex **4a** (0.6 g, 2.26 mmol), according to Section 4.2, was purified via flash column chromatography (silica gel, 10% ethylacetate–hexane) to give **9** (0.55 g, 1.88 mmol, 83%) as a yellow oil [5]. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.28 (t, $J = 7.3$ Hz, 1H); 1.98–2.03 (m, 3H); 2.04 (d, $J = 6.4$ Hz, 3H); 2.47 (t, $J = 6.8$ Hz, 1H); 2.57 (m, 1H); 3.95 (m, 1H); 4.01 (m, 1H); 4.16 (q, $J = 7.3$ Hz, 2H); 4.94 (t, $J = 12.4$ Hz, 1H). ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 14.2; 20.1; 26.9; 33.5; 34.3; 60.5; 84.5; 87.7; 104.9; 172.9; 205.0; 207.5. IR (CH_2Cl_2): 3067; 3046; 2992; 2982; 2087; 2035; 2006; 1728; 1424; 1256; 1155; 929 cm^{-1}.

4.7. Formation of (σ, η^3-allyl)Fe(CO)$_3$ complex (**18**)

The crude mixture obtained from intramolecular cyclization of complex **15** (0.6 g, 2.26 mmol), according to Section 4.2, was purified via flash column chromatography (silica gel, 10% ethylacetate–hexane) to give **18** (0.55 g, 1.88 mmol, 83%) as a yellow oil [5]. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.30 (t, $J = 7.3$ Hz, 3H); 2.03 (d, $J = 6.8$ Hz, 3H); 2.36 (m, 1H); 2.65–2.79 (m, 2H); 3.84 (m, 1H); 4.00 (m, 1H); 4.19 (q, $J = 7.3$ Hz, 2H); 5.02 (t, $J = 12.2$ Hz, 1H). ^{13}C-NMR ($CDCl_3$, 400 MHz); 14.2; 20.1; 30.1; 35.7; 60.8; 84.8; 86.2; 105.2; 172.2; 205.2; 205.5; 207.2. IR (CH_2Cl_2): 3005; 2967; 2087; 2037; 2006; 1730; 1628; 1564; 1433; 1416; 1375; 1292; 1109; 924 cm^{-1}.

4.8. Formation of (σ, η^3-allyl)Fe(CO)$_3$ complex (**19**)

The crude mixture obtained from intramolecular cyclization of complex **16** (0.5 g, 1.79 mmol), according to Section 4.2 was purified via flash column chromatography (silica gel, 10% ethylacetate–hexane) to give **19** (0.46 g, 1.50 mmol, 83%) as a yellow oil [5]. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.27 (t, $J = 6.8$ Hz, 3H); 1.64–1.78 (m, 3H); 2.04 (d, $J = 6.3$ Hz, 3H); 2.17 (m, 1H); 2.37 (t, $J = 7.4$ Hz, 2H); 2.54 (m, 1H); 3.96–3.99 (m, 2H); 4.15 (q, $J = 6.8$ Hz, 2H); 4.91 (t, $J = 12.7$ Hz, 1H). ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 14.3; 20.1; 24.5; 31.4; 34.0; 34.9; 60.4; 84.3; 88.7; 104.8; 173.3; 205.1; 205.2; 207.6. IR (CH_2Cl_2): 3383; 3067; 2992; 2982; 2085; 2035; 2004; 1728; 1427; 1419; 1289; 1242; 1182; 1153 cm^{-1}.

4.9. Formation of (σ, η^3-allyl)Fe(CO)$_3$ complex (**20**)

The crude mixture obtained from intramolecular cyclization of complex **17** (0.5 g, 1.70 mmol), according to Section 4.2 was purified via flash column chromatography (silica gel, 10% ethylacetate–hexane) to give **20** (0.48 g, 1.40 mmol, 87%) as a yellow oil [5]. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.27 (t, $J = 6.9$ Hz, 3H); 1.42–1.78 (m, 4H); 1.97 (m, 2H); 2.03 (d, $J = 6.3$ Hz, 3H); 2.33 (t, $J = 7.3$ Hz, 2H); 2.52 (m, 1H); 3.95 (m, 2H); 4.13 (q, $J = 7.3$ Hz, 2H); 4.91 (t, $J = 12.2$ Hz, 1H). ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 14.2; 20.1; 24.7; 28.7; 31.6; 34.1; 34.9; 60.3; 84.1; 89.2; 104.8; 173.6; 205.2; 207.7. IR (CH_2Cl_2): 3084; 3029; 2938; 2085; 2033; 2004; 1728; 1566; 1437; 1414; 1302; 1103 cm^{-1}.

4.10. Tricarbonyl(η^4-2-allylidenecyclopentan-1-one)iron (**21a**)

The crude mixture obtained from intramolecular Friedel–Crafts acylation (Section 4.3) of complex **4a** (0.75 g, 2.69 mmol) was purified via flash column chromatography (silica gel, 10% ethylacetate–hexane) to give **21a** (0.60 g, 2.29 mmol, 85%) as a yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz); δ 1.85 (m, 2H); 2.03 (m, 2H); 2.14 (m, 2H); 2.40 (m, 2H); 5.51 (m, 1H); 5.62 (d, $J = 4.0$ Hz, 1H). ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 20.7; 37.8; 38.1; 46.0; 73.7; 88.1; 89.8; 209.7. IR (CH_2Cl_2): 3011; 2970; 2056; 1987; 1676; 1454; 1408; 1334; 1103 cm^{-1}. EI MS m/z (%) of major fragments: 262 (M^+, 2%); 234 (22); 206 (40); 178 (106); 152 (20). High-resolution MS for $C_9H_{10}O_2Fe(M^+–2CO)$: Anal. Calc.: 206.0030. Found: 206.0038.

4.11. Tricarbonyl[η^4-2(trans-3-methylallylidenecyclopentan-1-one)]iron (**21b**)

The crude mixture obtained from intramolecular Friedel–Crafts acylation (Section 4.3) of complex **4b** (0.70 g, 2.34 mmol) was purified via flash column chromatography (silica gel, 10% ethylacetate–hexane) to give **21b** (0.49 g, 1.78 mmol, 64%) as a yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.50 (d, $J = 6.4$ Hz, 3H); 1.82 (m, 2H); 1.97 (m, 1H); 2.13 (m, 1H); 2.39 (m, 1H); 2.46 (m, 1H); 2.84 (m, 1H); 5.31 (dd, $J = 9.5$, 5.7 Hz, 1H); 5.44 (d, $J = 5.4$ Hz, 1H). ^{13}C-NMR ($CDCl_3$ 400 MHz): δ 19.9; 20.5; 37.8; 37.9; 64.4; 73.2; 83.4; 93.1; 210.0. IR (CH_2Cl_2): 3069; 3048; 2986; 2048; 1981; 1672; 1609 cm^{-1}. El MS m/z (%) of major fragments: 248 (M^+–CO, 23%); 220 (35); 192 (100); 164 (34); 121 (29); 95 (17); 84 (34); 56 (47). High-resolution MS for $C_{12}H_{12}O_4Fe(M^+)$: Anal. Calc.: 276.0085. Found: 276.0094.

4.12. Tricarbonyl[η^4-(2-methylallylidenecyclopentan-1-one)]iron (**21c**)

The crude mixture obtained from intramolecular Friedel–Crafts acylation (Section 4.3) of complex **4c** (0.70 g, 2.34 mmol) was purified via flash column chromatography (silica gel, 10% ethylacetate–hexane) to give **21c** (0.49 g, 1.78 mmol, 76%) as a yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.85 (m, 2H); 1.99 (m, 1H); 2.13 (m, 3H); 2.22 (s, 3H); 2.40 (m, 2H); 5.52 (s, 1H). ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 20.6; 24.4; 37.66; 37.9; 48.4; 70.2; 87.9; 107.2; 209.7. IR (CH_2Cl_2): 3067; 3046; 2984; 2058; 1984; 1676; 1582; 1424; 1265; 1248; 1095; 914; 875; 756 cm^{-1}. EI MS m/z (%) of major fragments: 248 ($M^+ - CO$, 25%); 220 (40); 192 (100); 176 (82); 149 (62). High resolution MS for $C_{11}H_{12}O_3Fe(M^+ - CO)$: Anal. Calc.: 248.0136. Found: 248.0131.

4.13. Tricarbonyl[η^4-2-(trans-3-phenylallylidenecyclopentan-1-one)]iron (**21d**)

The crude mixture obtained from intramolecular Friedel–Crafts acylation (Section 4.3) of complex **4d** (0.36 g, 1.00 mmol) was purified via flash column chromatography (silica gel, 10% ethylacetate–hexane) to give **21d** (0.15 g, 0.46 mmol, 46%) as a red orange powder: m.p. (dec.) 144°C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.86 (m, 2H); 2.01 (m, 1H); 2.22 (m, 1H); 2.40 (m, 1H); 2.53 (m, 1H); 3.97 (m, 1H); 5.63 (d, $J = 8$ Hz, 1H); 6.04 (d, $J = 8$ Hz, 1H); 7.27 (m, 5H). ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 20.0; 37.6; 37.8; 66.9; 72.9; 84.3; 87.0; 127.5; 127.9; 129.3; 139.9; 212.2. IR (CH_2Cl_2): 3065; 3045; 2993; 2050; 1986; 1703; 1676; 1612 cm^{-1}. EI MS m/z (%) of major fragments: 254 (M^+–3CO, 32%); 198 (94); 155 (21); 141 (100); 115 (38); 91 (28); 71 (7). High-resolution MS for $C_{14}H_{14}OFe(M^+–3CO)$: Anal. Calc.: 254.0394. Found: 254.0396.

4.14. Tricarbonyl[η^2-(trans-3-naphthylallylidenecyclopentan-1-one)iron (**21e**)

The crude mixture obtained from intramolecular Friedel–Crafts acylation (Section 4.3) of complex **4e** (0.35 g, 0.86 mmol) was purified via flash column chromatography (silica gel, 10% ethylacetate–hexane) to give **21e** (0.11 g, 0.28 mmol, 33%) as a deep red powder: m.p. 118–120°C. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0 1.91 (m, 2H); 2.06 (m, 1H); 2.31 (m, 1H); 2.48 (m, 1H); 2.70 (m, 1H); 4.79 (d, $J = 16$ Hz, 1H); 5.74 (d, $J = 8$ Hz, 1H); 6.31 (dd, $J = 16$, 8 Hz, 1H); 7.25–8.15 (m, 7H). ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 20.0; 37.9; 38.22; 61.5; 73.0; 85.6; 86.7; 121.6; 123.6; 125.6, 126.7; 127.3; 128.5; 129.3; 132.5; 134.6; 135.9; 212.9. IR (CH_2Cl_2): 3053; 3045; 2974; 2050; 1986; 1674; 1608; 1452 cm^{-1}. EI MS m/z (%) of major fragments: 388 (M^+, 1.7%); 304 (100); 191 (24); 165 (33); 152 (28); 56 (9). High-resolution MS for $C_{18}H_{16}OFe(M^+–3CO)$: Anal. Calc.: 304.0551. Found: 304.0552.

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