Intramolecular Friedel–Crafts acylation of acyclic \((\eta^4\text{-diene})\text{Fe(CO)}_3\) complexes

Ming-Chang P. Yeh *, Suen-Chi Chang, Ching-Ju Chang

Department of Chemistry, National Taiwan Normal University, 88, Ding-Jou Road, Section 4, Taipei 117, Taiwan, ROC

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Abstract

Intramolecular cyclization of \((\eta^4\text{-diene})\text{Fe(CO)}_3\) complexes bearing a carboxylic acid chloride functionality at the terminal side chain of the diene ligand produces \((\eta^5\text{-allyl})\text{Fe(CO)}_3\) complexes, whereas treatment of the acid chloride complexes with \(\text{Et}_3\text{N}\) and \(\text{AlCl}_3\) provides \((\eta^4\text{-diene})\text{Fe(CO)}_3\) complexes containing a cyclopentanone moiety. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The chemistry of \((\eta^4\text{-diene})\text{Fe(CO)}_3\) 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 \((\eta^4\text{-butadiene})\text{Fe(CO)}_3\) 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 \((\eta^4\text{-diene})\text{Fe(CO)}_3\) complexes, for example 1, afforded the bicyclic ketone 2 upon treating 1 with oxalyl chloride, \(\text{Et}_3\text{N}\) and \(\text{AlCl}_3\) in methylene chloride. Complex 1 presumably underwent double bond migration in the presence of \(\text{AlCl}_3\) 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 \((\eta^4\text{-diene})\text{Fe(CO)}_3\), complexes bearing an acid chloride at the terminal position of the diene ligand using \(\text{AlCl}_3\) and \(\text{Et}_3\text{N}\) generates iron–diene complexes containing a cyclopentanone ring.

* Corresponding author. Fax: +886-2-29324249.
E-mail address: cheyeh@scc.ntnu.edu.tw (M.-C.P. Yeh)

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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 \((\eta^5\text{-pentadienyl})\text{Fe(CO)}_3\) 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 Grignard reagent to \((\eta^4\text{-trans-2,4-pentadien-1-yl})\text{Fe(CO)}_3\) (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$_2$O furnished acid complex 4d in 90% yield.

Complex 4e bearing a naphthyl moiety was synthesized in the similar sequence starting from the naphthyl Grignard reagent and complex 5 in 41% overall yield (four steps) (Scheme 1).

2.2. Formation of \((\sigma, \eta^3\text{-allyl})\text{Fe(CO)}_3\) complexes

Our cyclization study began with complex 4a. Oxalyl chloride (two molar equivalents) was added to a solution of acid complex 4a in CH$_2$Cl$_2$ 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 \((\sigma, \eta^3\text{-allyl})\text{Fe(CO)}_3\) 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–iron diene complex 4g [5]. It is important to mention that the isolation of \((\sigma, \eta^3\text{-allyl})\text{Fe(CO)}_3\) 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 \((\sigma, \eta^3\text{-allyl})\text{Fe(CO)}_3\) 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 \((\sigma, \eta^3\text{-allyl})\text{Fe(CO)}_3\) complex.

The isolation of ester \((\sigma, \eta^3\text{-allyl})\text{Fe(CO)}_3\) 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 \(\eta\)-carbon of 11 into the iron center would generate the iron–hydride intermediate with the relative
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.

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\(_2\)N (1.2 molar equivalents) in CH\(_2\)Cl\(_2\) at 0°C for 45 min. Addition of AlCl\(_3\) (1.5 molar equivalents) in CH\(_2\)Cl\(_2\) 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\(_2\)N also produced the expected cyclopen-
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 $21e$.

It is important to mention that the intramolecular Friedel–Crafts acylation of acyclic (π$^3$-diene)Fe(CO)$_3$ complexes is limited to the formation of cyclopen
tanone 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$_4$Cl solution.

3. Conclusions

The reactions of the iron–diene complexes bearing an acid functionality with oxalyl chloride afford (σ, π$^3$-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
\( \eta^1\)-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 and 1.2 molar equivalents of triethylamine. 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 under nitrogen and added slowly 1.2 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 water (3 x 100 ml) and brine (3 x 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 cooled to −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 x 100 ml) and brine (3 x 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 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)CH_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 x 100 ml) and brine (3 x 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. 1H-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 x 100 ml) and brine (3 x 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; 1H-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). 13C-NMR (CDCl_3, 400 MHz): δ 27.8; 29.1; 33.2; 58.4; 89.0; 126.0; 126.5; 128.6; 140.1; 178.6; 201.9. IR (CH2Cl2): 3397; 3062; 3032; 3052; 3048; 2987; 2307; 2044; 1974; 1748; 1709; 1604; 1452 cm⁻¹. EI MS m/z (%): 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; 1H-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). 13C-NMR (CDCl_3, 400 MHz):
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]. 1H-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). 13C-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]. 1H-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). 13C-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]. 1H-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). 13C-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]. 1H-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). 13C-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-allyldienecyclopentan-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. 1H-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). 13C-NMR (CDCl_3, 400 MHz): δ 20.7; 37.8; 38.1; 46.0; 73.7; 88.1; 89.8; 207.9. 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_21H_18O_4Fe(M^+) : Anal. Calc.: 206.0030. Found: 206.0038.

4.11. Tricarbonyl[η^4,2-(trans-3-methyldienecyclopentan-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. 1H-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). 13C-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\(^{-1}\). EI 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_{21}H_{18}O_4Fe(M^+) : Anal. Calc.: 276.0085. Found: 276.0094.
4.12. Tricarbonyl[η^4-(2-methylallylidenedicyclopentane-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.

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1H-NMR (CDCl3, 400 MHz): δ 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). 13C-NMR (CDCl3, 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 (CH2Cl2): 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 C15H16OFe(M^+–3CO): Anal. Calc.: 304.0551. Found: 304.0552.

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